

# SYMPOSIUM NM02

Nanometal—Synthesis, Properties and Applications  
November 26 - November 29, 2018

## Symposium Organizers

De-en Jiang, University of California, Riverside  
Grant Johnson, Pacific Northwest National Laboratory  
Mika Pettersson, University of Jyväskylä  
Jianping Xie, National University of Singapore

## Symposium Support

Nanoscale | Royal Society of Chemistry

\* Invited Paper

SESSION NM02.01: Atomically Precise Nanometal: Structure, Ligands and Doping  
Session Chairs: De-en Jiang and Grant Johnson  
Monday Morning, November 26, 2018  
Sheraton, 3rd Floor, Commonwealth

### 8:45 AM \*NM02.01.01

**Tailoring Nanoparticles at Single-Atom, Single-Electron Level** Rongchao Jin; Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Nanoparticles play a central role in the rapidly growing nanoscience and nanotechnology fields. Atomic level tailoring of nanoparticles is of great importance in order to map out the structure-property relationships. Recent success in the synthesis of atomically well-defined nanoparticles has offered exciting opportunities to pursue many fundamental issues that were difficult to tackle with polydisperse nanoparticles. This talk will present several cases of single-atom, single-electron level manipulations of metal nanoparticles, such as doping a single Ag or Cu atom into a gold nanoparticle and site-specific “surgery” of surface motifs of a nanoparticle with controlled charge state. Such atomic-level manipulations provide unique opportunities for investigating how the structure and composition precisely impact the particle’s properties and functionality at the single-atom, single-electron level. New strategies for achieving such goals have been devised. Overall, the pursuit of single-atom level tailoring opens up new opportunities for controlling nanoparticles on an atom-by-atom basis.

### 9:15 AM NM02.01.02

**Toward Total Synthesis of Thiolate-Protected Metal Nanoclusters** Qiaofeng Yao and Jianping Xie; Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore.

Total synthesis, where desired organic- and/or bio-molecules could be produced from simple precursors *at atomic precision* and *with known step-by-step reactions*, has prompted centuries-lasting bloom of organic chemistry since its conceptualization in 1828 (Wöhler synthesis of urea). Such expressive science is also highly desirable in nanoscience, since it represents a decisive step towards *atom-by-atom customization of nanomaterials* for basic and applied research. Although total synthesis chemistry is less established in nanoscience, recent years have witnessed seminal advances and increasing research efforts devoted into this field. In this talk, I will discuss our recent work on introducing and developing total synthesis routes and mechanisms for atomically precise metal nanoclusters (NCs). Due to their molecular like formula and properties (e.g., HOMO-LUMO transition, strong luminescence and stereochemical activity), atomically precise metal NCs could be regarded as “molecular metals” (or metallic molecules / molecular-like metals), holding potential applications in various practical sectors such as biomedicine, energy, catalysis and many others. More importantly, the molecular-like properties of metal NCs are sensitively dictated by their size and composition, suggesting total synthesis of them as an indispensable basis for reliably realizing their practical applications.

### 9:30 AM \*NM02.01.03

**Precise Synthesis of Platinum and Alloy Clusters and Elucidation of Their Structures** Yuichi Negishi; Tokyo University of Science, Tokyo, Japan.

In recent years, it has become possible to synthesize gold clusters, silver clusters, and alloy clusters with atomic precision using thiolate or phosphine (PR<sub>3</sub>) as a ligand. The electronic/geometric structures and size-specific physical/chemical properties of these metal clusters have also been investigated extensively. Similar to these metal clusters, platinum (Pt) clusters have also attracted much interest. An attractive feature of Pt clusters is their high catalytic activity in a variety of reactions. In the precise synthesis of these Pt clusters, carbon monoxide (CO) or PR<sub>3</sub> is used as the main ligand. However, little information has been obtained on the electronic structure and physical/chemical properties of Pt<sub>n</sub>(CO)<sub>m</sub>(PR<sub>3</sub>)<sub>l</sub> clusters to date. In this research, the final objective is to obtain experimental information about the largely unknown electronic structure of Pt<sub>n</sub>(CO)<sub>m</sub>(PR<sub>3</sub>)<sub>l</sub> clusters. To this end, we precisely synthesized a Pt<sub>17</sub> cluster ([Pt<sub>17</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>n+</sup>; n = 1, 2) protected by CO and triphenylphosphine (PPh<sub>3</sub>) by a simple method and studied its geometric and electronic structure. Mass spectrometry, elemental analysis, and single-crystal X-ray structural analysis of the product revealed that the obtained Pt<sub>17</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>8</sub> comprises positively charged [Pt<sub>17</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>+</sup> and [Pt<sub>17</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>8</sub>]<sup>2+</sup>, having a geometric structure similar to that<sup>36</sup> of neutral Pt<sub>17</sub>(CO)<sub>12</sub>(PEt<sub>3</sub>)<sub>8</sub>. The optical absorption spectroscopy and electrochemical measurements of [Pt<sub>17</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>8</sub>][SbF<sub>6</sub>]<sub>n</sub> (n = 1, 2) demonstrated that [Pt<sub>17</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>8</sub>][SbF<sub>6</sub>]<sub>n</sub> (n = 1, 2) has a discrete electronic structure. Furthermore, the emission spectroscopy revealed that [Pt<sub>17</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>8</sub>][SbF<sub>6</sub>]<sub>n</sub> (n = 1, 2) exhibits photoluminescence in the near-infrared region. In this presentation, I also talk about our recent results on the precise synthesis and one-dimensional structures of alloy clusters including Pt element.

10:00 AM BREAK

#### 10:30 AM NM02.01.04

**Attractive Interactions at the Metal-Ligand Interface of Coordinated Clusters** Katsuki Konishi, Md. Abu Bakar, Mitsuhiro Iwasaki, Shipeng Wang and Yukatsu Shichibu; Hokkaido University, Sapporo, Japan.

Ligand-protected gold clusters with defined compositions and structures have attracted special attention because of diverse geometric structures and unique optical/electronic properties associated with their molecule-like features. During our recent studies on phosphine-ligated gold clusters in the subnanometer regime (nuclearity ~10), some examples of peculiar interactions at the metal-ligand interface, such as weak attractive forces involving heteroatoms and  $\pi$ -functionalities in the ligand moieties, have been found [1]. Herein we report unusual Au...H-C hydrogen bonds, which were characterized by X-ray crystallography and solution NMR [2].

The cluster we used here is core+exo type Au<sub>6</sub> cluster carrying *m*-phenylene-bridged diphosphines. The crystal structure showed close contacts of the gold framework to the bridging *m*-phenylene units. The hydrogen atoms at the 2-position of the bridges (H-2) are located in proximity to the tetrahedral core with Au-H distances of 2.60 – 2.65 Å, which are shorter than the sum of the van der Waals radii (2.86 Å). Accordingly, the distances to the C-2 atoms (3.641 – 3.699 Å) were shorter than that estimated with the assumption that C, H and Au atoms are aligned with van der Waals Au-H contact (3.95 Å). These observations imply the presence of hydrogen-bond-type interactions between the H-2 atoms and the Au cluster unit. It should be noted that the Au...H-C interactions were also observed in solution NMR, which showed <sup>1</sup>H and <sup>13</sup>C NMR signals due to the C-H units at considerably downfield regions ( $\delta_{\text{H}} = 11.6$ ,  $\delta_{\text{C}} = 147.3$ ); The downfield shifts from normal aromatic protons were more than 4 and 10 ppm for <sup>1</sup>H and <sup>13</sup>C, respectively. We also show similar metal-H hydrogen bonds in related cluster systems. These results not only demonstrate the unique capability of small gold cluster to interact with unfunctionalized C-H groups but also shed light on the elucidation of recently emerging gold cluster catalysis.

[1] K. Konishi, et al. *J. Phys. Chem. Lett.* 2016, 7, 4267 [2] Md. A. Bakar, K. Konishi et al, *Nature Commun.* 2017, 8, 576).

#### 10:45 AM \*NM02.01.05

**Ligand Effects of Alkynyls on the Structures and Properties of Gold Nanoclusters** Quan-Ming Wang; Tsinghua University, Beijing, China.

Ligand-protected gold nanoclusters have been attracting great interest, because they display aesthetical structural diversity and are promising materials for both fundamental research and applications in catalysis, biosensing, luminescence and molecular electronics, etc. Their precise compositions and well-defined sizes are very helpful for understanding the structure-property relationships of metal clusters and nanoparticles.

Beyond the conventional thiolate and phosphine ligands, alkynyl groups have emerged as a promising ligand in protecting gold nanoclusters. As the ligand space is further broadened, new cluster compositions, structures and interfaces can be discovered. We will provide an atomic-level view of alkynyl-protected gold nanoclusters. The syntheses of a series of gold nanoclusters with “direct reduction” method will be reported. The total structure determination of these clusters will be described. The stability and optical properties of these nanoclusters will be discussed based on electronic structural analysis. In addition, ligand effects on the catalytic performance of gold nanoclusters will be presented. We believe the success in these systems will stimulate more effort in discovering new aspects this class of gold nanoclusters with alkynyl groups in the protective layer.

#### 11:15 AM NM02.01.06

**Overview of the Ligand-Gold Interfaces and the Case of the N-Heterocyclic Carbenes** De-en Jiang; University of California, Riverside, Riverside, California, United States.

Ligands play an important role in the stabilization and functionalization of Au nanostructures and in self-assembled monolayers. Despite the increasing number of organic groups capable of stabilizing gold in addition to the popular thiolate ligands and the emerging alkynyl groups, there has been no systematic comparison of organic ligands regarding their binding strength to gold. To facilitate the future experimental design of promising ligands for gold surfaces, nanostructures, and nanoclusters, we provide a comprehensive view of the ligand-gold interface for six types and 27 ligands from first principles dispersion-corrected density functional theory. We find a surprising contrast between simple and bulky N-heterocyclic carbenes (NHCs). The bulk NHCs benefit from greater van der Waals contributions and additional Au...H-R hydrogen bonds. In fact, we find that alkynyl groups and bulky NHCs demonstrate the strongest binding with the gold surfaces. We further explore the computational design and show the viability of NHC-protected gold nanoclusters of magic stability. The overall trend from the present work not only confirms the emerging role of alkynyl ligands but also predicts the very promising direction of using bulky NHCs to achieve stable gold nanoclusters and interfaces.

#### 11:30 AM NM02.01.07

**Structural Control of Quarternary Ammonium Cationic Gold Nanoclusters** Tetsu Yonezawa, Yohei Ishida, Mai Thanh Nguyen, Kunihiko Narita and Ryan D. Corpuz; Hokkaido Univ, Sapporo, Japan.

Quaternary ammonium is a cationic group which is always show positive charge at any pH conditions. Many reports have been published on thiolate-gold nanoclusters but almost all of them were covered by non-ionic or anionic thiol compounds. Only a few reports of amino-thiol-stabilized gold nanoclusters can be found but no report of quaternary ammonium thiolate-stabilized ones. For the first time, we prepared quaternary ammonium-stabilized fluorescent gold nanoclusters by sputtering processes. Furthermore, we have successfully prepared Au<sub>25</sub> clusters stabilized by quaternary ammonium thiols. In this case, counter anion plays an important key. Bromides cannot well stabilize Au<sub>25</sub> clusters and they decomposed rapidly. But after changing this counter anion to PF<sub>6</sub><sup>-</sup> or other soft anions, very stable fully cationic Au<sub>25</sub> nanoclusters could be obtained.

#### 11:45 AM NM02.01.08

**Tailoring the Atomic Structure of Gold Nanoclusters by Doping—Using an 23-Gold-Atom Nanocluster as an Example** Qi Li and Rongchao Jin; Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

In this work, we demonstrate three different doping modes when an atomically-precise nanocluster: [Au<sub>23</sub>(SR)<sub>16</sub>]<sup>-</sup> is doped with different metals (Cd, Cu, Ag), including (i) simple substitution, (ii) surface reconstruction and (iii) total structure transformation. Both experimental and theoretical results demonstrate that the dopant concentration is critical: the original structure of [Au<sub>23</sub>(SR)<sub>16</sub>]<sup>-</sup> is retained under slight doping, but it starts to change under high concentrations of Cd and Ag dopants. Our results suggest that doping in nanoclusters is not just a simple substitution of original atoms or filling a vacant site; instead, it can be explored as a useful method to tailor the structure of nanoclusters partially (e.g., Cd doping of Au<sub>23</sub>) or totally (e.g., Ag doping of Au<sub>23</sub>). Overall, this work greatly expands doping chemistry for tailoring the structures of nanoclusters and is expected to open new avenues for designing nanoclusters with novel structures using different dopants.

**1:30 PM \*NM02.02.01**

**Au<sub>68</sub> and Au<sub>144</sub> 3-MBA Protected Nanoparticles—From Atomic 3D Structural Determination to Tracking Them Inside Human Cells by Electron Microscopy** [Maia Azubel](#); Structural Biology, Stanford University, Stanford, California, United States.

The first atomic structure of a gold nanoparticle (AuNP) was determined by X-ray crystallography (1). The atomic structure that identified the Au<sub>102</sub>NP as a molecule led to the idea of the gold cluster as a "super-atom", and revealed a layer of alternating gold and ligand molecules at the interface (2). Subsequent X-ray structures of smaller organo-soluble AuNPs have supported the super-atom idea, and have shown a similar gold-thiol surface layer (3). Nevertheless, using X-ray crystallography as a general method for solving AuNP structures has been limited by the capability of forming well-ordered crystals. The structure determination of AuNPs at atomic resolution by aberration corrected electron microscopy (EM) was demonstrated (4,5). The successful structural determination was due to the implementation of a low dose strategy combined with a homogeneous sample that could be subjected to single particle reconstruction. Last but not least, the new structures do not respond to the super-atom model. Yet, they are well-defined particles of remarkable stability and reactivity. Such reactivity makes possible to form bio-conjugates that can be used to monitor traffic of small proteins inside human cells by cryo-electron tomography.

(1) Jazdzinsky et al. Science (2007).

(2) Walter, et al. Proc. Natl. Acad. Sci. (2008)

(3) Häkkinen. Nature Chemistry (2012).

(4) Azubel et al. Science (2014).

(5) Azubel et al. ACSNano (2017)

**2:00 PM NM02.02.02**

**Probing the Surface Chemistry of Ultrasmall Gold Nanoparticles by In-Depth NMR Spectroscopy** [Tatjana Ruks](#)<sup>1</sup>, Christine Beuck<sup>2</sup>, Torsten Schaller<sup>3</sup>, Felix Niemeier<sup>3</sup>, Manfred Zachres<sup>4</sup>, Kateryna Loza<sup>1</sup>, Marc Heggen<sup>5</sup>, Ulrich Hagemann<sup>6</sup>, Peter Bayer<sup>2</sup>, Christian Mayer<sup>4</sup> and Matthias Eppele<sup>1</sup>; <sup>1</sup>Inorganic Chemistry and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Essen, Germany; <sup>2</sup>Institute of Biology and Center for Medical Biotechnology (CMB), University of Duisburg-Essen, Essen, Germany; <sup>3</sup>Organic Chemistry, University of Duisburg-Essen, Essen, Germany; <sup>4</sup>Physical Chemistry, University of Duisburg-Essen, Essen, Germany; <sup>5</sup>Ernst Ruska-Center for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich GmbH, Jülich, Germany; <sup>6</sup>Interdisciplinary Center for Analytics on the Nanoscale (ICAN) and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Duisburg, Germany.

Ultrasmall nanoparticles with a diameter below 2 nm are promising as specialized carriers for targeted drug delivery. Functionalized with specific binding motifs, they open up innovative opportunities in a wide range of applications, e.g. nanomedicine. A possible application is the specific targeting of protein-epitopes.

A versatile approach to the functionalization with specific epitope-binding motifs, i.e. peptides and proteins, is covalent binding of the gold-surface with sulfur-containing molecules. NMR spectroscopy gives valuable insights into the characteristics of the binding situation on the surface.

L-cysteine as a typical sulfur-containing biomolecule was chosen to elucidate the binding of ligands to ultrasmall gold nanoparticles ( $d < 2$  nm). Cysteine is the only thiol-containing amino acid and therefore an ideal model compound for the binding to gold nanoparticles.

The nanoparticle preparation was carried out by reduction of HAuCl<sub>4</sub> with NaBH<sub>4</sub>. L-cysteine was directly attached to the gold nanoparticles via gold-sulfur binding. The purification of the cysteine-capped nanoparticles was performed by multiple centrifugation and washing steps.

To investigate the binding of L-cysteine to the gold nanoparticle surface, isotope-labeled L-cysteine (<sup>13</sup>C and <sup>15</sup>N) was used. 2D <sup>1</sup>H-DOSY, <sup>13</sup>C-DOSY and 3D <sup>1</sup>H-<sup>13</sup>C-HSQC-iDOSY NMR spectroscopy of the gold nanoparticles enabled the determination of the hydrodynamic particle diameter in excellent agreement with the metallic core diameter by high-resolution transmission electron microscopy.

The binding of L-cysteine to the gold nanoparticles via the thiol group was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and 2D-NMR spectroscopy (<sup>1</sup>H, <sup>1</sup>H-COSY, <sup>1</sup>H, <sup>13</sup>C-HSQC and <sup>13</sup>C, <sup>13</sup>C-INADEQUATE). To exclude the binding of L-cysteine to the gold nanoparticles via the amino group, <sup>15</sup>N NMR spectroscopy was carried out.

Quantitative <sup>13</sup>C NMR spectroscopy and atomic absorption spectroscopy enabled the calculation of a loading of approximately 100 L-cysteine molecules on each gold nanoparticle. By X-ray photoelectron spectroscopy, 95% elemental gold was identified whereas about 5% was oxidized. This confirms the existence of metallic gold nanoparticles, functionalized with L-cysteine as model compound.

We show that NMR spectroscopy is especially well suited to analyze ultrasmall gold nanoparticles due to their small particle size, leading to excellent spectra of dispersed nanoparticles that elucidate the binding situation of L-cysteine on the gold surface.

**2:15 PM NM02.02.03**

**Electron Beam Induced Growth of Metal Nanoparticles in Metal-Polydopamine Complex** [Haoqi Li](#), Yao Zhao and Fei Ren; Temple University, Philadelphia, Pennsylvania, United States.

Polydopamine (PDA) is a nature inspired biopolymer that can be synthesized through self-assembly under mild controlled environment. Due to the catechol functional groups, PDA can form coordination bonding with various metallic ions. In our work, we utilized the strong affinity between PDA and various metal cations, including Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Co<sup>2+</sup>, to obtain metal ion doped PDA (mPDA). The mPDA powders were irradiated under electron beam using a transmission electron microscope. As the electron beam intensity increased, nucleation and growth of nanoscale precipitates were observed. Electron diffraction and EDX analysis indicated these precipitations were metal nanocrystals. The morphology of the metal nanoparticles varied depending on the metal specie. This discovery indicates electron and perhaps other irradiation sources can be used to induce nanoparticle in metal-doped PDA, which may be useful to modify the properties of PDA-based thin film materials. On the other hand, our study implies PDA can be used as a platform for growth of nanoparticles, which may have potentials in various engineering applications.

### 2:30 PM NM02.02.04

**Superlinear Photoluminescence from Pt Nanoclusters Embedded in Silica and Sapphire Matrices** [Jhovani Bornacelli](#)<sup>1</sup>, Carlos Torres Torres<sup>1</sup>, Alejandro Crespo-Sosa<sup>2</sup>, Juan-Carlos Cheang-Wong<sup>2</sup> and Alicia Oliver<sup>2</sup>; <sup>1</sup>Sección de Estudios de Posgrado e Investigación, Escuela Superior de Ingeniería Mecánica y Eléctrica Unidad Zacatenco, Instituto Politécnico Nacional, Ciudad de México, Mexico; <sup>2</sup>Instituto de Física, Universidad Nacional Autónoma de México (UNAM), Mexico City, Mexico.

In recent years, small metal nanoclusters (with sizes below 2 nm) have emerged as quite interesting materials because their optical properties differ from those of larger clusters or plasmonic nanoparticles. One of the new properties exhibited by these systems is their photoluminescence, probably due to the discretization of the electron density of states. Light emission from metal nanoclusters can be relevant in technological applications as primary nanosource of light or as a nanoantenna to enhance light-matter interaction. Herein, we study the photoluminescence (PL) emission from Pt metal nanoclusters embedded in silica and sapphire plates, by using the ion implantation technique. The PL signal ranges from 400 nm to 600 nm, with a peak at 550 nm for all samples irrespective of the matrix type. We have observed a gradual change in the behavior of the PL intensity as increasing the power density of picosecond pulse excitation in the UV range. PL intensity increases linearly at lower pump excitation and reaches a saturation behavior for intermediate power density. However, as the excitation power increases above  $\sim 7 \text{ kW/m}^2$ , the PL response become more intense, and it can be considered as superlinear with respect the excitation laser intensity. This optical behavior is in clear contrast compared with the usual observations in semiconductor quantum dots, where the PL intensity saturates at higher fluence excitation. The observed superlinear PL from Pt nanoclusters is analyzed in terms of multi-photon excitations.

### 2:45 PM NM02.02.05

**Investigating Mechanisms of Non-Equilibrium Etching of Nanocrystals Using Liquid Cell TEM** [Matthew Hauwiler](#)<sup>1</sup>, Layne Frechette<sup>1</sup>, Matthew R. Jones<sup>2</sup>, Justin Ondry<sup>1</sup>, Phillip Geissler<sup>1</sup> and A. P. Alivisatos<sup>1</sup>; <sup>1</sup>University of California-Berkeley, Berkeley, California, United States; <sup>2</sup>Rice University, Houston, Texas, United States.

The emergent properties of colloidal nanomaterials are dependent on their shape and exposed facets, so mechanistic understanding of atomic formation and removal is critical. Non-equilibrium synthetic methods are powerful tools for making energetically unfavorable shapes and facets, but studying these processes is challenging. Liquid cell Transmission Electron Microscopy (TEM) enables single nanoparticle dynamics to be monitored in their native liquid environment with the necessary spatial and temporal resolution to observe shape and facet evolution. Studying non-equilibrium etching of gold nanocrystals has provided insight into fundamental formation mechanisms of nanocrystals with high-energy facets.

Graphene liquid cell TEM encapsulates small pockets of liquid between graphene sheets for imaging using a transmission electron microscope. Oxidative etching of gold nanocrystals in the graphene liquid cell was induced through a combination of pre-loaded iron chloride and oxidative species generated by electron beam induced radiolysis. Control of the chemistry in the graphene liquid cell pockets allowed the nanocrystal dynamics and mechanisms to be related back traditional synthetic techniques. The electron beam dose rate controlled the rate of atom removal, and the initial concentration of iron chloride established the potential of the oxidative etching.

Pre-synthesized gold nanocubes and nano-rhombic dodecahedra (RDD), with  $\{100\}$  and  $\{110\}$  surface facets respectively, were oxidatively etched while monitoring the effect of chemical potential on the facet trajectories. Both the cubes and RDD transformed to intermediate tetrahedra (THH) shapes with  $\{hk0\}$  surface facets. When etching the cubes in this non-equilibrium regime, lower initial concentrations of iron chloride led to intermediate  $\{hk0\}$  facets with lower  $h/k$  values. However, etching the RDD at differing initial iron chloride concentrations led to same intermediate THH with  $\{hk0\}$  facets of  $h/k = 2.5$ . Monte Carlo simulations corroborated the role of chemical potential in controlling the facets for the cubes but not the RDD. Zero temperature kinetic models show that removing a 6-coordinated edge atom on the nanocrystals reveals 7-coordinate inner atoms for cubes but 6-coordinate inner atoms for RDD. Therefore, chemical potential controls the facets for cubes by modulating the probability ratio of removing inner versus edge atoms. This fundamental understanding of kinetically-driven shape transformations will aid efforts to make nanocrystals with high-energy facets.

Through these in situ TEM studies, the formation of non-equilibrium nanocrystal structures were watched at the single particle level in solution, and the mechanisms of etching were elucidated. This mechanistic understanding of nanocrystal etching will hopefully inform future synthetic efforts to control facets and structures for energetically unfavorable shapes.

### 3:00 PM BREAK

### 3:30 PM \*NM02.02.06

**Hydrogen-Doped Gold-Based Superatoms—Synthesis, Structure and Transformation** [Tatsuya Tsukuda](#)<sup>1,2</sup>; <sup>1</sup>University of Tokyo, Tokyo, Japan; <sup>2</sup>Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto, Japan.

Gold clusters protected by ligands or stabilized by polymers are viewed as superatoms from the analogy of the electronic structures with those of the conventional atoms. It has been demonstrated that H atom mimics Au atoms in bare Au clusters: the electronic and geometric structures of Au clusters are retained after replacement of the Au atom with H atom [1]. A recent theoretical study proposed that an H atom behaves as an Au atom in the Au cluster  $\text{Au}_{25}(\text{SR})_{18}$  (SR = thiolate) and contributes its 1s electron to the superatomic electron count [2]. Small nonplasmonic Au clusters stabilized by polymer exhibit localized surface plasmon resonance in the presence of  $\text{NaBH}_4^-$  due to electron donation from the adsorbed H atoms [3,4]. These results suggest that structures and properties of gold superatoms can be tuned through doping H atoms. However, a molecular-level understanding has not been attained about the interaction between H and Au superatoms.

The present work focuses on the interaction of H with phosphine-protected Au-based clusters  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$  and  $[\text{PdAu}_8(\text{PPh}_3)_8]^{2+}$  which can be viewed as oblate superatoms with 6 electrons. We observed by mass spectrometry and NMR spectroscopy that a hydride ( $\text{H}^-$ ) was doped into these gold-based oblate superatoms upon the reaction with  $\text{NaBH}_4^-$ . Density functional theory calculations of the products  $[\text{Au}_9\text{H}(\text{PPh}_3)_8]^{2+}$  and  $[\text{PdHAu}_8(\text{PPh}_3)_8]^{2+}$  demonstrated that hydride is bonded to a coordinatively unsaturated site at the center and that the  $(\text{Au}_9\text{H})^{2+}$  and  $(\text{PdHAu}_8)^+$  core can be viewed as nearly spherical superatom with closed electronic shells. The hydride-doped superatoms  $(\text{Au}_9\text{H})^{2+}$  was successfully converted to the well-known  $\text{Au}_{11}^{3+}$  superatoms by the reaction with Au(I) complexes, while the hydride in the  $(\text{PdHAu}_8)^+$  remained during the growth to  $(\text{PdHAu}_{10})^+$ . These hydride-mediated growth processes will provide a new atomically precise synthesis of Au clusters via bottom-up approach.

[1] Buckart, S.; Ganteför, G.; Kim, Y. D.; Jena, P. *J. Am. Chem. Soc.* **2003**, *125*, 14205.

[2] Hu, G.; Tang, Q.; Lee, D.; Wu, Z.; Jiang, D.-e. *Chem. Mater.* **2017**, *29*, 4840.

[3] Ishida, R.; Yamazoe, S.; Koyasu, K.; Tsukuda, T. *Nanoscale* **2016**, *8*, 2544.

[4] Ishida, R.; Hayashi, S.; Yamazoe, S.; Kato, K.; Tsukuda, T. *J. Phys. Chem. Lett.* **2017**, *8*, 2368.

### 4:00 PM NM02.02.07

**Stronger-Than-Pt Hydrogen Adsorption in a Au<sub>22</sub> Nanocluster for the Hydrogen Evolution Reaction** [Guoxiang Hu](#)<sup>1</sup>, Zili Wu<sup>2</sup> and De-en Jiang<sup>1</sup>; <sup>1</sup>University of California, Riverside, Riverside, California, United States; <sup>2</sup>Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Atomically precise metal nanoclusters have recently emerged as a novel class of catalysts for the hydrogen evolution reaction. From first-principles density functional theory, we show that the eight coordinatively unsaturated (cus) Au atoms in the  $\text{Au}_{22}(\text{L}^8)_6$  cluster [ $\text{L}^8 = 1,8\text{-bis}(\text{diphenylphosphino})\text{ octane}$ ] can adsorb H stronger than Pt, thereby being a potentially promising catalyst for the hydrogen evolution reaction (HER). We find that up to six H atoms can adsorb onto the  $\text{Au}_{22}(\text{L}^8)_6$  cluster and they have close-to-zero Gibbs free adsorption energies ( $\Delta G_{\text{H}}$ ). From the HOMO–LUMO gaps, frontier orbitals, and Bader charge analysis, we conclude that H behaves as a hydride or electron-withdrawing ligand in the  $\text{Au}_{22}(\text{L}^8)_6$  clusters, in contrast to the metallic H in thiolate-protected Au nanoclusters. Our study demonstrates that ligand-protected Au clusters with cus Au sites will be the most promising candidates for realizing Au–H nanoclusters and can act as excellent electrocatalysts for the HER.

**4:15 PM \*NM02.02.08**

**Dissecting the Structure-Property Interplay of Nanometals Using Ultrafast Two-Dimensional Electronic Spectroscopy (2DES)** Kenneth L. Knappenberger, Hongjun Zheng and Patrick Herbert; The Pennsylvania State University, University Park, Pennsylvania, United States.

Monolayer-protected clusters (MPCs) represent a class of nanomaterials that can be synthesized and isolated with structural (both compositional and geometric) specificity. Hence, MPCs provide model systems for understanding the nanoscale structure-function interplay. We have recently shown that femtosecond time-resolved two-dimensional electronic spectroscopy (2DES) can be used to isolate carrier dynamics of specific MPC electronic states. Here, 2DES studies of a family of MPCs in the 1-2 nm size range will be presented. These results show that the optical, electronic, and spin-state properties of MPCs are extremely sensitive to the electronic configuration of nanometal orbitals. For example, the magnetic properties of  $\text{Au}_{25}(\text{SR})_{18}$ , where SR represents an alkanethiol, can be switched reversibly by oxidative opening of the eight-electron Superatom P orbital. Electronic interactions between assembled MPCs also exhibit spin-dependent magnetic phenomena not present in the isolated building blocks. Ultrafast spectroscopy on dimerized 20-atom MPCs reveal inter-particle spin-dependent dynamics not observed for the monomer. In contrast to the discrete carrier dynamics typical for MPCs, larger nanoparticles exhibit collective electronic behavior. I will provide a comprehensive description of how 2DES can be employed to describe the dynamics of metals spanning the non-metallic cluster and metallic particle domains.

SESSION NM02.03 Poster Session I  
Session Chairs: De-en Jiang and Grant Johnson  
Monday Afternoon, November 26, 2018  
8:00 PM - 10:00 PM  
Hynes, Level 1, Hall B

**NM02.03.01**

**Gold Treatment of Silver Nanoparticles and Their Enhanced Antimicrobial Activity** Takuro Niidome<sup>1</sup>, Kaung Kyaw<sup>1,2</sup>, Hiroaki Ichimaru<sup>1</sup>, Masayuki Tsushida<sup>3</sup>, Yuta Miyazawa<sup>4</sup> and Daigou Mizoguchi<sup>4</sup>; <sup>1</sup>Faculty of Advanced Science and Technology, Kumamoto University, Kumamoto, Japan; <sup>2</sup>Department of Chemical Engineering, Yangon Technological University, Yangon, Myanmar; <sup>3</sup>Technical Division, Faculty of Engineering, Kumamoto University, Kumamoto, Japan; <sup>4</sup>Dai Nippon Toryo Co., Ltd., Otawara, Japan.

It has been known that silver ions released by silver nanoparticles have bactericidal effect against a wide spectrum of bacteria. Silver ions can induce redox reactions on the membrane transport proteins of bacteria thereby deactivating them. Silver ions are also capable of impairing the energy transfer mechanism of bacteria during respiration process. However, the nanoparticles are unstable and easily form aggregates, which decreases their antibacterial activity.

To improve the dispersion stability of silver nanoparticles in aqueous media, and to increase their effectiveness as antibacterial agents, we coated triangular plate-like silver nanoparticles (silver nanoplates, Ag NPLs) with one or two layers of gold atoms ( $\text{Ag@Au1L}$  NPLs and  $\text{Ag@Au2L}$  NPLs, respectively). These gold coatings improved the dispersion stability in aqueous media with high salt concentrations.  $\text{Ag@Au1L}$  NPLs showed stronger antibacterial activity on pathogenic bacteria than Ag NPLs and  $\text{Ag@Au2L}$  NPLs. Furthermore, the  $\text{Ag@Au1L}$  NPLs decreased the number of bacteria living in RAW 264.7 cells. The  $\text{Ag@Au1L}$  NPLs displayed no cytotoxicity towards RAW 264.7 cells, and the  $\text{Ag@Au1L}$  NPLs could be used as an antibacterial agent for intracellular bacterial infections.

Next, we prepared hollow-shaped alloy nanoparticles made of silver and gold atoms (Ag/Au NPs) by treating silver nanoparticles with gold ions, not core-shell type gold-coated silver nanoparticles as described in the previous section. The antibacterial activity of the hollowed Ag/Au alloy nanoparticles was stronger than the original silver nanoparticles. Additionally, the release of silver ions from the hollowed Ag/Au nanoparticles was higher than the original silver nanoparticles.

The gold atoms on the surface of silver nanoparticles or in the alloy nanoparticles made of silver and gold atoms affected the oxidation of the silver atoms in the nanoparticles. Since chloride ions can affect the migration of gold atoms on silver, in turn, the migration of gold atoms might affect the exposure of silver metals to the culture medium and the subsequent release of silver ions. These gold treatments are effective methods to improve the antimicrobial activity of silver nanoparticles.

**NM02.03.02**

**Surface Architecting in Palladium Nanoparticle Synthesis** Nam Heon Cho, Hye-Eun Lee, Hyo-Yong Ahn and Ki Tae Nam; Seoul National University, Seoul, Korea (the Republic of).

Morphology dependent properties of nanoparticles have been utilized in various applications and especially nanoparticles composed of high-index facets have attracted significant attention in catalysis with its high density of atomic steps serving as active sites for reactions. However, despite vigorous efforts for delicate control of nanoparticle morphology, controlled fabrication of specific surface structures within a few nanometer scale still remains as a big challenge due to instability of high-index facets. Previously, we demonstrated aqueous based seed-mediated two step growth method to synthesize high-indexed gold nanoparticles with morphological variations by control of reaction parameter and introduction of organo-thiol shape controlling additives. Strong interactions between the organo-thiol based additives and the metal surface induces directional growth depending on the shape-modifier structures. Herein, based on this established system, we demonstrate precise surface structure control with organo-thiol additive during palladium nanoparticle synthesis. Resulting nanoparticles show multi-stepped surface structures which varies from cubic based planar step patterns to spiral step patterns composed of multiple high-index facets. We demonstrate superior catalytic activity of “multi-stepped” nanoparticles. Morphology variation is originated from collaborative interactions between kinetic modifiers and shape modifying additives during the growth step. Reduction kinetic was controlled by growth solution pH, where various types of acids were introduced to the growth solution. Higher proton concentration in the synthesis environment induced slower electron withdrawing of reducing agent to affect geometrical shape and uniformity. Additionally, dramatic change in nanoparticle morphology was observed respect to the acid type when shape modifying organo-thiol group was introduced to the reaction solution. These anion

dependent morphology change is related to specific interactions between organo-thiol molecule and anions to modify growth directionality. Our study provides crucial design constraints for fine morphology tuning during nanoparticle synthesis which allows systematic control of nanoparticle surface structures for potential catalysis application.

#### NM02.03.03

**Correlation Between Positive Surface Charge Density on Silver Nanoparticles and Separation Performances in Facilitated Olefin Transport Membranes** Moon G. Hyeon, Yebin Eum, Il Seok Chae and Yong Soo Kang; Hanyang University, Seoul, Korea (the Republic of).

It has been accepted that the separation performance of olefin/paraffin mixtures has been improved through composite membranes containing silver nanoparticles (Ag NPs) dispersed in a common polymeric matrix when their surface is positively charged by electron acceptor. Here, a correlation between the surface positive charge density, represented by the binding energy, on Ag NPs and the separation performance was explored. The binding energy of Ag atom was reached a maximum value as increasing the concentration of an electron acceptor such as nitroaromatic compounds (NACs). At the highest binding energy, the highest gas separation performance was also obtained: the remarkably high mixed-gas selectivity above 150 for a 50/50 (v/v) propylene/propane mixture and the propylene permeance about 0.9 GPU. The correlation between the surface positive charge density and the gas separation performance was observed to be linear regardless of the electron acceptor used. This correlation thus suggests that the major determinant of the olefin/paraffin gas separation performance is not the chemical characteristics of electron accepting compounds, but the induced surface positive charge density on Ag NPs. Therefore, it is concluded that surface charge density of Ag NPs is a key factor in determining the separation performance of facilitated olefin transport membranes.

#### \*NM02.03.04

**Micro/Nanostructured Lamella Phases Make 2205 Stainless Steel Have Superior Strength and Ductility** Peiqing La, Yu Shi, Keliang Wang and Yi Song; State Key Laboratory of Advanced Processing and Recycling of Nonferrous Metals, Lanzhou University of Technology, Lanzhou, China.

Strength and ductility are mutually trade off usually in steels and alloys. Grain refinement to nanoscale can make the conventional steels several times stronger, but invariably leads to poor ductility. Here we demonstrate a micro/nanostructured lamellar phases in 2205 stainless steel prepared by aluminothermic reaction and followed hot rolling that produced a superior yield strength of 780MPa, ultimate tensile strength of 979 MPa and elongation of 54%. The elongation is the highest in the reported steels with that level of strength. The product of tensile strength and elongation exceeds 50 GPa% and is the highest value that was reported in the literatures. The steel consists of micro/nanostructured lamellar ferrite phase and micro/nanostructured lamellar austenitic phase in which the dislocation free hard nano grains dispersed in soft coarse grains. The high strength is attributed to strengthening of dislocation free nano grains and interface between the two phases. The unusual high ductility originates from cracks propagation resistance by the nano grains and the two phase interfaces.

#### NM02.03.05

**Highly Efficient Ni-B Amorphous Alloyed Catalysts on Ni Foam for Nitrobenzene Hydrogenation** Gang Chen<sup>1,2</sup>, Xun Zhu<sup>1,2</sup>, Rong Chen<sup>1,2</sup>, Qiang Liao<sup>1,2</sup>, Dingding Ye<sup>1,2</sup> and Biao Zhang<sup>1,2</sup>; <sup>1</sup>Key Laboratory of Low-grade Energy Utilization Technologies and Systems (Chongqing University), Chongqing, China; <sup>2</sup> Institute of Engineering Thermophysics, Chongqing University, Chongqing, China.

In this work, Ni-B amorphous alloyed catalysts used for a gas-liquid-solid three phase reaction were synthesized on Ni foam by electroless plating method, which was evaluated by the reference reaction of nitrobenzene hydrogenation. Such design offered several advantages. First of all, the low-cost Ni-B amorphous alloyed catalysts showed superior catalytic activity and selectivity towards the hydrogenation reaction. Besides, the use of Ni foam as the support materials could increase the surface area for loading the Ni-B amorphous alloyed catalysts. Moreover, its interconnected macropore structure was beneficial for the transport of the gas/liquid reactants to the active sites. The morphologies and size distributions and the chemical composition of the prepared Ni-B amorphous alloyed catalysts were characterized by SEM, XRD and XPS, respectively. The actual loading of the Ni-B amorphous alloyed catalysts was analyzed using ICP-MS technology. The hydrogen chemisorption on the Ni-B amorphous alloyed catalysts was characterized by temperature programmed desorption of H<sub>2</sub> (H<sub>2</sub>-TPD) analyses. Finally, the catalytic performance was evaluated by nitrobenzene hydrogenation in a continuous flow monolithic microreactor under various parameters. The experimental results indicated that the developed Ni-B amorphous alloyed catalysts deposited on the Ni foam was able to improve the catalytic performance.

#### NM02.03.06

**Effect of Nanoparticles on Liquid State Dewetting of Bismuth Thin Films** Krishna Kumar, Mrudula Kavuri and Parasuraman Swaminathan; Indian Institute of Technology Madras, Chennai, India.

Metallic thin films are unstable in as deposited state. These films tend to break up and agglomerates when annealed. This is known as dewetting and driven by surface energy minimization of the film – substrate interface. Dewetting occurs in both solid and liquid state and while it can be detrimental, where high temperature performance is required, it can also be used to fabricate nanoparticles arrays on substrate for different applications [1].

Enhancing the thermal stability of metallic thin films is of importance, especially for high temperature applications. Recently, we reported that addition of silver nanoparticles on copper thin films suppresses the solid state dewetting of copper thin film [2]. In this work, we explore the effect of added nanoparticles on the liquid state dewetting behaviour of bismuth thin films. We study three system, copper, silver and gold nanoparticles deposited on bismuth thin films on amorphous carbon TEM grids. Transmission electron microscopy results shows that gold and silver nanoparticles accelerate bismuth dewetting, while copper nanoparticles suppress the process. A model is presented to explain these differences.

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#### NM02.03.07

**Inkjet Printed Encapsulation of Gold Nanoparticles inside Cell-Adhesive Chitosan Hydrogels** Álvaro Artiga<sup>1,2</sup>, Sonia García-Embid<sup>1,2</sup>, Inés Serrano-Sevilla<sup>1,2</sup>, Gabriel Alfranca<sup>1</sup>, Laura De Matteis<sup>3,2</sup>, Scott G. Mitchell<sup>1,2</sup>, Carlos Sánchez-Somolinos<sup>1,2</sup> and Jesús M. de la Fuente<sup>1,2</sup>; <sup>1</sup>Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC/University of Zaragoza, Zaragoza, Spain; <sup>2</sup>CIBER-BBN, Instituto de Salud Carlos III, Madrid, Spain; <sup>3</sup>Instituto de Nanociencia de Aragón (INA), University of Zaragoza, Zaragoza, Spain.

The unique physicochemical properties of gold nanoparticles (AuNPs) make them highly applicable for drug release, optoacoustic imaging, biosensing and photothermal therapy, among others. This work highlights unique methodologies for the encapsulation of AuNPs in chitosan hydrogels to increase their applicability and efficacy in health-related applications, in particular for photothermal therapy (PTT).

In PTT, AuNPs are employed to convert light energy into heat for the selective ablation of target cells. Anisotropic AuNPs such as nanoprisms, rods and stars, are frequently employed because they absorb near-infrared light that is harmless for surrounding cells. In previous work, we have compared the heating capability, cellular internalization, toxicity and thermoablation capacity of two different types of anisotropic AuNPs: gold nanorods (AuNRs) and nanoprisms (AuNPrs) [1]. Although both AuNPs were highly efficient photothermal converters, AuNRs possessed a more efficient heating capability. However, the *in vitro* thermoablation studies clearly demonstrated that AuNPrs were more effective at inducing cell death by PTT due to their greater cellular internalization, while AuNRs could not be employed for this purpose due to their extremely low cellular internalization.

We succeeded in improving the PTT application of AuNRs by entrapping them inside a cell-adhesive chitosan hydrogel using anionic polyoxometalates (POMs) as gelling agents [2]. These functional nanocontainers remained non-cytotoxic and presented the ability to adhere to the cytoplasmic membranes of cells avoiding any need for cellular internalization, thus rendering them as highly efficient PTT agents. However, one key disadvantage of this entrapment methodology is the lack of control of the size and size-dispersion of the nanocontainers.

In order to improve these drawbacks, we have developed a novel strategy for AuNP microencapsulation in chitosan hydrogel by inkjet printing [3]. Inkjet printing, as a high-throughput, continuous and automatic technology poses relevant industrial potential for microencapsulation. In particular, our approach has showed a high rate of production, excellent control of the microcapsules size, high encapsulation efficiency and ease of scale-up; obtaining almost monodisperse chitosan microcapsules containing AuNPs. We are currently studying the use of these chitosan hydrogels for oral administration of gold nanoparticles *in vitro* and *in vivo*.

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#### NM02.03.08

**Fabrication and Morphological Control of Palladium Film with Three-Dimensional Nano-Network Structure as a Hydrogen Gas Sensing Material by Organic Acid Chelation** Takuji Ube, Akizumi Kawamoto, Tomoya Nishi and Takashi Ishiguro; Department of Material Sciences, Tokyo University of Science, Tokyo, Japan.

The large specific surface area of nano-porous materials realizes both high catalytic activity and resource savings. Thin film materials have homogeneity in large areas and can be applied to sensor devices or electrode materials for batteries. The traditional and general method of fabricating a nano-porous noble metallic thin film is the dealloying method, i.e., the selective corrosion of an alloy of a noble metal and a base metal by a strong acid, such as hydrochloric acid or sulfuric acid. In this study, we fabricated a palladium (Pd) thin film with three-dimensional (3D) nano-network structure (3DPdNNF) by the dealloying method without discharging any material with possibly high environmental impact, such as waste solution containing heavy metals or strong acids. The dealloying was conducted in aqueous solutions of organic chelating agents of citric acid and ethylene-diamine-tetraacetic acid (EDTA) and sodium carbonate. All agents are used as a food additive and have environmentally friendly characteristics. Furthermore, the base metal used was aluminum (Al). However, Pd has a hydrogen-storage property with hydrogen gas selective permeation, and it is expected to be useful for developing sensor devices to detect only hydrogen gas. However, pure Pd metal has low repetitive durability for hydrogen gas exposure due to irreversible deformation and destruction caused by its hydrogen-storage property. In this study, we aimed to fabricate a 3DPdNNF by the above method and utilize its stress relaxing action due to the nano-network structure to apply it to a hydrogen gas sensor with repetitive durability.

The thin film preparation was performed using the RF-sputtering method, and Al-Pd alloy (82at% Al–18 at% Pd) films were deposited on substrate (glass, Si wafer, and elastic carbon film) to a thickness of 70 nm. The dealloying process was conducted in mixed aqueous solution of organic chelating acid (100  $\mu\text{mol/L}$ ) and sodium carbonate for pH adjustment. The optimized pH value and temperature were 10.0 and 368 K, respectively.

The Al-Pd film was reformed to uniform 3DPdNNF with high Pd purity (> 99 at% Pd). The pore size of the network could be controlled to within the range of 2.90–12.5 nm by three parameters of the gas conditions during the sputtering deposition and the pH values and chelating agents in the dealloying processes. Furthermore, we evaluated the hydrogen gas sensing performance as a 3DPdNNF utilization of a high Pd purity and large specific surface area film. The fabricated 3DPdNNF showed a response to hydrogen gas by changing the electrical resistance in the  $\text{k}\Omega\text{cm}$  range with repetitive durability for hydrogen gas exposure.

#### NM02.03.09

**Sputter Deposition onto Liquid to Prepare Pt and Pt Alloy Nanoparticles** Lianlian Deng<sup>1</sup>, Mai Thanh Nguyen<sup>1</sup>, Tomoharu Tokunaga<sup>2</sup>, Syo Matsumura<sup>3</sup> and Tetsu Yonezawa<sup>1</sup>; <sup>1</sup>Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Japan; <sup>2</sup>Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Nagoya, Japan; <sup>3</sup>Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, Fukuoka, Japan.

Platinum (Pt) and Pt-based (e.g. Pt/Cu, Pt/Au, Pt/Ag) alloy nanoparticles (NPs) have been demonstrated as high performance catalysts. Usually Pt and Pt-based alloy NPs have been synthesized via chemical reduction methods. However, impurity and incomplete removal of byproducts and toxic reductants can hinder catalytic properties. On the other hand, due to the difference in reduction potential of metal salts and/or difference in decomposition temperature of metal complexes, core-shell structure or phase segregation were observed in the formed bimetallic NPs. This is often seen in bimetallic NPs of immiscible elemental components in the bulk state such as Pt/Au. In our research, we have proposed to prepare highly uniform Pt and Pt alloy NPs, such as Pt/Cu and Pt/Au alloy NPs, by sputtering at room temperature onto a low vapor pressure liquid, polyethylene glycol (PEG, Mw 600). The method combines the advantages of sputtering to produce atoms and clusters for any metals from the bulk counterparts and the suppression and control of particle growth by the liquid medium in vacuum sputtering chamber. Thus varying the sputtering parameters allows for particle size control and tunable alloy NPs' composition. Sputtering was performed onto PEG and TEM grid. Sputtering current applied to each magnetron was separately controlled and varied in order to tune the composition in the resulting bimetallic NPs. Various characterization methods such as UV-Vis, XRD, XPS, TEM, HRTEM and STEM-HAADF and STEM-EDX mapping have been used to analyze the obtained NPs. TEM, HRTEM and STEM showed that Pt NPs with tunable sizes from 0.9 nm to 1.4 nm and narrow size distribution were produced. In addition, we found that negligible particle aggregation happened in PEG and Pt NPs were stable even after keeping in the dark at room temperature for several months. The slight growth of Pt NPs in PEG during storage was found accompanied with the consumption of free Pt atoms in PEG. The method was applied for a Pt/Cu alloy target and the effect of sputtering parameters such as sputtering time, the rotation speed of PEG on particle size has been studied. Pt<sub>29</sub>Cu<sub>71</sub> alloy NPs have been synthesized by sputter deposition for the first time. Furthermore, we showed that we were able to produce Pt/Au alloy NPs using a double-target sputtering. The target design allowed us to finely control Pt/Au alloy NPs' composition via simultaneous sputter deposition onto PEG. The results showed that particle size and composition are strongly correlated and can be tailored by varying the sputtering current. Increasing Pt content resulted in smaller particle size and particles with same composition had similar sizes. Moreover, the agglomeration of NPs is dependent on the Pt content. Our findings in the relation among particle size, particle composition, and aggregation state of the formed NPs with respect to its composition can shed light into the formation mechanism of Pt-based alloy NPs.

#### NM02.03.10

**The Role of Silver Nano-Particles/Colloids on Conduction Mechanisms of Current Through Ag Gridlines of Si Solar Cell** Keming Ren, Veysel Unsur, Ahrar A. Chowdhury, Tang Ye and Abasifreke Ebong; Chemistry, University North Carolina at Charlotte, Charlotte, North Carolina, United States.

Fire through dielectric (FTD) contact is the dominant technology for contacting a commercial silicon solar cell because of its low-cost and high throughput attributes. During the FTD process, the glass frits in the Ag paste melt and etch the dielectric (anti-reflecting layer) first, to have Ag metal contact directly to the bulk Si. The redox reaction between the glass frits melting and dielectric etching leads to the formation of a recrystallized glass layer, which distributes within the Ag gridlines and bulk Si emitter surface, and silver nano-particles, which are mainly silver alloys (Ag<sub>2</sub>Te and PbTe) encapsulated in the glass layer. When without the Ag<sub>2</sub>Te and PbTe nano-particles/colloids, due to the existence of glass layer, silver gridlines rarely directly contact with the bulk silicon and electrons have to tunnel through the glass layer. However, in this work, Ag<sub>2</sub>Te and PbTe are semimetals which have very narrow bandgaps. The existence of Ag<sub>2</sub>Te and PbTe nano-particles/colloids in the glass layer can change the electrical property of the glass layer. Thus, the specific contact resistance of silver gridlines cannot be calculated based on simplified metal-semiconductor contacts. The possible electron transport on the silver/silicon interface includes: 1. through silver gridline contact directly with bulk silicon; 2. tunneling through an ultrathin glass layer; 3. through Ag<sub>2</sub>Te and PbTe nano-particles assisted tunneling; 4. through multistep tunneling. This suggests that the contact resistivity in the presence of Ag<sub>2</sub>Te and PbTe nano-particles/colloids is independent of the inverse square root of emitter peak surface concentration. Lower contact resistances were measured in the presence of Ag<sub>2</sub>Te and PbTe nano-particles on the silicon emitter with relatively low peak surface concentration.

#### NM02.03.11

**Kinetics of Detwinning in Chemical Vapor Deposited Nickel—Critical Structures Determining the Stability of Nano-Twin Lamellas** Hao Sun; Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario, Canada.

Nickel carbonyl vapor deposition (CVD) is a novel metal-forming process used to produce thin-shell molds with a higher level of efficiency and a lower cost than traditional mold making techniques. Not only is the production process highly effective, but the deposited CVD Nickel shell is also both harder (a tensile yield strength of ~584MPa) than conventional polycrystalline Nickel (~100MPa) with a grain size of 10nm and more ductile (a failure strain of ~13%) than nanocrystalline electroformed Nickel (4-7%) with a grain size of 21-30nm. The combination of high strength and high ductility of the CVD Nickel shell is attributed to its unique bi-modal grain structure with large columnar grains embedded in a nanocrystalline matrix. A high density of nano-twins in large columnar grains significantly improve the working hardening capacity and ductility of CVD Nickel, but they are thermodynamically unstable. Most coherent twin boundaries (CTBs) transform into dislocation cells during annealing at temperature higher than 400 degree centigrade. While the driving force for detwinning is well-known, the mechanism by which CTBs disappear is still puzzling. Based on both experimental observation and simulation analysis, we found that although the driving force for detwinning is determined by the density of nano-twins, the thermal stability of each CTB in CVD Nickel is only determined by incoherent twin boundaries (ITBs) and its intrinsic grain boundary dislocations (IGBDs). Driven by the tensile strain originated from grain growth in the nanocrystalline matrix of CVD Nickel, IGBDs detach from CTB planes during detwinning. The emerging dislocations rearrange into sub-grain boundaries which then remove some CTBs during their migration. Twin lamellas terminated by ITBs transform back to the matrix stacking by the migrating ITBs which can also release sessile grain boundary dislocations into the crystal. Our results suggest that replacement of the nanocrystalline matrix in CVD Nickel with nano-twin structure can eliminate the tensile strain originated from grain growth, so nano-twins in CVD Nickel without nanocrystalline matrix might have a much higher level of thermal stability than that in CVD Nickel with bi-modal grain size distribution.

#### NM02.03.12

**Electrochemical Synthesis of Ag-Cu Bimetallic Nanostructure for Oxygen Reduction Reaction (ORR)** Jianan Chen and Shien Ping Feng; The University of Hong Kong, Hong Kong, Hong Kong.

Highly active and economic catalysts for oxygen reduction reaction (ORR) are always important for renewable energy technique. Since more than half of the voltage loss in fuel cell comes from the cathodic ORR process, and most of the commercial available catalysts for ORR is Pt-based. Herein, a new Ag-Cu bimetallic nanostructure was developed by electrochemical method, the fabricated Pt-free material shows a great performance towards ORR, which is comparable to the Pt/C commercial catalyst. The selectivity of the catalyst was carefully studied by scanning electrochemical microscope (SECM). Result shows the ORR by Ag-Cu bimetallic nanostructure prefer a four-electron reduction process, with H<sub>2</sub>O as the main product and trace amount of H<sub>2</sub>O<sub>2</sub> can be detected. However, similar pure Ag nanostructure presents a much lower selectivity, which indicates the introduction of Cu is essential. Possible model was established to explain the enhancement as well. This Ag-Cu bimetallic nanostructure suggests a potential to be developed as cathodes in fuel cell, with a highly activity and relative low cost.

#### NM02.03.13

***In Vitro* and *In Vivo* Toxicity of Metal-Doped Titanium Oxide Nanoparticles** Su-Eon Jin<sup>1</sup>, Seok Won Hong<sup>3</sup> and Hyo-Eon Jin<sup>2</sup>; <sup>1</sup>Inha University, Incheon, Korea (the Republic of); <sup>2</sup>Aju University, Suwon, Gyeonggi-do, Korea (the Republic of); <sup>3</sup>Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Metal-doped titanium oxide (TiO<sub>2</sub>) nanoparticles were developed as enhanced photocatalysts with disinfection and purification potential. However, they can be hazardous to both the environment and human health. In this study, the toxicity of nickel (Ni) and platinum (Pt)-doped TiO<sub>2</sub> nanoparticles (Ni-TiO<sub>2</sub> and Pt-TiO<sub>2</sub> nanoparticles) to skin and eye cells and a mouse skin model was evaluated. Physicochemical properties of nanoparticles were characterized using field emission-scanning electron microscopy, field emission-transmission electron microscopy, and X-ray photoelectron spectroscopy. Cytotoxicity was also evaluated at concentrations of 0.0001 to 10 mg/mL in HaCaT and ARPE-19. To investigate *in vivo* acute toxicity, 1 to 123 mg nanoparticles/1.5 cm<sup>2</sup> were applied to hair-removed dorsal skin in a mouse model, and skin tissues and body condition were monitored. Metal-doped TiO<sub>2</sub> nanoparticles had a spherical crystalline shape with nanoscale sizes less than 100 nm. In nanoparticles, 1.0% Ni<sub>2</sub>p and 0.26% Pt<sub>4</sub>f were detected at 871.2 eV and 74.4 eV for Ni-TiO<sub>2</sub> and Pt-TiO<sub>2</sub> nanoparticles, respectively. Cell viability in HaCaT was higher than that in ARPE-19 at a range of 0.1 - 10 mg/mL nanoparticles. In ARPE-19, superior cell viability was observed at 1.0 mg/mL and more than 1.0 mg/mL Ni-TiO<sub>2</sub> nanoparticles compared with Pt-TiO<sub>2</sub> nanoparticles. *In vivo*, body weight and AST/ALT levels were not significantly altered by Ni-TiO<sub>2</sub> nanoparticle exposure. Histology, skin thickness, and inflammation grade were also comparable to control mice. Thus, metal-doped TiO<sub>2</sub> nanoparticles show minimal toxicity in skin cells and a mouse skin model, indicating their potential for various applications.

#### NM02.03.14

**Morphological and Microstructural Evolution of Polycrystalline Thin Films** Resego Phiri; Chemical, Materials and Metallurgical Engineering, Botswana International University of Science and Technology, Palapye, Botswana.

Modern thin film industries require precise tailoring of thin films properties to have excellent performance at specific applications intended. Atomic scale understanding of the microstructure of polycrystalline thin films is necessary for the control and manipulation of the film properties for a wide range of industrial applications. Thin film growth of thin films influence grain shapes, distribution of grains and the crystallographic orientation of the grains thereby affecting their reliability and performance. This article reviews the present understanding of the mechanism(s) determining the microstructural

evolution of polycrystalline films and the related structure zone models. General trends in microstructural evolution, grain morphology and texture formation mechanisms are discussed in terms of their fundamental kinetic processes. The temperature dependency of the film microstructure is described using Thornton structure zone models.

#### NM02.03.15

**Synthesis and Characterization of Redox-Sensitive Mixed Metal Complexes** [Joseph T. Race](#), Lauren Knappenberger and Scott Williams; Rochester Institute of Technology, Rochester, New York, United States.

A mixed metal inorganic complex which resembles redox sensitivity will be presented. Molecular switches experience a reversible physical change due to various external stimuli such as: high energy radiation, electrical current, heat, magnetic fields, and ultraviolet or visible light. We have synthesized a series of Group IVB and VB complexed to VIIIIB metals that undergo intermolecular electron transfer upon high energy exposure resulting in a state change. In addition, we have found that substituting a Group IVB with selected Lanthanide metals results in fluorescently active compounds. We will present how the structure dictates the function of these complexes as sensors by analysis using nuclear magnetic resonance spectroscopy (NMR), Fourier-transform infrared spectroscopy (FT-IR), Raman spectroscopy, ultraviolet and visible spectroscopy (UV-Vis), fluorescence spectroscopy, energy dispersive x-ray spectroscopy, and cyclic voltammetry.

#### NM02.03.16

**Ni/Co Nanocrystalline Film and Nanowires Grown via High Speed Electrodeposition on Untreated Titanium** [Gaurab Panda](#)<sup>1</sup>, Mohammed S Hussien<sup>2</sup>, Virginia M. Ayres<sup>1</sup>, Haozhi Dong<sup>1</sup>, Kan Xie<sup>1</sup>, Jun H. Ro<sup>1</sup>, Usienemfon Adia-Nimuwa<sup>1</sup> and Harry Shaw<sup>3</sup>; <sup>1</sup>Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan, United States; <sup>2</sup>Birmingham City University, Birmingham, United Kingdom; <sup>3</sup>NASA Goddard Space Flight Center, Greenbelt, Maryland, United States.

A high-speed electrodeposition regime that enables nanocrystalline nickel (Ni), cobalt (Co) and alloy (Ni-Co) film depositions with excellent adhesion characteristics on untreated titanium (Ti) surfaces was recently reported by our group [1]. This was the first report of strong adhesion to an untreated Ti surface without any pretreatment, displacement reaction, or intermediate layer pre-deposition to mitigate the thin tenacious oxide that renders adhesion to Ti a challenge. Under conditions that combined the high flow rate electrodeposition with a higher current density than previously investigated, a new and additional mechanism was enabled that resulted in the growth of highly crystalline Ni, Co and Ni-Co nanowires in addition to the nanocrystalline film. Excellent quality nanowires for high melting point metals are difficult to grow using the standard electrodeposition into nanoporous anodized aluminium templates method [2,3]. The new template-less growth conditions reported here indicate that an alternative method to produce highly crystalline nanowires for high melting point metals has been identified. Novel roles for oxygen, carbon and chlorine chemistries in the nanocrystallite and nanowire growth processes are identified. We identify specific growth models for both nanocrystal and nanowire from quantitative TEM, SEM, SAED, EDS and AFM results.

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#### NM02.03.17

**Fabrication of a Transparent Conducting Electrode Based on Silver Nanowires for Organic Photovoltaic Devices** [Heejeong Shin](#) and Hyosung Choi; Chemistry, Hanyang University, Seoul, Korea (the Republic of).

A solution-processed transparent conducting electrode was fabricated via layer-by-layer (LBL) deposition of graphene oxide (GO) and silver nanowires (Ag NWs). First, graphite was oxidized with a modified Hummer's method to obtain negatively-charged GO sheets, and Ag NWs were functionalized with cysteamine hydrochloride to acquire positively-charged silver nanowires. Oppositely-charged GO and Ag NWs were then sequentially coated on a 3-aminopropyltriethoxysilane modified glass substrate via LBL deposition, which provided highly controllable thin films in terms of optical transmittance and sheet resistance. Next, the reduction of GO sheets was performed to improve the electrical conductivity of the multilayer films. The resulting GO/Ag NWs multilayer was characterized by a UV-Vis spectrometer, field emission scanning electron microscope, optical microscope and sheet resistance using a four-point probe method. The best result was achieved with a 2-bilayer film, resulting in a sheet resistance of  $6.5 \Omega \text{ sq}^{-1}$  with an optical transmittance of 78.5% at 550 nm, which values are comparable to those of commercial ITO electrodes. The device based on a 2-bilayer hybrid film exhibited the highest device efficiency of 1.30% among the devices with different number of graphene/Ag NW LBL depositions.

Ag NWs films exhibited low sheet resistance and high optical transmittance, which are comparable to those of commercial ITO electrode. We fabricated an organic photovoltaic device based on Ag NWs as the anode/V2O5 as the HTL/P3HT:PCBM/Al, and optimized device with Ag NWs exhibited power conversion efficiency of 1.30% and 1.72%.

#### NM02.03.18

**Highly Sensitive Temperature Sensors with Ag Nanocrystal Thin Films** [Bang JunSung](#), Oh Soong Ju, Junhyuk Ahn and Ho Kun Woo; Nanocrystal Electronics Laboratory, Korea University, Seoul, Korea (the Republic of).

We introduce a strategy to design a highly sensitive temperature sensors using Silver (Ag) nanocrystal (NC) thin films. Resistive temperature sensors were fabricated on using poly(dimethylsiloxane) (PDMS) substrate through ligand exchange process [1] and interfacial engineering process. We take advantages of high thermal expansion coefficient of PDMS to control the interparticle distances of Ag NCs, and eventually to improve the sensitivity. We achieved a very sensitivity with temperature coefficient of resistance of 0.1/K. We discussed the origin of the high sensitivity by investigating structural, chemical, electrical, and electromechanical properties as well as the charge transport mechanisms. We also examine the stability, reliability, and sensitivity of our sensors. This work offers an effective way to design low-cost and high-performance sensors.

### NM02.03.19

**Designing Wearable Strain Sensors with Ag Nanocrystals Thin Film Through Halide Ligand Exchange Strategies** [Junhyuk Ahn](#), Soongju Oh, Bang JunSung and Ho Kun Woo; Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of).

Through all solution-processed methods, wearable strain sensors with high gauge factor are demonstrated using thin film of Ag nanocrystals (Ag NCs). Controlling of interval between Ag NCs enables to control a flow of electrons through hopping mechanism and/or tunneling effect, which can enhance gauge factor. In this study, halides ligand treatment is proposed to design interval between nanoparticles to obtain high performances at solid state. Higher sensitivity of ligand treatment with I<sup>-</sup> is demonstrated by comparisons of experimental results of halides; Br<sup>-</sup>, Cl<sup>-</sup>, I<sup>-</sup>. The origin of the higher performance is discussed with various characterization methods. Careful studies to further enhance the sensitivity is conducted by controlling various conditions in ligand exchange process. These high sensitivity thin film Ag NCs strain gauge sensors allow to measure a delicate movement or signal from various objects. This work provides a low cost and simple method to design high sensitivity wearable sensors for various field such as robotics, or healthcare systems.

### NM02.03.20

**Encoded Silver Nanoshells as Surface-Enhanced Raman Spectroscopic Nanoprobes for Diagnosis of Alzheimer's Disease** [In-Jun Hwang](#), Jin-Kyoung Yang, Sin Lee and Jong-Ho Kim; Hanyang University, Ansan, Korea (the Republic of).

Recently, early diagnosis of Alzheimer's disease (AD) has attracted considerable attention in the field of nanomedicine and biosensing. In particular, detection of plasma biomarkers specific for AD, including amyloid beta (A $\beta$ 40 and A $\beta$ 42), is considered a promising, cost-effective, and non-invasive method for diagnosis of AD. Herein, we present a facile approach for designing a nanoprobe based on surface-enhanced Raman scattering (SERS) for the sensitive and selective detection of A $\beta$ 40 and A $\beta$ 42 in blood. To this end, Ag nanoshells (AgNSs) bearing Raman labels were synthesized in a single step under very mild conditions (25 °C and 60 min). As-prepared AgNSs had a uniform shell thickness and nanogaps of 2 nm, resulting in significant electromagnetic field enhancement. In addition, each AgNS exhibited a unique and intense SERS signal without overlapping, allowing the multiplex and sensitive detection of A $\beta$ 40 and A $\beta$ 42. The AgNSs conjugated with a specific antibody for A $\beta$ 40 or A $\beta$ 42 was able to detect each target protein at concentration as low as 100 fg/ml in a fast and simple manner.

### NM02.03.21

**Evaluation of Thin-Film Interfacial Properties Using Single Nanoindentation Test** [Jinwoo Lee](#), Woojoo Kim, Ohmin Kwon and Dongil Kwon; Seoul National University, Seoul, Korea (the Republic of).

Nano technology is developed consistently in all kind of industry like chemical, Bio, Energy. Especially thin-film process improvement and material changes is researching actively. Through variety material and processing, High quality thin film element must have clearly purpose for electric and optical ability and also request a reliable device which is over standard mechanical properties. A thin film's reliable question is depend on interfacial characterization, so evaluating interfacial characterization is the most important things in this test. So far, Peel off test, 4 point bending test and scratch test are usually using among lots of test in order to evaluate a thin film's feature. But those test is inconvenience to make sample, and hard to check a characteristic evaluation of characteristic interface because of mechanical properties. So, this research is introduced how to test a thin-film by indentation test, and confirmed availability of interfacial properties by nanoindentation test.

Determination of the mechanical properties of thin films on substrates by nanoindentation has always been difficult because of the influence of the substrate and interface on the measured properties. In order to measure film-only properties, a commonly used rule of thumb is to limit the indentation depth to less than 10% of the film thickness. As the film gets harder, the substrate and interfacial effects appear at lower indentation depth. Many researchers derived the conclusion from the theoretical and experimental methods. In the case of thin films which have thickness under than from nanometers to micrometers, it has no choice but must include the substrate and interfacial effects. Owing to the quantitative consideration about interfacial effects was hard, modeling equations with no interfacial effects is used.

### NM02.03.22

**Stress-Induced Chemical Reaction of Ti/Si Multilayered Nano-Films** [Hiroyuki Hirakata](#)<sup>1</sup>, Takashi Kawai<sup>2</sup>, Toshiyuki Kondo<sup>2</sup> and Kohji Minoshima<sup>2</sup>; <sup>1</sup>Department of Mechanical Engineering and Science, Kyoto University, Kyoto, Japan; <sup>2</sup>Department of Mechanical Engineering, Osaka University, Osaka, Japan.

When a sufficient energy is applied at a local point in multilayered nano-films composed of alternating layers with a thickness of 10 nm order, an exothermic reaction occurs and a compound is generated at the local region. The generated heat then spreads into an adjacent unreacted region. If the temperature in the neighboring region becomes high sufficient to cause additional mixing, a self-sustained propagating reaction (SPR) occurs. SPR is induced by not only by electrostatic discharge, electrical heating, and laser irradiation, but also by mechanical impact. SPR by mechanical impact can be divided into two phenomena: i.e., (i) initial reaction by mechanical loading and (ii) ignition and propagation of reaction wave. Many studies have been conducted on (ii) SPR properties such as the ignition threshold and the speed of propagation. On the other hand, for (i), the detailed mechanisms of the initial chemical reaction due to mechanical loading has been unclear. This chemical reaction occurs at well below melting points and eutectic temperature, implying that the chemical reaction can occur by solid-state reaction. The atomic mixing in the solid-state can be brought about by diffusion or plastic deformation. Since the reaction occurs in very short time, we focus the role of plastic deformation.

The purpose of the study is to clarify the mechanisms of initial chemical reaction of Ti/Si multilayered nano-films by mechanical loading. Since the multilayered nano-films have structural anisotropy, the deformation mechanism depends on the loading mode with respect to the stacking direction. In this study, we focus the deformation and chemical reaction under compression loading in the stacking direction as a basic mode. We fabricated truncated cone-shaped specimens by focused ion beam from a polycrystalline-Ti/amorphous-Si multilayered nano-films (bilayer thickness: ~30 nm) deposited by electron beam evaporation, and then conducted compression experiments under *in situ* observation by field emission scanning electron microscopy. We evaluated the chemical reaction or change in crystal structure by transmission electron microscopy (TEM) observation and selected-area electron diffraction to the deformed specimens.

The specimens yielded at a true stress of ~3 GPa under compression, and showed gradual hardening behavior. TEM observation confirmed that each layer was plastically deformed or thinned, and then the mixing of Ti and Si occurred. The selected-area electron diffraction revealed that a new crystal structure, estimated to be Ti<sub>3</sub>Si<sub>4</sub> or TiSi, was generated on the Ti/Si interface and in the Ti layer. These results indicated that the mixing of each layer was induced by plastic deformation due to compressive stress and the compound of Ti and Si was generated. The exothermic reaction can be controlled or generated at a desired site by the local mechanical loading, and so it can be used for various applications such as local heating in large-scale devices.

Tuesday Morning, November 27, 2018  
Sheraton, 3rd Floor, Commonwealth

**8:30 AM \*NM02.04.01**

**Confined Growth of Metal Nanostructures** [Yadong Yin](#); University of California, Riverside, Riverside, California, United States.

Metal nanostructures have been studied quite extensively in the research area of heterogeneous catalysis long before the introduction of the concept of nanoscience and nanotechnology. The significant progress achieved in the past twenty years in chemical synthesis has enabled precise control over not only the size but also the shape of the metal nanostructures, and therefore attracted intense interest not only in catalysis but also optoelectronics due to the well-known effect of localized surface plasmon resonance. In this presentation, I will introduce our recent progress in the synthesis of colloidal metal nanostructures in confined spaces using various templating methods, and further manipulation of their secondary structures. By combining the confinement of templates with the seed-mediated growth strategy, we demonstrate the significant advantages of this general method over the conventional ones in creating a large variety of nanomaterials with novel plasmonic properties.

**9:00 AM NM02.04.02**

**Near Surface Nucleation and Particle Mediated Growth of Colloidal Au Nanocrystals** [Maria Sushko](#), Yingwen Cheng, Jinhui Tao, Guomin Zhu, Jennifer Soltis, Elias Nakouzi, James J. De Yoreo and Jun Liu; Pacific Northwest National Laboratory, Richland, Washington, United States.

During non-classical growth of nanostructures via assembly of primary nuclei, nucleation and assembly are assumed to be distinct processes: nanoparticles nucleate randomly and aggregate to form extended structures through Brownian motion in the presence of long-range attractive interactions. Here we investigate the relationship between these two processes by using *in situ* AFM, *in situ*, *ex situ* and *cryo* TEM and UV-Vis spectroscopy to observe growth of colloidal gold and simulations to develop a mechanistic model of the process. Our results reveal an inexorable link between nucleation and assembly with nuclei forming almost exclusively within a  $\sim 1$  nm interfacial region of existing particles. The new particles immediately close the gap either through a diffusive jump or via growth of a neck between the seed and new particle, generating aggregates exhibiting features commonly attributed to oriented attachment of independently nucleated particles. In addition, pH was identified as a control parameter for manipulating crystallization pathway through shifting the balance of chemical potentials of solution species. The results demonstrate that creation of initial particle interfaces leads to local environments that redirect growth towards non-classical processes.

**9:15 AM \*NM02.04.03**

**Controlling Absolute Dimensions of Gold Nanorods** [Catherine J. Murphy](#); University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Gold nanoparticles of controlled size and shape display brilliant optical properties throughout the visible and near-infrared portions of the electromagnetic spectrum. Gold nanorods, usually 15-20 nm in diameter with tunable lengths of 20, 30, 40, 50, 60 nm, show two plasmon bands corresponding to transverse and longitudinal excitations. The length/width ratio (aspect ratio) of gold nanorods is well-known to dictate the relative positions of the two plasmon bands. Recently in my laboratory we have developed a synthesis of "mini gold nanorods" in which the particle diameters are 5-8 nm, and lengths are 10, 20, 30 etc. nm. These absolutely smaller nanorods display similar plasmon bands to their larger counterparts, but the relative proportion of light scattering compared to light absorption differs. This talk will describe the synthetic procedures to create mini-rods as well as comparisons of properties between mini-rods and "regular" rods.

**9:45 AM NM02.04.04**

**Symmetry Breaking and Shape Control in Gold Nanorod Growth—From Conception to Old Age** [Joanne Etheridge](#), Wenming Tong, Michael Walsh, Hadas Katz-Boon and Alison Funston; Monash University, Monash University, Victoria, Australia.

Symmetry-breaking is the essential step required for an isotropic seed particle to grow into an anisotropic shape. Using specially designed electron microscopy methods and strategically-chosen synthetic routes, we investigate the mechanisms behind symmetry breaking and shape control in gold nanorod growth, from conception to old age [1-4]. We observe the symmetry-breaking event that triggers the formation of the embryonic nanorod; an asynchronous formation of new surface structures in the cuboctahedral gold seed particles [1,3]. We show that the size at which the seed particle breaks symmetry depends sensitively on the Au/Ag ion ratio and describe a mechanism as to how this, in turn, controls the initial nanorod aspect ratio [2,3]. After observing the initial symmetry breaking event, we investigate the evolution of the nanorod morphology over an extended timeframe, for periods up to 3 orders of magnitude longer than the conventional 1 - 2 hours [4]. Following initial rapid anisotropic growth, the nanorods grow isotropically, and over longer times (weeks), tend ultimately towards the same reduced aspect ratio, irrespective of the AgNO<sub>3</sub> concentrations. Furthermore, we measure the orientation and stability of different facets [5,6] and show how the nanorod transitions from faceted to curved when allowed to grow for extended periods [4]. Collectively, these observations suggest that the ultimate final aspect ratio is dictated by the surface energetics of the cylindrical sides compared to the hemispherical tips, with little dependence on the initial AgNO<sub>3</sub> concentration. In other words, the AgNO<sub>3</sub> concentration mainly asserts control over aspect ratio at the symmetry breaking point, rather than during later growth. Altogether, these observations provide a rational framework for controlling width, aspect ratio and facet orientation in the growth of single crystal gold nanorods.

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**10:00 AM BREAK**

#### 10:30 AM NM02.04.05

**Quantitative Chemical Mapping of Soft-Hard Interfaces on Gold Nanorods** Blanka Janicek<sup>1</sup>, Joshua G. Hinman<sup>2</sup>, Jordan Hinman<sup>2</sup>, Hwei-Huei Chang<sup>2</sup>, Kenneth Suslick<sup>2</sup>, Catherine J. Murphy<sup>2</sup> and Pinshane Huang<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; <sup>2</sup>Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Soft-hard interfaces at the surface of nanoparticles (NPs) determine interaction potentials, including the mechanisms of growth, spatial reactivity, colloidal stability, and nanoparticle functionality [1]. For example, soft molecular ligands are thought to guide growth and symmetry breaking in anisotropic NPs. These ligands can also act as soft templates for site-selective deposition of functional coatings [2, 3]. Thus, quantitative details of the local attachment, distribution, and structure of soft-hard interfaces would enable the development of methods for high-yield, monodisperse NP synthesis.

Conventional techniques to characterize soft-hard NP interfaces—such as nuclear magnetic resonance, small angle x-ray scattering, and other bulk methods—lack the spatial resolution necessary to probe key details, including how the surface structure and chemistry varies within and between individual particles [1]. Yet in NPs, polydispersity is a defining characteristic, and surface energies and interactions vary widely based on local facet, curvature, and composition. While electron microscopy can address this challenge, an ideal approach requires a combination of: low-background substrates, the ability to quantify elemental distributions of small molecules, and the efficiency necessary to probe multiple NPs. Here we report a particle-by-particle analysis of soft-hard interfaces on gold nanorods (AuNRs) using aberration-corrected scanning transmission electron microscopy and electron energy loss spectroscopy (EELS) spectrum imaging on graphene substrates.

In order to demonstrate the ability of electron microscopy methods to probe soft-hard interfaces, we investigate anisotropic mesoporous silica functionalization of AuNRs. Mesoporous silica can be deposited with site selectivity to either the ends or the sides of AuNRs. Such growth is thought to be templated by the anisotropic distribution of capping ligand cetyl trimethylammonium bromide (CTAB) [2, 3]. We deposit AuNRs onto suspended graphene substrates and use EELS spectrum imaging to map the presence of carbon, silicon, and oxygen. We directly observe a mesoporous silica frame with carbon containing pores and an increased carbon signal on the surface of the rods, indicating the presence of a residual CTAB shell surrounding the particle. Using graphene as a reference, we quantify the CTAB present before and after silica deposition. These results indicate that before deposition, AuNRs are coated with a few-nm thick CTAB layer corresponding to ~5,000 ligands/particle. This density is small when compared to the ~60,000 ligands/particle on silica-coated AuNRs. Our methods thus represent the first direct, quantitative chemical analysis of soft-hard interfaces of metal nanoparticles.

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#### 10:45 AM \*NM02.04.06

**Visualizing Dynamic Reorganization of Surface-Bound Ligands on Gold Nanorods** Katherine Willets; Temple University, Philadelphia, Pennsylvania, United States.

A key way to impart specific function to metallic nanoparticles is to functionalize their surface with ligands, allowing a range of applications including chemical and biological sensing; theranostics; and catalysis. For gold nanoparticles, this typically involves incubating nanoparticles in solutions containing thiol-terminated ligands and allowing the ligands to self-assemble on the surface of the gold through the formation of gold-thiol bonds. However, the structure and organization of the resulting ligand shell at the metal-organic interface is difficult to visualize. This talk will describe how single molecule fluorescence and super-resolution microscopy provide insight into surface organization of DNA-functionalized gold nanorods as a function of different preparation strategies. In cases when the DNA binds in a collapsed, disordered configuration, plasmon heating facilitates dynamic surface reorganization to a more ordered, upright geometry. By understanding how changes in surface preparation protocols impact the resulting ligand shell, we will be able to synthesize more reproducible functionalized nanostructures.

#### 11:15 AM NM02.04.07

**Amplification of Chirality Transfer to Nematic Liquid Crystals by an Enhancement of the Anisotropy Factor in Chiral Ligand-Capped Gold Nanorods** Ahlan Nemat<sup>1</sup>, Sasan Shadpour<sup>1</sup>, Lin Li<sup>1</sup>, Lara Querciagrossa<sup>2</sup>, Taizo Mori<sup>3</sup>, Claudio Zannoni<sup>2</sup> and Torsten Hegmann<sup>1,4</sup>; <sup>1</sup>Liquid Crystal Institute, Chemical Physics Interdisciplinary Program, Kent, Ohio, United States; <sup>2</sup>Department of Industrial Chemistry, University of Bologna, Bologna, Italy; <sup>3</sup>National Institute for Materials Science, Center for Materials Nanoarchitectonics (MANA), Ibaraki, Japan; <sup>4</sup>Department of Chemistry & Biochemistry, Kent, Ohio, United States.

Understanding the behavior of chiral molecules in macroscopic systems requires amplification. Here we investigate the amplification of chirality by biocompatible chiral ligand-functionalized gold nanorods (GNRs) in a nematic liquid crystal. We synthesized two aspect ratios of cholesterol-capped and 1,1'-binaphthyl-capped GNRs. Both types of GNRs, featuring either centrally or axially chiral ligands, were fully characterized by NMR, transmission electron microscopy, TEM, UV-vis-NIR spectroscopy, TGA, and CD spectropolarimetry. Characterization of mixtures of these GNRs in 5CB with induced CD spectropolarimetry and polarized light optical microscopy (free surface, homeotropic boundary conditions, and Cano wedge cells) show that the GNRs not only induce chirality in the N-LC phase but also that the chirality in both systems is remarkably amplified in comparison to quasi-spherical gold nanoparticles (NPs) functionalized with the same ligands.<sup>1,2</sup>In each case the helical pitch ( $p$ ) of the induced N\*-LC phase was measured and the molar helical twisting power ( $\beta_M$ ) of the chiral GNRs calculated to elucidate the chirality transfer efficiency of the chiral ligand-functionalized GNRs.<sup>3</sup>The  $\beta_M$  value significantly increases by altering the shape from NPs to NRs due to an enhancement of the anisotropy factor. This result is coherent with other data on the anisometric shape of GNRs with enhanced anisotropy or Kuhn's dissymmetry factors.<sup>4</sup>

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#### 11:30 AM NM02.04.08

**In Situ X-Ray Scattering Guides the Synthesis of Functional Nanocrystals** Liheng Wu<sup>1,2</sup>, Christopher J. Tassone<sup>2</sup> and Matteo Cargnello<sup>1</sup>; <sup>1</sup>Department of Chemical Engineering, Stanford University, Stanford, California, United States; <sup>2</sup>Stanford Synchrotron Radiation Lightsource, SLAC National

Accelerator Laboratory, Menlo Park, California, United States.

Synthesizing nanocrystals with precisely controlled size, shape, and structure is of great importance for understanding their properties. Although significant developments have been achieved in colloidal synthesis, it remains challenging to synthesize nanocrystals in a predictive way due to a lack of mechanistic understanding of the synthesis. In this talk, I will discuss my recent research efforts on precise syntheses of nanocrystals guided by *in situ* synchrotron X-ray scattering.

The first part of this talk describes using *in situ* small angle X-ray scattering (SAXS) under "realistic" synthetic conditions to elucidate the formation kinetics of monometallic Pd nanocrystals in the presence of different ligands, which enables precise synthesis of a broad library of monodisperse Pd nanocrystals with 1 nm size control.<sup>[1]</sup> The real-time SAXS also allows us to observe an unprecedented rapid crystallization of nanocrystals into three-dimensional superlattices at high temperatures and their continuous growth within the superlattices, which provides new insights on interparticle interactions during colloidal synthesis.<sup>[2]</sup> In the second part of the talk, I will demonstrate a mechanistic understanding of the formation of bimetallic PtSn nanocrystals at the atomic scale using simultaneous SAXS and wide angle X-ray scattering (WAXS).<sup>[3]</sup> This type of *in situ* characterization can be readily extended to other nanocrystal systems to advance their rational synthesis.

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#### 11:45 AM NM02.04.09

**Measuring the Facet-Selective Electrochemistry that Drives Anisotropic Growth of Metal Nanostructures** Myung Jun Kim<sup>1</sup>, Samuel Alvarez<sup>1</sup>, Zihao Chen<sup>2</sup>, Kristen A. Fichthorn<sup>2</sup> and Benjamin Wiley<sup>1</sup>; <sup>1</sup>Duke University, Durham, North Carolina, United States; <sup>2</sup>Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States.

The number of applications for anisotropic metal nanocrystals in biomedicine, catalysis, and electronics has grown rapidly over the last decade. However, the origins of anisotropic growth of metal nanocrystals in solution remain unclear due to the lack of experimental methods that can test previously proposed hypotheses. For pentagonally-twinned nanowires of Cu, Ag, and Au, researchers have hypothesized that organic capping agents selectively inhibit atomic addition to the {100} facets on the sides of nanowires, and thereby induce anisotropic nanowire growth through atomic addition to {111} facets on the ends of nanowires. However, there is little experimental evidence to support this hypothesis, and it does not explain why most syntheses require halide ions to grow Cu, Ag, and Au nanowires.

This presentation will show how electrochemical measurements on single crystals can be used to test hypotheses for how anisotropic growth of a metal nanocrystal occurs. In one study with Cu(100) and Cu(111), rather than acting as a capping agent, ethylenediamine (EDA) increased the rate of atomic addition to nanowire ends by keeping the Cu(111) surface relatively free of surface oxidation in the highly basic growth solution (>12 M NaOH). In another synthesis of Cu nanowires that involves the reduction of CuCl<sub>2</sub> in the presence of hexadecylamine (HDA), we show that this capping agent passivates both Cu(100) and Cu(111) surfaces equally. However, the introduction of chloride ions in a narrow range of concentrations disrupts the alkylamine monolayer on Cu(111) but not Cu(100), causing Cu to preferentially deposit onto {111} facets on the ends of the nanowires. As in experiments, DFT calculations reveal there is an intermediate Cl coverage window in which HDA chemisorbs to Cu(100) but physisorbs to Cu(111), enabling the selective addition of Cu atoms to the less-protected {111} facets on nanowire ends. This study shows single-crystal electrochemistry, in combination with DFT, can reveal unexpected mechanisms for how anisotropic growth occurs.

SESSION NM02.05: Plasmonic Structures  
Session Chairs: Grant Johnson and Jianping Xie  
Tuesday Afternoon, November 27, 2018  
Sheraton, 3rd Floor, Commonwealth

#### 1:30 PM \*NM02.05.01

**Plasmonic Nanocrystals with High Refractive Index Sensitivity and Thermal Stability** Sara E. Skrabalak; Indiana University, Bloomington, Bloomington, Indiana, United States.

Seed-mediated co-reduction is a versatile route to multimetallic nanocrystals with shape definition. This method has been used to achieve stellated Au-Pd nanocrystals with high symmetry, which is guided by the shape of the seeds used for bimetallic deposition. This presentation will highlight recent studies into the tunable optical properties of these nanocrystals for use as LSPR sensors and photothermal agents. As will be shown, compared to all-Au nanocrystals, the Au-Pd nanocrystals display higher sensitivity to changes in local refractive index as well as greater shape stability when heated. This presentation will be coupled with a detailed discussion of multimetallic nanocrystal synthesis by seeded methods and a broader discussion of the challenges associated with characterizing and modeling the composition of multimetallic nanostructures.

#### 2:00 PM NM02.05.02

**Peptide-Directed Synthesis of Chiral Plasmonic Gold Nanoparticles** Hye-Yong Ahn, Hye-Eun Lee and Ki Tae Nam; Material Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

The integration of chirality with plasmonic materials offers a new possibility for nanophotonics including polarization control, enantiomeric sensing, and negative refractive index in the visible range. Since the light manipulation of chiral plasmonics relies on delicate nanostructure, a majority of chiral nanostructure was created by precise lithographic techniques and molecular self-assembled template. Although remarkable chiral structures have been made by these techniques, spontaneous formation of three-dimensional inorganic nanostructure without mirror symmetry is an important challenge and still has not been achieved on a single nanoparticle.

In this study, we developed a peptide-directed strategy for synthesizing chiral plasmonic nanoparticle that allows for the precise control over handedness and chiroptical responses.<sup>[1-3]</sup> We demonstrated that interactions between peptides and gold surface enable "chirality transfer" to drive the spontaneous

development of chirality during the nanoparticle growth. The intrinsic chirality at kink of inorganic high-Miller-index  $\{h k l\}$  planes ( $h \neq k \neq l \neq 0$ ) served a critical role to provide an enantioselective binding site for peptide on crystalline facets of gold nanoparticles. These unique peptide-gold interactions led to the evolution of asymmetric structure in an individual nanoparticle and consequently created a novel helicoid morphology with a 100-nm size.

The highly twisted feature of chiral components in the helicoid gold nanoparticles gave rise to remarkably strong plasmonic optical activity; dissymmetry factor of the randomly dispersed nanoparticle solution reached 0.2 at visible wavelengths and can be further controlled by sequence, handedness, and an enantiomeric ratio of peptides. Theoretical calculation clarified that this optical activity is associated with the formation of strong chiral nearfield at high-order plasmonic mode. Surprisingly, based on the wavelength-dependent polarization rotation ability, a solution of the helicoid gold nanoparticle can modulate the color of transmitted light in a wide range of visible wavelengths. This color transformation operates in real-time by rotating a polarizer and can be observed in naked-eye. In this regard, we expect that our peptide-directed approach will promote the rational design and fabrication of three-dimensional chiral plasmonic metamaterial, as well as improve an understanding of the enantioselective interaction of peptide and inorganic material.

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### 2:15 PM \*NM02.05.03

**New Earth-Abundant Metallic Nanoparticles for Plasmonics** John S. Biggins<sup>3</sup>, Josee Richard-Daniel<sup>4</sup>, Sadegh Yazdi<sup>5</sup> and Emilie Ringe<sup>2, 1</sup>; <sup>1</sup>Department of Chemistry, Rice University, Houston, Texas, United States; <sup>2</sup>Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; <sup>3</sup>Department of Engineering, University of Cambridge, Cambridge, United Kingdom; <sup>4</sup>COPL, Université Laval, Quebec, Quebec, Canada; <sup>5</sup>Renewable and Sustainable Energy Institute (RASEI), Joint Institute with NREL, University of Colorado Boulder, Boulder, Colorado, United States.

Nanoparticles (NPs) of some metals (commonly Cu, Ag, and Au) sustain oscillations of their electron cloud called localized surface plasmon resonances (LSPRs). These resonances can occur at optical frequencies and be driven by light, generating enhanced electric fields and spectacular photon scattering, opening applications including photocatalysis, photothermal therapy, and enhanced spectroscopies, to name a few. However, current plasmonic metals, in particular Ag and Au, are rare, expensive, and have a limited resonant frequency range. Recently, much attention has been focused on earth-abundant Al, but Al NPs have interband transitions that damp LSPRs in the IR. Here we report earth-abundant Mg NPs that may surmount this limitation. Our colloidal synthesis forms 100-300 nm diameter, 30-50 nm thick hexagonal nanoplates, reflecting Mg's simple hexagonal lattice, as shown by SEM and HRSTEM (Figure 1). STEM-EDS and STEM-EELS mapping reveals a self-limiting layer of oxide analogous to that observed in Al NPs, protecting the metallic core, even for weeks in air. Mg NPs sustain multiple LSPRs with size-dependent frequencies spanning from UV to IR, which we precisely characterize by combining STEM-EELS, optical dark-field scattering, and numerical simulations. Colloidally synthesized Mg thus offers a route to inexpensive NPs with novel shapes and resonances spanning the UV-vis-IR spectrum, making them a flexible addition to the nanoplasmonics toolbox.

### 2:45 PM NM02.05.04

**Plasmon Driven Alignment of Silver Nanoparticles** Ivan Shutsko, Christian Böttge, Maik Meudt, Andreas Henkel, Till H. Hoffmann and Patrick Görrn; Chair of Large Area Optoelectronics, Bergische Universität Wuppertal, Wuppertal, Germany.

The growth of metal nanoparticles on a solid substrate with precise control over their positions is one of the main challenges of plasmonics. Here, we introduce a facile approach based on photoinduced deposition of metal nanoparticles from the liquid phase on a solid substrate, driven and controlled by plasmons. The solid substrate consists of nano gaps in a silver stripe covered by a flat polystyrene film. Surface plasmons excited at the nano gaps initiate and control the growth of silver nanoparticles. We demonstrated that by confinement of light in this way highly ordered lines of silver nanoparticles can be grown with a width of 200nm over the whole laser spot area. Moreover, the near-field intensity pattern formed by the incoming laser light and the light scattered at the surface plasmons (SPs) is able to form much smaller (70nm in width) silver nanoparticle lines experimentally observed in our work. This facile approach opens a new path towards photochemical and plasmon-mediated fabrication of different sophisticated nanostructures. It does not require the usage of an expensive light source, materials or vacuum condition. Only photosensitive chemicals and a suitable light confining structure are needed.

### 3:00 PM BREAK

### 3:30 PM \*NM02.05.05

**Describing Light-Driven Catalysis on Surface-Doped Plasmonic Metals via Embedded Correlated Wavefunction Theories** John Mark P. Martirez and Emily A. Carter; Princeton University, Princeton, New Jersey, United States.

Nanoplasmonic catalysis is a potentially transformative method for photo-driven heterogeneous catalysis under mild conditions. Many reactions have been experimentally demonstrated to benefit from nanoplasmonics, e.g., room temperature H<sub>2</sub> activation, CO oxidation with O<sub>2</sub>, organic cross-coupling reactions, water splitting, and catalytic reduction of CO<sub>2</sub> with H<sub>2</sub> to CH<sub>4</sub> or CO. Insights into the role of localized surface plasmon resonances (LSPRs) in enhanced catalysis however is still scarce and often speculative; thus the field benefits from quantum mechanical atomic-scale calculations. Density functional theory (DFT) is the workhorse method used in understanding heterogeneous catalysis at the atomic scale from first principles. However, ground-state DFT does not adequately treat excited-state phenomena. *Ab initio* quantum mechanical correlated wavefunction (CW) methods, while more accurate and able to treat electronically excited states, scale poorly with system size. We thus employ embedded CW methods *via* density functional embedding theory, which enables explicitly modeling of small metal clusters while accounting for the extended metal surface via an embedding potential. We first determine the chemical pathways in the adiabatic ground electronic state from periodic DFT, and subsequently evaluate the effects of local electronic excitations, centered at surface reaction sites, on the reaction energetics using embedded CW. We then examine whether accessing available excited states will enable overcoming energy barriers for reactions that are otherwise kinetically forbidden to proceed in the ground state. Since there are only a few metals that exhibit strong LSPRs (Al, Cu, Ag, and Au), we explore surface doping as means to facilitate catalysis of reactions that are not possible on these metals. For example, we investigate the possible role of plasmonics on N<sub>2</sub> dissociation and CH<sub>4</sub> activation on Mo-doped Au(111) and on Ru-doped Cu(111), respectively.

### 4:00 PM NM02.05.06

**Enhancing Mo:BiVO<sub>4</sub> Solar Water Splitting with Patterned Au Nanospheres by Plasmon-Induced Energy Transfer** Xinjian Shi and Xiaolin Zheng; Stanford University, Stanford, California, United States.

Plasmonic metal nanostructures have been extensively studied to improve the performance of metal oxide photoanodes for photoelectrochemical (PEC) solar water splitting cells. Most of

these studies have focused on the effects of those metal nanostructures on enhancing light absorption and enabling direct energy transfer via hot electrons. However, several recent studies have shown that plasmonic metal nanostructures can improve the PEC performance of metal oxide photoanodes via another mechanism known as plasmon-induced resonant energy transfer (PIRET). However, this PIRET effect has not been yet tested for the molybdenum-doped bismuth vanadium oxide (Mo:BiVO<sub>4</sub>), regarded as one of the best metal oxide photoanode candidate. Here, we constructed a hybrid Au nanosphere/Mo:BiVO<sub>4</sub> photoanode interwoven in a hexagonal pattern to investigate the PIRET effect on the PEC performance of Mo:BiVO<sub>4</sub>. We find that the Au nanosphere array not only increases the light absorption of the photoanode as expected but also improves both its charge transport and charge transfer efficiencies via PIRET, confirmed by time-correlated single photon counting and transient absorption studies. Incorporating the Au nanosphere array increases the photocurrent density of Mo:BiVO<sub>4</sub> by ~ 2.2-fold, thereby outperforming all the other hybrid Au/metal oxide photoanodes in the literature.

#### 4:15 PM NM02.05.07

**Plasmon Manipulated Magnetization in Au-Fe<sub>3</sub>O<sub>4</sub> Nanostructures** Shuai He<sup>1</sup>, Zheng Gai<sup>2</sup>, Alexander Puzosky<sup>2</sup> and Wei D. Wei<sup>1</sup>; <sup>1</sup>Department of Chemistry and Center for Catalysis, University of Florida, Gainesville, Florida, United States; <sup>2</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Manipulation of photo-electron interactions provides great opportunities for the integration of nano-photonics with electronics and spintronics.<sup>[1]</sup> Researches have demonstrated that the highly spin-polarized electronic states in metal oxides significantly enhance the optical response of the magnetoplasmonic nanostructures.<sup>[2],[3],[4],[5],[6]</sup> However, it still remains unclear how the plasmon excitation of metallic nanoparticles influence the magnetization of the magnetic materials. Herein, we demonstrate the use of Au plasmon to change the magnetization of Fe<sub>3</sub>O<sub>4</sub> in a Au-Fe<sub>3</sub>O<sub>4</sub> dumbbell nanostructure. We conclusively exclude the plasmon-mediated hot electron transfer and light-induced system temperature increase and identify the plasmon-mediated energy transfer as the primary driving force for the observed magnetization decrease upon optical excitation. Furthermore, it is elucidated that the Au SPR significantly enhanced the confined optical field in Fe<sub>3</sub>O<sub>4</sub>, which facilitated the generation of excitons and led to the spin disordering through the excitation-spin exchange-coupling.<sup>[7]</sup> Taken together, these findings illustrate the ability to modulate the magnetization of ferromagnetic materials via plasmon excitation and provide new insights for the understanding of plasmon-mediated spin dynamics.

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#### 4:30 PM NM02.05.08

**Near-IR Photothermal Ag Nanoparticles-Polymer Nanocomposite Layers with Controlled Plasmonic Coupling for Biofilm Eradication** Shuzhi Zhou, Padryk Merkl and Georgios A. Sotiriou; Karolinska Institute, Solna, Sweden.

With the ever-growing threat of catheter-associated infections, the development of highly effective treatments against bacterial biofilms is crucial while at the same time challenging. For this reason, physical ways to eradicate biofilms are sought, with a popular one the local temperature increase by plasmonic metals and near-IR laser light that is typically induced by expensive gold (nanoshells, nanorods) and complex silver (nanotriangles) nanostructures. Here, a stimuli-responsive polymer nanocomposite simulating the surface of polymer catheters incorporating plasmonic photothermal nanoparticles was designed aiming to destroy biofilms by heat and/or heat-triggered antibiotic drug release. The agglomeration degree during flame nanoparticle synthesis and, thus, controlled plasmonic coupling of inexpensive spherical silver (Ag) plasmonic nanoparticles supported on inert amorphous SiO<sub>2</sub> was optimized by adjusting the deposition time on substrates and SiO<sub>2</sub> content in the particle films. This enhanced the localized surface plasmon resonance and light absorption in the near-IR region and facilitated efficient heat conversion upon irradiation with an 808 nm laser. Heat generated from the PDMS-Ag nanoparticle layer-PDMS nanocomposite under near-IR irradiation inhibited the viability of *clinically-relevant* biofilms. Additionally, laser-induced heat was able to trigger drug release from poly(2-hydroxyethyl methacrylate) hydrogels that were coated on the polymer nanocomposites surface, enabling these nanocomposites to achieve on-demand, heat-triggered antibiotic release against biofilms. The facile, scalable and inexpensive fabrication method of the developed anti-biofilm polymer surfaces based on plasmonic photothermal layers liberates the field from the use of expensive materials and processes facilitating their broad employment and clinical translation.

#### 4:45 PM NM02.05.09

**Solution-Derived Plasmonic Metal Surfaces for Optical and Thermal Applications** Jyotirmoy Mandal and Yuan Yang; Columbia University, New York, New York, United States.

Solution-based processes, such as galvanic displacement reactions, are a simple method for creating plasmonic metal nano- and micro-structures. However, despite their simplicity, their potential to fabricate metasurfaces tailored for thermal and optical applications remains to be explored in detail. In this talk, we present galvanic displacement reactions as a facile pathway to make plasmonically active metasurfaces tailored to function as, among other examples, selective solar absorbers, super-broadband absorbers/emitters, and stray light absorbers for astronomical and imaging applications. For instance, galvanic displacement reactions are known to yield solar absorbers with solar absorptance > 0.95 and hemispherical thermal emittance < 0.1 [1]. Similar reactions can yield super-broadband absorbers with excellent, wide-angle absorptance (e.g. ~ 0.95 at incidence angles > 60°) from the visible to

infrared wavelengths of light. Additional functionalities arising from the optical selectivity of the surfaces and combination with other materials will also be discussed.

With regard to synthesis, galvanic displacement reactions are attractive, as they can be conveniently **tuned to yield specifically tailored plasmonic surfaces** for different optical and thermal applications. Furthermore, they are **simpler, less expensive and greener** than currently used fabrication techniques (e.g. vacuum deposition). Lastly, they are **compatible with unexotic metals or alloys** such as steel, which broadens their applicability. Considering the above uses, these aspects make galvanic displacement-based reaction pathways viable and highly attractive for making plasmonic metasurfaces.

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SESSION NM02.06: Poster Session II  
Session Chairs: De-en Jiang and Grant Johnson  
Tuesday Afternoon, November 27, 2018  
8:00 PM - 10:00 PM  
Hynes, Level 1, Hall B

#### NM02.06.02

**Facile Synthesis of the Silver-Cobalt Oxide Nanocrystals for Oxygen Reduction Reaction via Plasma Discharge in Water** [SangYul Lee](#)<sup>1</sup>, Jung-Wan Kim<sup>2</sup> and Sung-Min Kim<sup>3</sup>; <sup>1</sup>Korea Aerospace University, GoYang, Korea (the Republic of); <sup>2</sup>Incheon National University, Incheon, Korea (the Republic of); <sup>3</sup>Korea Institute of Industrial Technology, Incheon, Korea (the Republic of).

The development of non-Pt electrocatalysts with enhanced ORR activity is highly sought but still remains a significant challenge. Recently plasma discharge in solution has been paid much attention to for the synthesis of noble nanoparticles with various shapes and compositions as a plasma discharge in the liquid phase provides various excited chemical species, which results in an intrinsically high chemical reactivity compared to ordinary reaction media. The silver-cobalt oxide core-shell nanocrystals ( $\text{Ag@Co}_3\text{O}_4$ ) were synthesized using bi-polar pulsed plasma discharge in water for catalytic oxygen reduction in alkaline solutions. Microstructural and compositional analysis using HRTEM equipped with high resolution EDX elemental mapping verified that the reactive oxygen species generated from plasma-assisted decomposition of water molecules played important role in controlling the phase structure of the nanoparticles. In the presence of abundant oxygenated species, the  $\text{Ag@Co}_3\text{O}_4$  core-shell was formed by the preferential oxidation of Co at the surface. The electrochemical measurements for oxygen reduction reaction revealed that the electrocatalytic activity of the  $\text{Ag@Co}_3\text{O}_4$  core-shell nanocrystals were higher than that of pure Ag and  $\text{Co}_3\text{O}_4$  nanoparticles. This enhanced catalytic activity could be attributed to the electronic effects induced by an upshift in the d-band center via charge transfer between Ag and Co. For the  $\text{Ag@Co}_3\text{O}_4$  core-shell architecture, the active Ag interacted more extensively with the  $\text{Co}_3\text{O}_4$  monolayer shell at the surface. Owing to this favorable structure, the ORR activity was higher on the core-shell surface than for the subcluster-segregated nanoalloys. This was unlike uniform contacts, and it led to weakened electronic effects. Thus, it was concluded that  $\text{Ag@Co}_3\text{O}_4$  core-shell electrocatalysts will be promising candidates for potential applications in catalysis.

#### Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grants funded by the Korea Government (NRF-2016R1D1A1A09918072)

#### NM02.06.03

**Mechanical and Electrical Properties of Nanowire-Based Flexible Galvanic Skin Response Sensor** [Sun Hwa Park](#), Ji Hye Park and Jae Yong Song; KRIS, Daejeon, Korea (the Republic of).

Monitoring systems to read human bio-signal have been developed with increasing healthcare applications. Among them, galvanic skin response (GSR) sensor has been used to measure skin conductance, defined as electrical conductance between two regions of skin. GSR sensor can help to evaluate a stress and a lie detection because skin conductance is changed by the sweat gland activity indicating a psychological or physiological arousal. Recently, GSR sensors have been fabricated in the forms of fingerband, armband, hairband and patch. However, these sensors have some limitation due to low sensitivity and large volume for wearable devices.

In this study, we introduce a low-cost and facile fabrication of highly flexible GSR nanosensor (less than 5 mm in size and 6  $\mu\text{m}$  in thickness) which is composed of vertically aligned Ag/Au core-shell nanowires (200 to 300 nm in diameter) embedded in a polyimide matrix. Vertical configuration of the nanowires within GSR nanosensor enables the sensor to measure skin conductance through thickness direction while the nanosensor is insulating in the in-plane direction. The nanowire based GSR sensor is flexible enough to be easily adapted to the curved skin. Experimental results show that the nanowire based GSR sensors have more excellent sensitivity than commercial GSR sensor. The bending and cycling tests showed that the sensitivities of the GSR sensors are reliably maintained for three months.

#### NM02.06.04

**Regulation of EGFR Signal Transduction by Dynamic Receptor Clustering** [Qianyun Zhang](#); Chemistry, Boston University, Boston, Massachusetts, United States.

Epidermal growth factor receptor (EGFR) is a transmembrane receptor tyrosine kinase, whose dysregulation and abnormality have been associated with oncogenesis. Current EGFR targeted therapeutic approaches have failed to meet expectations due to the mutation of EGFR or the resistances of tumor to the treatment. So the development of an efficient receptor targeted drug would be successful only if the molecular mechanism underlying the EGFR signaling pathway are fully understood. It has been known that clustering of receptors play important roles in cell signaling. Thus, we will study the distribution of the epidermal growth factor receptors on the cellular membrane as well as in early endosome in the response to the ligand binding.

Noble gold nanoparticles (NPs) has been used as tool in biosensing and tracking due to their unique optical properties. The most useful property of NPs is that they can induce plasmon coupling, then leads to a spectral shift in the scattering spectrum of the coupled NPs labels. This shift can be conveniently detected by conventional far-field light microscopy, so called Plasmon Coupling Microscopy (PCM). Heterogeneous EGFR distribution will be optically indicated by EGF conjugated gold NPs clusters with different size and colors. Thus, we will develop a gold plasmon ruler that can characterize the compartmentalization of growth factor in cancerous cell lines. The first aim is to investigate the regulation of surface receptor clustering to signaling strength. To do that, it is necessary to correlate the spatial organization of EGFR clustering, as measured by PCM, with the receptor activation. The

triggered EGFR signaling can be quantified by detecting its phosphorylation levels by specific antibodies.

The next question is that how receptor tyrosine kinases determine different cell-fate decisions despite sharing the same signaling cascades. One hypothesis is the tight control of the endosomal distribution of EGF could serve to regulate signal transmission. The cell respond to higher EGF concentration by increasing the number of endosomes, and the average number of phosphorylated EGF receptors in each endosome remains almost constant. If we expose cell to gold NPs with different EGF ligand density, the endosome contained NPs cluster would be different. Thus, we could test hypothesis by quantitatively analyzing the endosomal distribution of EGFR and downstream signaling outcome.

The correlation of EGFR clustering and signaling activation will explicit explain how growth factor activation of this process depend on receptor clustering. Furthermore, we will address the question that whether intercellular EGFR clustering facilitates the decisions of signaling outcome. Therefore, the study of the mechanism of tyrosine kinase receptor in signaling pathway could help to augments efficacy of EGFR targeted therapeutic treatments in the future.

#### **NM02.06.05**

**Seed-Mediated Co-Reduction Synthesis of Intermetallic Au-Cu Nanocrystals—Insight into the Size-Dependent Disorder-Order Transformation** [Hannah M. Ashberry](#), Jocelyn T. Gamler and Sara E. Skrabalak; Indiana University, Bloomington, Indiana, United States.

Intermetallic nanoparticles often show increased catalytic efficiencies and durability towards electrocatalytic processes, such as the oxygen reduction reaction and reduction of carbon dioxide. Typical syntheses of intermetallic materials include thermal annealing of the alloyed counterpart and colloidal chemical syntheses. While both methods can produce intermetallic nanoparticles, little is known about the transformation from the random alloy to intermetallic phase. Previously demonstrated in the Skrabalak group was a size-dependent disorder-to-order transformation from random alloy to intermetallic with Pd-Cu nanoparticles. Such a size dependent transformation has also been observed in semiconductor systems. Here, this size-dependent transformation is explored with Au-Cu nanoparticles. Specifically, monodisperse AuCu and Au<sub>3</sub>Cu intermetallic nanoparticles were synthesized by seed-mediated co-reduction using Au-Cu random alloys as seeds. The study of the growth mechanism by analyzing reaction aliquots by TEM and XRD supports that such a disorder-to-order transformation is a general feature that can be exploited with seed-mediated co-reduction to achieve high quality intermetallic samples. This demonstration advances understanding of intermetallic nanoparticle formation in colloidal synthesis, which can expedite the development of electrocatalysts.

#### **NM02.06.06**

**Selective Heterogeneous Growth of Polyhedral Cu Nanoshell for Plasmonic Light Scattering Enhancement and Quantitative Naked-Eye Bio-Detection** [Jae-Ho M. Kim](#), Jeong-Eun Park, Mouhong Lin, Sungi Kim, Gyeong-Hwan Kim and Jwa-Min Nam; Chemistry, Seoul National University, Seoul, Korea (the Republic of).

Nanoparticles (NPs) such as AuNPs have wide applications in molecular detection, labelling, and imaging due to their compatible size, large surface area, availability of various conjugation methods, richness in core-shell chemistry, as well as geometry-dominant optical properties such as localized surface plasmon resonance and plasmonic coupling properties. The magnitude of the intrinsic optical properties of individual NP probes are, however, insufficient to detect targets at trace levels. Further, the simplicity, assay speed, and portability are critical elements, especially in developing fast but reliable naked-eye-based bioassays. To address these issues, Ag-based enhancement, known as silver staining, has been extensively studied so far to amplify Rayleigh scattering, surface-enhanced Raman scattering, colorimetric signals and electrical signals. However, the lack of specificity on detection label and low controllability of Ag shell formation limited its practical applications.

Here, we introduce a selective heterogeneous growth of polyhedral Cu nanoshell on Au nanoparticle. This is based on highly controllable polyethyleneimine(PEI)-mediated Cu polyhedral nanoshell (CuP) formation chemistry, specifically formed on AuNP probes, and used this CuP formation method for straightforward, intensive and quantifiable optical signal enhancement. The optical signals from one-to-one overgrown metallic polyhedral nanoshells are amplified about two orders of magnitude, and readily detectable with naked-eyes or an ordinary smartphone camera. In the case of DNA assay (anthrax sequence), we detected 8 fM DNA on an archetypal DNA microarray chip with a dynamic range from 8 fM to 800 pM in this manner. Also for virus detection (norovirus target in this case), clinical stool samples were used, and as low as 2,700 virus copies were detected with >2-orders of dynamic range. The high sensitivity and quantification capability of this CuP enhancement were superior to any other previously reported bio-detection methods detectable with naked eyes. The Cu nanoshell formation chemistry provides a new paradigm in controlling optical properties from selectively overgrown Cu shell nanostructures and their use in bio-detections.

#### **NM02.06.07**

**Enhanced Radiation Shielding with Conformal Light-Weight Nanoparticle-Polymer Composite** [Qingxuan Li](#), Qilin Wei and Ming Su; Northeastern University, Boston, Massachusetts, United States.

This abstract reports a new property enabled by nanoparticles, where bismuth nanoparticles added in a polymer matrix can block X-ray radiation several times more efficient than microparticles at the same mass ratio. Bismuth nanoparticles are made with cellulose nanofibers and dispersed evenly into a polymer. A four time reduction in the mass of bismuth material is identified at 2% mass ratio when nanoparticles (3 nm diameter) are used in composite to shield a given flux and energy of radiation, in relative to those of microparticles (5 μm diameter). The enhancement in radiation shielding is primarily attributed to close packing of nanoparticles along projection direction of incoming X-ray, which is enabled by strong affinity of nanoparticles to interstitial space of cellulose nanofibers and even distribution of nanoparticles in polymer. Given its low cost, light weight and structure conformability, bismuth nanoparticle-polymer composite will find its use in a wide range of fields related to personal radiation protection.

#### **NM02.06.08**

**A Quantitative Electron Microscopy Study of the Bending of Seed-Mediated Grown Gold Nanorods** [Xin Wen](#)<sup>1,2</sup>, Torben N. Pingel<sup>2</sup>, Kasper Moth-Poulsen<sup>1</sup> and Eva Olsson<sup>2</sup>; <sup>1</sup>Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden; <sup>2</sup>Department of Physics, Chalmers University of Technology, Gothenburg, Sweden.

Gold nanorods are promising candidates for applications in medicine, optics, electronics and chemistry since they have attractive optical and physical properties, especially strong absorption of localized surface plasmon resonance<sup>1,4</sup>. In order to manipulate absorption of light in unprecedented ways, researchers have studied how to bend gold nanorods using lasers<sup>5</sup>. However, we have observed gold nanorods synthesized by a binary-surfactant seed-mediated growth method<sup>3</sup> using high resolution transmission electron microscopy (TEM) and found that they were bending a few degrees spontaneously. The study on formation of bending structure and the deformation in the rods also benefits to understanding the dynamic process of gold nanorods' growth<sup>6</sup>. Further researches on TEM have shown that the gold crystal lattice is tilting a small angle (less than 10 degree) around [010] zone axis continuously, which is also transversal axis of the rod. Besides, there is no lattice defects observed on the bending gold nanorod in high resolution images. In order to

understand bending mechanism, the distribution of silver element added in growth solution was studied by Energy-dispersive X-ray spectra. We found very little amount of silver concentrated on the outer layer of a gold nanorod, which is the possible reason that causes the bending structure.

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#### NM02.06.09

**Perturbation Effects of Proximal  $\pi$ -Systems in Small Gold Clusters** Mitsuhiro Iwasaki<sup>1</sup>, Yukatsu Shichibu<sup>1,2</sup> and Katsuaki Konishi<sup>1,2</sup>; <sup>1</sup>Graduate School of Environmental Science, Hokkaido University, Sapporo, Japan; <sup>2</sup>Faculty of Environmental Earth Science, Hokkaido University, Sapporo, Japan.

Recent progress in the crystal structure determination of ligand-stabilized gold clusters has revealed that not only nuclearity but also geometrical structures of inorganic units affect their electronic structures and optical properties. The perturbation effect of the ligand environment is an important feature for developing designer clusters with specific functions, but the role of the organic units is still elusive. In this work, we placed focus on the effect of proximal  $\pi$ -system of organic unit on the optical properties of the gold cluster. A series of core + exo type Au<sub>8</sub> clusters decorated by diphosphine (dppp=Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>), arylthiolate and arylacetylde ligands were synthesized, and their optical properties were studied to obtain insights into the perturbation effect of the organic ligands.

Various thiolate and acetylde ligand were induced on the Au<sub>8</sub> framework via the reaction of divalent Au<sub>8</sub> cluster ([Au<sub>8</sub>(dppp)<sub>4</sub>]<sup>2+</sup>) with the corresponding alkyne and thiol. The produced clusters were characterized by electrospray ionization mass spectrometry and elemental analysis. Pyridinethiolate-substituted Au<sub>8</sub> clusters [Au<sub>8</sub>(dppp)<sub>4</sub>(SPy)<sub>2</sub>]<sup>2+</sup> exhibited absorption and photoluminescence responses to protonation events of pyridyl moieties. Upon protonation, 2- and 4-pyridinethiolate clusters showed larger red shifts of absorption and photoluminescence bands than 3-pyridinethiolate, suggesting that the observed band shifts are associated with the resonance structure of the pyridinethiolate units. On the other hand, emission intensities of all regioisomer increased largely. X-ray crystallographic and NMR analyses revealed the electron-deficient pyridinium rings form  $\pi$ -stacks with proximal phenyl groups of dppp in the protonated form. Thus, it was suggested that the rigidity of the ligand environment induced by  $\pi$ - $\pi$  interactions leads to the enhancement of emission efficiency. These results indicate that optical properties of small gold clusters can be modulated through the electronic and steric perturbations by surrounding organic unit.<sup>[1],[2]</sup>

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#### NM02.06.10

**Rapid and Direct Assembly of Colloidal Plasmonic Nanoparticles via Photothermal Convection Lithography** Chang Min Jin<sup>1</sup>, Wooju Lee<sup>2</sup>, Tae Ho Kang<sup>1</sup>, Seungki Lee<sup>1</sup>, Yunjeong Lee<sup>1</sup>, Dongchoul Kim<sup>2</sup>, Taewook Kang<sup>3</sup> and Inhee Choi<sup>1</sup>; <sup>1</sup>Department of Life Science, University of Seoul, Seoul, Korea (the Republic of); <sup>2</sup>Department of Mechanical Engineering, Sogang University, Seoul, Korea (the Republic of); <sup>3</sup>Department of Chemical and Biomolecular Engineering, Sogang University, Seoul, Korea (the Republic of).

Pinpoint assembly of colloidal nanoparticles onto solid substrate has been employed in a wide range of applications in microelectronics, nanophotonics, and nanomedicine. In order to precisely assemble colloidal nanoparticles onto a designated position against their thermal diffusion, chemical bonding or capillary interaction with pre-patterned solid substrate has been utilized. However, the direct assembly of colloidal nanoparticles without chemical linkers and pre-patterned substrates remains challenging. Here, we propose a novel approaches for rapid and direct positioning of colloidal plasmonic nanoparticles onto diverse solid substrates via photothermal convection lithography. It is based on the photothermal conversion effect of plasmonic nanoparticles by resonant light focusing, which induces convective flow. The convective flow further forces the colloidal nanoparticles to assemble at the illumination point of light. The size of the assembly is increased by either increasing the light intensity or illumination time. Also, we accelerate the assembly by modulating of experimentally controllable variables such as light intensity and solvent viscosity. We show that three types of colloidal gold nanoparticles with different shapes (rod, star, and sphere) can be quickly assembled by resonance matching with light. One assembly with a diameter of tens of micrometers can be completed within a minute, and patterned arrays of this assembly can also be prepared rapidly. We believe that our proposed method will have a huge impact on the future development of optical and electronic systems, as well as the building-up of plasmonic nanomaterials.

#### NM02.06.11

**Convenient and Inexpensive Highly-Efficient Nickel Nanowire Catalysts** Tomasz Wasiak, Lukasz Przepis, Krzysztof Walczak and Dawid Janas; Silesian University of Technology, Gliwice, Poland.

Recently, metal nanoclusters and nanowires have received a significant amount of attention due to the range of remarkable properties that they offer. A wide spectrum of these nanostructures can be created. Ranging from superconducting (YBCO), metallic (Ni, Pt, Au), semiconducting (Si) to isolating (SiO<sub>2</sub>, TiO<sub>2</sub>), it seems that many possible applications can be matched appropriate nanomaterial. Nickel nanowires (NiNWs) are particularly interesting due to the fact that they offer very promising properties while the material can be created from inexpensive precursors [1,2]. In this contribution we present how NiNWs of tuned diameter distribution can be made using a simple reduction of Ni ions in liquid medium [3]. The material created by this method was found to offer a number of advantages over commonly employed catalytic systems [3,4]. A range of chemical transformations carried out with ease using this system will be shown.

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#### NM02.06.12

**Size and Composition Effects in Compression of Ni-Fe Particle Prepared by Solid State Dewetting of Bilayers** Amit Sharma<sup>1</sup>, James Hickman<sup>2</sup>, Yuri Mishin<sup>2</sup> and Eugen Rabkin<sup>1</sup>; <sup>1</sup>Department of Materials Science and Engineering, Technion-Israel Institute of Technology, Haifa, Israel; <sup>2</sup>Department of Physics and Astronomy, George Mason University, Fairfax, Virginia, United States.

Small scale testing of single crystalline metallic particles offers a unique opportunity to understand the nucleation-mediated plasticity mechanisms. Single crystalline Nickel-Iron (Ni-Fe) particles with different iron content were prepared by solid state dewetting of Ni-Fe bilayers on sapphire substrate. The solid state dewetting process results in defect- and impurity-free single crystalline particles. The as-received particles were tested in compression employing in-situ nanoindentation in the field emission scanning electron microscope.

We demonstrate that faceted single-crystalline Nickel and Ni-Fe alloy nanoparticles exhibit an ultrahigh compressive strength unprecedented for crystalline metals. Most of the particles yielded with a large strain burst, and their strength exhibited a strong dependence of on the particle size. The strength of Nickel is consistent with all available estimates of the theoretical strength of Ni. Three factors are responsible for this record-high strength: (1) large shear modulus of Ni (78 GPa), (2) smooth edges and corners of the nanoparticles that reduce the stress concentration during the compression, and (2) thin oxide layer on the particle surface that softens the contacts with the substrate and indenter. This experimental discovery is augmented by molecular dynamics simulations that closely mimic the experimental conditions, including the degree of particle roundness, the softening of the particle contacts with the substrate/indenter, and the testing temperature.

#### NM02.06.13

**Self-Organized Formation of Multilayer Structure in a High Nitrogen Stainless Steel During Solution Treatment** Xuan Wang<sup>2</sup>, Rui Zhou<sup>2</sup>, Derek O. Northwood<sup>1</sup> and Cheng Liu<sup>2</sup>; <sup>1</sup>Mechanical, Auto and Materials Engineering, University of Windsor, Windsor, Ontario, Canada; <sup>2</sup>Mechanical Engineering, Yangzhou University, Yangzhou, China.

Compared with traditional stainless steels, high nitrogen stainless (HNS) steels have been widely used due to their high strength, toughness along with excellent corrosion resistance and low cost, by partial replacement of Ni (austenite-forming element) by N element. The evolution of the microstructure of a Cr<sub>19</sub>Mn<sub>19</sub>Mo<sub>2</sub>N<sub>0.7</sub> stainless steel is investigated by solution treatments at 1010, 1060, 1200 and 1250 degree Celsius for 30min, respectively. A complex multilayer structure has been found. A ferritic layer with nano-scaled particles precipitated along ferrite boundaries, at the surface, is formed. The subsurface layer with full austenitic structure and an internal microstructure comprising of austenite and ferrite are detected. With increasing the solution temperature, the thicknesses of both surface and subsurface layer show an increasing trend. However, the increase of surface layer thickness is greater compared with subsurface. This is attributed to an outward diffusion, a diffusive retardation and an abnormal accumulation of nitrogen during solution treatments. The precipitation of nano-scaled particles in the ferritic surface layer indicates possible diffusion barriers for nitrogen from subsurface to surface. This self-organized formation of multilayer structure can broaden the application of HNS steel to magnetic functional areas.

#### NM02.06.14

**Surfactant-Free Synthesis of Cu<sub>2</sub>O Yolk-Shell Cubes Decorated with Pt Nanoparticles for Enhanced H<sub>2</sub>O<sub>2</sub> Detection** Jian Lv<sup>1,2</sup>, Chuncai Kong<sup>1</sup>, Sen Yang<sup>1</sup> and Zhimao Yang<sup>1</sup>; <sup>1</sup>Department of Materials Physics, Xi'an Jiaotong University, Xi'an, China; <sup>2</sup>Department of Nanoengineering, University of California, San Diego, San Diego, California, United States.

Cu<sub>2</sub>O yolk-shell cubes decorated with Pt nanoparticles were synthesised by a liquid-phase, surfactant-free and multi-step route (Figure 1a). Zn<sup>2+</sup> ions and O<sub>2</sub> dissolved in solution lead to the formation of the yolk-shell Cu<sub>2</sub>O cubes. The as-prepared yolk-shell Cu<sub>2</sub>O cubes were used as the substrate to hold the growth of Pt nanoparticles through a commonly used photo-reduction reaction without damage of the yolk-shell structures. Then, the as-prepared Pt-Cu<sub>2</sub>O composites were used as the active materials for the fabrication of the nonenzymatic sensor for H<sub>2</sub>O<sub>2</sub>. Decorating Pt nanoparticles hugely increased the electrochemical sensing performance of Cu<sub>2</sub>O, compared with the bare yolk-shell Cu<sub>2</sub>O cubes. Meanwhile, the Pt-Cu<sub>2</sub>O based H<sub>2</sub>O<sub>2</sub> sensors show good electrochemical selectivity to the reduction of the H<sub>2</sub>O<sub>2</sub>, indicating its great promise to serve as the electrocatalytic materials for the sensing of the H<sub>2</sub>O<sub>2</sub>.

#### NM02.06.15

**Retention of Anti-Cancer Activity of Curcumin after Conjugation with Gold Quantum Clusters—An *In Vitro* and *In Vivo* Xenograft Study** Puneet Khandelwal<sup>2,1</sup>, Aftab Alam<sup>3</sup>, Arpan Kumar Choksi<sup>3</sup>, Samit Chattopadhyay<sup>4</sup> and Pankaj Poddar<sup>2</sup>; <sup>1</sup>Indian Institute of Technology Kanpur, Kanpur, India; <sup>2</sup>CSIR-National Chemical Laboratory, Pune, India; <sup>3</sup>NCCS, Pune, India; <sup>4</sup>IICB, Kolkata, India.

Cancer is a leading cause of death worldwide. However, a significant progress has happened in the cancer theranostics, a huge scope of the development is still exist. Chemotherapy is the most commonly used modality for cancer treatment. Curcumin is one of the very important therapeutically important drug molecules which has applications in wide range of diseases but could not be used clinically much because of its poor water solubility. The nanoparticles based platforms are used to enhance the solubility of curcumin. Since last two decades, metal nanoclusters are becoming increasingly popular for biomedical applications because of their very small size around 1-2 nm, biological inertness, a wide range of luminescence from UV to NIR. Therefore, in the present work, gold quantum clusters (Au QCs) are used to increase the curcumin water solubility by using it as both reducing and capping agent for the synthesis of Au QCs. These curcumin conjugated Au QCs (C-Au QCs) were studied for their cytotoxicity to normal (NIH3T3) as well as cancer cells (MCF7). The curcumin conjugated gold nanoparticles (C-Au NPs) and GSH conjugated Au QCs were also synthesized to evaluate the effect of size and capping agent on the anticancer property. The cytotoxicity mechanism of Au QCs was studied in detail using FACS and western blot analysis. Further, the antitumor activity of C-Au QCs was studied in xenograft mice model and found that C-Au QCs were able to effectively inhibit the tumor growth. The major organ section analysis showed that the C-Au QCs did not exhibit cytotoxicity to the organs. Based on the results, the C-Au QCs are believed to be a promising candidate to treat cancer effectively in near future.

#### NM02.06.17

**Visible Migration of Gold Based on Localized Plasmon Effect on a Paper Substrate** Nobuko Fukuda<sup>1</sup>, Sakae Manaka<sup>1</sup> and Toshiharu Enomae<sup>2</sup>; <sup>1</sup>National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; <sup>2</sup>University of Tsukuba, Tsukuba, Japan.

We visually observed color changes of a paper substrate on which gold particles were deposited during a period since deposition. The isolated gold particles are formed on the coated paper by thermal vapor deposition with 0.01 nm/s of the deposition rate for 500 s. The size of each gold particle is about a few 10s nm just after deposition, according to the surface image of the paper collected with a scanning electron microscope (SEM) and an atomic force microscope (AFM). The reflection spectrum for the surface measured with an integrating sphere spectrophotometer shows a high reflection from 400 to 510 nm and the surface color is bluish. The color is derived from localized surface plasmon resonance of the gold particles. After it was placed in air at room temperature for 6 months, the color changed from bluish to reddish. The spectrum shows a high reflection at more than 600 nm. The size of the gold particles after 6 months widely varies from a few 10s nm to 100s nm. Some particles seem to coalesce and the space between grains obviously has widened according to SEM observation. These results suggest that migration of the gold particles on the coated paper occurs at room temperature. In the case that the thermal vapor deposition with 0.01 nm/s was carried out for 1000 s, an incomplete gold sheet with gaps is formed on the paper substrate. The sheet thickness is about 10 nm. The reflection spectrum shows a high reflection at more than 500 nm and the surface color is yellowish and slightly metallic. After it was placed in air at room temperature for 6 months, the color changed from yellowish to reddish. The SEM and AFM images of the surface after 6 months passed shows isolated gold particles with more than 100 nm in diameter and more than 100 nm in height. It seems that dewetting, isolating, and coalescence of the gold have sequentially occurred on the coated paper. In addition, we expect that the rate of the color changes based on the migration of

gold depends on the surface conditions such as roughness, surface free energy, adhesive force, and so on.

#### NM02.06.18

**Preparation and Characterization of NiMn<sub>2</sub>O<sub>4</sub> Particles Toward Supercapacitor Application** [Hikaru Ishitsuka](#) and Yoshikazu Suzuki; Graduate School of Pure and Applied Science, University of Tsukuba, Tsukuba, Japan.

Recently, with the increase in worldwide energy demand, rechargeable energy devices and materials are actively studied. Especially, supercapacitor is a promising application in energy storage devices due to its high power density, good reversibility and cycle characteristics. Manganese oxide-based transition metal compounds are candidates for supercapacitor materials. NiMn<sub>2</sub>O<sub>4</sub> has excellent conductivity, stability and electrostatic capacity and does not contain noble metal.

NiCO<sub>3</sub>·2Ni(OH)<sub>2</sub>·4H<sub>2</sub>O (1 mmol), Mn<sub>2</sub>O<sub>3</sub> (3 mmol) and urea (15 mmol) were dissolved in 30 mL distilled water to obtain homogeneous solutions. The solutions were hydrothermally treated at 120-160 °C for 6 h, and Ni-Mn precursors were obtained. The as-prepared precursors were calcined at 350 °C for 3 h.

The obtained powder samples were characterized by XRD, and the microstructure was investigated by SEM and TEM. The specific surface area was evaluated by N<sub>2</sub> adsorption method.

#### NM02.06.19

**Nano-Phase Separation Sintering in Titanium-Magnesium Alloys** Kathrin Graetz<sup>2,1</sup>, [Jonathan Paras](#)<sup>1</sup> and Christopher A. Schuh<sup>1</sup>; <sup>1</sup>Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; <sup>2</sup>Mubea Performance Wheels, Gurten, Austria.

While mechanical milling reliably produces nano-sized grains in metal alloy powders, consolidating as-milled powders into bulk parts—while still retaining the desirable nanocrystalline structure—remains a challenge. This work seeks to use alloying to lower the free energy of grain boundaries and decrease the driving force for coarsening in nanocrystalline Ti alloys, permitting solid-state sintering to high density. Mg is identified as a nano-grain stabilizer for Ti, and the effects of Mg composition on powder consolidation by pressureless sintering are explored. The mechanical milling of Ti-Mg alloys produces grain sizes on the order of 20 nm along with a supersaturation of Mg solute in Ti. Accelerated sintering occurs upon heating, triggered by nano-phase separation of Mg out of solution, in some cases leading to relative densities >95% at low processing temperatures, while maintaining ultrafine grain sizes. The thermal stability of the grain structure is also characterized over a range of temperatures and a kinetic relationship for the coarsening behavior of Ti-Mg alloys is determined.

#### NM02.06.20

**Surface Versus Incorporated Pd on SnO<sub>2</sub>—Influence on Gas Sensing** [Sebastian Keller](#), Nicolay J. Pineau, Andreas T. Güntner and Sotiris E. Pratsinis; ETH Zurich, Zurich, Switzerland.

Size, shape and location of catalytic active Pd on SnO<sub>2</sub> has a strong impact on gas sensing properties. In specific, it greatly enhances the sensitivity of gas sensors and reduces response and recovery times and is therefore often applied.<sup>1</sup> However, the exact role of Pd size, location and amount is rarely investigated and remains a trial and error approach. Here, the location (i.e. surface or incorporated) and size of Pd on SnO<sub>2</sub> and its role on gas sensing are systematically investigated and optimized at the nanoscale. In a first step, SnO<sub>2</sub> nanoparticles with different amounts and locations of Pd were prepared by flame aerosol and wet chemical synthesis. The amount of incorporated and surface Pd was investigated by X-ray diffraction, tunnelling electron microscopy and Pd-leaching. Sensing films of these particles were obtained by doctor blading them onto substrates with interdigitated electrodes. The optimized gas sensors exhibit superior sensitivity to trace analytes even at relevant low ppb levels and could therefore readily be used to detect environmental pollutants<sup>2</sup>, monitoring food quality<sup>3</sup>, detect entrapped humans after a calamity<sup>4</sup>, as well as in medical breath analysis<sup>5</sup>.

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#### NM02.06.21

**Design of Localized Surface Plasmon Absorption in Square-Shaped Silver Nanoparticles** [Abhishek Ramachandran](#), Anmol Walia and Madhusudan Singh; Indian Institute of Technology Delhi, New Delhi, India.

Shaped nanoparticles are known to enhance absorption in a tailored manner due to the enhancement of electric field modes in incident light. Various fabrication techniques have made it possible to produce nanoparticles with accurate sizes and in a variety of external media resulting in a controlled red shift in the absorption spectrum. This control is valuable in the design of absorbers for potential detector and photovoltaic applications, besides optical coatings. In this work, the dependence of the absorption spectrum on various parameters such as square nanoparticle edge length, height, aspect ratio, wavelength and polarization of incident light, external medium as well as the effect of a proximal conductive substrate was investigated using finite difference time domain numerical techniques, and enhancement factors derived. Absorption peaks were found to redshift from ~625 nm to ~890 nm upon an increase of the edge length from 150 nm to 250 nm (height constant), but blue shift upon increasing height of the nanoparticles (edge length constant). The peak location is found to be strongly dependent on the aspect ratio, but not the volume of the nanoparticles. Higher refractive indices resulted in redshift of the absorption (fixed distance to the conductive substrate). Resonant energy transfer is seen to happen through enhanced absorption for in-plane polarization of light. These results are expected to provide a better path to the rational design of optical absorption through localized surface plasmon resonance of square nanoparticles produced through techniques such as chemical synthesis and e-beam lithography.

#### NM02.06.22

**Correlating Interfacial Solvent Structures with Catalytic Behavior by Total Scattering** Mirco Eckardt and [Mirijam Zobel](#); University of Bayreuth, Bayreuth, Germany.

Noble metal nanoparticles (NP) play a major role in modern heterogeneous catalysis. Reaction conditions like temperature and pressure impact the catalytic activity and selectivity. [1] Although a solvent effect is commonly accepted as a decisive parameter in liquid-phase catalysis, its fundamental understanding on a molecular level is still missing. Pair distribution functions (PDF) analysis based on high-energy X-ray scattering experiments can access the size of and the molecular ordering within solvation shells around colloidal NPs. [2] To correlate solvent-dependent catalytic activity with the interfacial solvent structure, we performed the selective hydrogenation of styrene to ethylbenzene under atmospheric hydrogen pressure in various organic solvents like tetrahydrofuran (THF) and toluene. Dodecanethiol stabilized palladium (Pd) NPs with an average diameter of 3 nm acted as catalyst. The difference-PDF signal of the THF dispersions reveals four restructured layers of THF molecules stretching 2 nm away from the NP surface. Corresponding catalytic studies

(gas chromatography) allow a structure-activity correlation. Finally, GC-MS can be coupled to in-operando PDF measurements (1 min time resolution) to track structural changes of both NP and interfacial solvent layers in liquid-phase catalysis.

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#### NM02.06.23

**Control of Nanoporous Pd-Al Film Structure by Dealloying Reaction of Al-Pd Alloy Film Using Organic Acids as Chelating Agents** Takashi Ishiguro, Akizumi Kawamoto and Takuji Ube; TUS, Tokyo, Japan.

Nanoporous materials are applied to sensors, catalysts, etc. because of their large specific surface area. For example, since palladium (Pd) selectively reacts with hydrogen gas, application as a sensor is expected. One of the most usual methods to form the nanoporous materials is dealloying, which is chemical or electrochemical dissolution process of the base metal from the precursor alloy with target material. In this case, strong acids such as hydrochloric acid and sulfuric acid or strong alkali are usually used. In contrast to this, we have proposed a dealloying process using environmentally friendly chemicals. Ultrafine nanoporous Pd-Al film had been successfully formed by citric acid-assisted hot-water-treatment of Al-Pd alloy film. (T. Harumoto, Y. Tamura, and T. Ishiguro, *AIP Advances* 5, 017146 (2015)). Here the citric acid played a role as a chelating agent for forming the complex with  $Al^{3+}$  ions. On the other hand, there was a disadvantage that the reaction rate was slow, e.g. it took 30 minutes for dealloying reaction of 70-nm-thick Al-Pd alloy films to be saturated. Therefore, in this study, in order to accelerate the dealloying reaction rate, pH value of the reaction solution was controlled from 4 to the alkaline side. In addition to the citric acid, as the reaction solution, ethylenediaminetetraacetic acid (EDTA) having high chelating ability was also examined. 70-nm-thick Al-Pd (82at%Al) alloy films were prepared by rf sputtering method using Al target with Pd sectors. pH value was controlled by adding  $NaHCO_3$  to citric acid solution or  $Na_2CO_3$  to EDTA solution. Time variation of the visible light transmittance (VLT) during dealloying processing at 370 K was measured by using a digital high-vision video camera. Structure of the film on elastic carbon film were observed by using scanning transmission electron microscope.

Saturation time of VLT in the pure citric acid solution at pH=4.0 was 30 min. By adding  $NaHCO_3$  to this citric acid solution, pH value changed to 9.0 and then saturation time of VLT was shortened to 9 min. Furthermore, when reacting with EDTA at pH=10.0, the saturation time was reduced to 90 sec. By changing chelating agent from the citric acid to EDTA, the film morphology also changed from high-density nanopore (diameter of about 10 nm) structure to nanopore network structure. In addition, the film composition after the dealloying treatment increased up to 92at%Pd in the case of EDTA (pH=10.0) from 85 at%Pd in the case of citric acid (pH=4.0).

It was considered that dissociation of citric acid and EDTA was promoted under the pH conditions on the alkaline side and the chelating ability was activated. As a result, it was found that by controlling the pH value according to the type of chelate, the dealloying reaction rate was accelerated to 20 times.

#### NM02.06.25

**Fullerene Nanopottery—Design, Shaping and Interconnecting Hollow Nanostructures** Fei Han and Hongyu Chen; Nanyang Technological University, Singapore, Singapore.

Hollow nanostructures have been widely applied in nanoscience, but their fabrication remains at a primitive level. Most hollow nanostructures are enclosed spheres. Even creating a bottle in nanoscale is extremely difficult, not to mention creating more complex shapes and assembling interconnected systems. Interconnected hollow system is one of the most fundamental structures both in living system and in human industry, e.g., blood vessel system and nerve system in livings, various tube systems in city, and modern buildings consisted by corridors and rooms. However, the concept of interconnecting hollow spaces still remains blank in nanoscale, which is critical to the synthesis of such structures.

We bring pottery, the oldest and simplest method to create and assemble hollow structures, into nanoscale, to realize the systematical design, synthesis, assembly, and interconnection of hollow nanostructures. Individual fullerene hollow structures of tailored shapes, such as bowls, bottles, and cucurbits, are synthesized through a bottom-up process within one-step. Most importantly, the method allows modularized interconnection of hollow units into interconnected hollow systems. The synthesized structures have a hydrophobic interior and a hydrophilic outer surface. As a proof-of-concept, we create multi-compartment nano-containers, with different hydrophobic nanoparticles isolated in the separate pockets. Hopefully, these findings could expand the synthetic freedom for hollow nanostructures, building a bridge from isolated hollow units to interconnected hollow systems, and hence, have the potential to broaden their applications in a wide range of fields.

#### NM02.06.26

**In Situ Analysis of Conductive Films Formation Using Cu Nanocrystals** Arnau Oliva Puigdomenech<sup>1</sup>, Filip Geenen<sup>2</sup>, Christophe Detavernier<sup>2</sup> and Zeger Hens<sup>1</sup>; <sup>1</sup>Chemistry, Ghent University, Ghent, Belgium; <sup>2</sup>Solid State, Ghent University, Ghent, Belgium.

##### Introduction

The constantly growing market of printed electronics requires the development of new materials that can be turned into conductive inks and allow for economic device fabrication. Hereof, due to its top-of-the-line conductivity and affordable cost, conductive inks based on copper nanocrystals have been extensively studied in the recent years. A particular focus of this work has been the prevention of copper oxidation, which can compromise the conductivity of the eventually printed copper. Typically, oxidation has been suppressed by the incorporation of antioxidants or the formation of a shell around the Cu nanocrystals. While effectively slowing down oxidation, such approaches come at the expense of costlier synthesis reagents and conditions.<sup>1</sup> Instead of preventing oxidation at all costs, we propose a flexible and economical synthesis route of Cu nanocrystals, demonstrate by in-situ x-ray diffraction that surface oxidation can be reversed upon sintering, and how the sintering conditions vary depending on the copper nanocrystal size and surface termination.

##### Results and Discussion

Cu nanocrystals were synthesized by thermal decomposition of copper formate in oleylamine. SEM and TEM imaging presented quasi-spherical nanocrystals; depending on the molar ratio between copper formate and oleylamine the particle size could be tuned from 4-200 nm. By means of solution NMR, we demonstrate that the ligands capping the copper nanocrystal surface can be readily exchanged, which enables us to modify the physicochemical properties of the nanocrystals. Using in-situ XRD carried out during the sintering of the deposited particles, we demonstrated a direct correlation between the characteristics of these ligands and the temperature at which copper oxide is reduced. Moreover, this dependency was also demonstrated in the case of different particle sizes, where we found that smaller nanocrystals are converted into pure copper at significantly lower temperatures. Similarly, in-situ 4-point probe resistance studies demonstrated a correlation between the reduction of copper oxide and a sudden drop on the resistivity of the films. Eventually, a resistivity down to 20  $\mu\Omega\bullet\text{cm}$  were obtained, a result that proves that conductive inks based on Cu nanocrystals are a viable technology for printed electronics.

##### Conclusions

We propose a flexible and efficient synthesis method that yields Cu nanocrystals. We use them as models to study the reduction of copper oxide in Cu nanocrystal films. We find that the unavoidable oxidation of the surfaces can be reversed via sintering. We prove that the temperature at which conversion to copper occurs markedly depends on the size and the surface termination of the nanocrystals. We demonstrate that sintered films attain a resistivity as low as 20  $\mu\Omega\bullet\text{cm}$ , which confirms the potential of nanocrystals for printed electronics.

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#### NM02.06.27

**Synthesis and Characterization of Biogenic Selenium Nanoparticles with Antimicrobial Properties Made by *Staphylococcus aureus*, Methicillin-Resistant *Staphylococcus aureus*(MRSA), *Escherichia coli* and *Pseudomonas aeruginosa*** David Medina, Gujje Mi and Thomas Webster; Northeastern University, Boston, Massachusetts, United States.

Antimicrobial resistance is a global concern that affects more than 2 million of people each year. Therefore, new approaches to kill bacteria are needed. Nanotechnology is one of the most promising approaches. While metallic nanoparticle synthesis methods are well studied, they are often accompanied by significant drawbacks such as cost, extreme processing conditions, and toxic waste production. In this work, we explored the environmentally safe synthesis selenium nanoparticles, which have shown promise in killing bacteria.

Using *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* subsp. *aureus* Rosenbach and Methicillin-resistant *Staphylococcus aureus*(MRSA) were used to synthesize biogenic selenium nanoparticles, 90-150 nm selenium nanoparticles were synthesized under standard conditions using an environmentally-safe approach. Bacterial cultures, prepared in Luria-Bertani (LB) media, were inoculated with 2 mM sodium selenite ( $\text{Na}_2\text{SeO}_3$ ) solution to activate the detoxification process that leads to the synthesis of nanoparticles. The nanostructures were characterized using Transmission Electron Microscopy, Energy Dispersive X-Ray (EDX) to determine the chemical compositions and Inductively coupled plasma mass spectrometry (ICP-MS) to validate the chemistry within the samples. Nanoparticles were also characterized and tested for their ability to inhibit the bacterial growth through optical density measurements in a SpectraMax M3 spectrophotometer, and colony forming unit assays. Besides, biocompatibility tests of the nanoparticles with human tissue were accomplished, growing human dermal fibroblast (HDF) cells in media in the presence of biogenic selenium nanoparticles. After an incubation time of 24 hours, the cell growth was analyzed using MTS assay.

It is demonstrated that the bacterial strains used can generate biogenic selenium nanoparticles. The antimicrobial activity of these biogenic selenium nanoparticles was tested against *Escherichia coli* and *Staphylococcus aureus* to discover their antibacterial ability. Nanoparticles can produce a decay in the standard bacterial growth. Besides, the growth of *Staphylococcus aureus* was significantly inhibited for those nanoparticles synthesized by *Staphylococcus aureus*. In vitro cytotoxicity assays were performed with human dermal fibroblasts (HDF) cells. The experiments showed that all nanoparticle concentrations tested did not inhibit the growth of cells while also confirming a high percentage of cell viability.

As a conclusion, selenium nanoparticles with small and uniformly shape were synthesized with a relatively homogeneous size distribution. Decay in the bacterial growth was achieved against both Gram-positive and Gram-negative bacteria, showing no significant cytotoxicity effect when they were cultured with human dermal fibroblasts (HDF) cells.

#### NM02.06.28

**Nanoshaping of Metallic Liquid by Stretching—Evading Lithography** Zhonglue Hu and Golden Kumar; Texas Tech University, Lubbock, Texas, United States.

Metal nanostructures are integral parts of nanoscale devices and fundamental studies on characterization of size-effects. However, these technological and scientific advancements are hampered by the complex and expensive lithography based fabrication techniques. Here, we present a novel lithography-free nanomanufacturing by elongation and rupture of glass forming metallic liquid. This approach allows facile fabrication of various structures such as nano-tips, nano-wires, and dog-bone-shaped nano-structures without lithography or expensive templates. The flow behavior of metallic liquids is tuned through temperature and strain-rate to control the shape of resulting structures upon elongation and rupture. Quantitative studies on individual structures are performed to understand the correlation between the initial size/shape, temperature (viscosity), elongation speed (strain-rate), and final shape/size.

#### NM02.06.29

**Multifunctional Vesicles from Self-Assembled Cluster-Containing Diblock Copolymer** Anastasia Voevodin, Luis Campos and Xavier Roy; Chemistry, Columbia University, New York, New York, United States.

The study of metal chalcogenide molecular clusters as functional units in macromolecular systems has rapidly expanded in recent years. Their tunable properties allow them to be used in a variety of applications, including energy storage, lighting, magnetics and catalysis. While the self-assembly of metal chalcogenide clusters in the solid-state is well studied, their incorporation into polymer systems has been limited. We report a new block copolymer containing a site-differentiated  $\text{Co}_6\text{Se}_8$  molecular cluster capable of multi-electron redox processes. The block copolymer system self-assembles in solution to form vesicle structures at the mesoscale whose walls can be further crosslinked after assembly. Moreover, the vesicles can be loaded with molecular cargo such as with a methylene blue dye. This talk will describe the synthesis, self-assembly and characterization of the novel cluster-containing diblock copolymer. The integration of a transition metal-containing molecular cluster into well-defined block copolymers offers exciting possibilities to develop multifunctional assemblies for further applications in catalysis, electrochemistry, and biomedicine. This cluster-containing polymer could also be used to direct hierarchical assembly of novel metal chalcogenide mesostructures.

#### NM02.06.30

**Investigation the Effect of Gold Nanoparticle on Alkaline Phosphatase Enzyme Activity for Using Influenza a Diagnosis Studies** Yasemin Budama Kilinc, Gunem O. Eren and Rabia Cakir Koc; Bioengineering Department, Yildiz Technical University, Istanbul, Turkey.

In our present study it is focused on examining of effect of colloidal gold nanoparticles which have 40 nm in diameter to ALP-IgY conjugate in order to use in Influenza A diagnosis applications. Influenza A affects all age groups worldwide, and causes significant loss of workdays, human suffering, and mortality every year. Matrix protein 2 (M2) is a structural protein of influenza A viruses and plays an important role in the virus life cycle. M2e is the high sequence conservation of extracellular domain among all known human influenza A viruses. Therefore, M2e peptide specific IgY antibodies were chosen in this study for development of ELISA methods based on gold nanoparticles conjugation.

Transmission Electron Microscopy (TEM-EDX) demonstrated that particles have 40 nm in diameter it is confirmed that IgY-ALP conjugate was

successfully bound to gold nanoparticle. Nano-ELISA results demonstrated that after one hour incubation at 37°C absorbance values of IgY-ALP conjugate was higher than IgY-ALP-Au conjugate in every concentrations. In addition kinetic rate was measured by UV-vis analysis and these results indicated that reaction rate of IgY-ALP-AuNPs was slower than IgY-ALP while absorbance values are higher when gold nanoparticle was bound to IgY-ALP conjugate. Fourier Transmission Infrared Spectroscopy (FTIR) results indicated that gold nanoparticle has effect on ALP enzyme structure. The transmittance peaks of amide I and amide II bonds of IgY-ALP-Au conjugate changed due to presence of gold nanoparticle when compared to IgY-ALP conjugate alone.

In result it can be said that gold nanoparticles have a negative effect on ALP enzyme kinetic rate when it used for enzyme-linked immunosorbent assays. Au-NPs increases the activation energy of ALP-substrate interaction due to conformational change and therefore absorbance values of IgY-ALP-Au complex are much lower than IgY-ALP conjugate in ELISA procedure.

#### **Funding and Acknowledgement**

This study was supported by the Scientific and Technological Research Council of Turkey with the project titled "The development of a rapid diagnostic kit using the immunochromatographic method of depending on an M2c peptide-specific IgY antibody for the diagnosis of influenza A infection" (Project No: 115S132).

Authors would like to thank the Scientific and Technological Research Council of Turkey.

#### **NM02.06.31**

**The Core-Shell Engineering on Energy Product of Magnetic Nanometals** Shenqiang Ren and Jingming Zhang; University at Buffalo, The State University of New York, Buffalo, New York, United States.

The exchange coupling between magnetically hard and soft materials possesses many desirable magnetic characteristics and thus is extensively explored for high energy product magnets. Here we demonstrate a solution-based growth of magnetically hard and soft FePt-FeCo (Core-shell) nanoparticles with the controllable shell thickness. The transition from spin canting to exchange coupling of FePt-FeCo core-shell nanostructures leads to a 28% increase in the coercivity (12.8 KOe) and a greater than two-fold enhancement in the energy product (9.11 MGOe), as compared to the FePt nanoparticles. Besides the traditional solution method, a eutectic molten salts method has been developed to synthesis L1<sub>0</sub> hard magnetic phase in one step. The benefit of this method is the ease of removal chemical residual after reaction, and reduce the total preparation time of the L1<sub>0</sub> phase of FePt. The as-synthesized FePt powder has a coercivity of 15 KOe while no further treatment was needed. The results shown here imply that the eutectic method and core-shell engineering have the potential to enhance the energy product of next-generation nano-magnets.

#### **NM02.06.32**

**The Role of Aminosilane Loading Density on the Formation of Gold-Coated Superparamagnetic Core/Shells with Enhanced Dual Surface Heating to Combat Tumor** Manal Almusaynid<sup>2,3</sup>, Roa Fardous<sup>2,3</sup>, Edreese H. Alsharaeh<sup>1</sup>, Abdulaziz Almalik<sup>3,2</sup> and Ali H. Alhasan<sup>2,3,1</sup>; <sup>1</sup>College of Science and General Studies, Alfaisal University, Riyadh, Saudi Arabia; <sup>2</sup>KACST-BWH/Harvard Centre of Excellence for Biomedicine, Joint Centers of Excellence Program, King Abdulaziz City for Science and Technology, Riyadh, Saudi Arabia; <sup>3</sup>National Center for Pharmaceutical Technology, Life Science and Environmental Research Institute, King Abdulaziz City for Science and Technology (KACST), Riyadh, Saudi Arabia.

Despite significant development in the therapeutic strategies for breast cancer, some challenges remain. Conventional treatments such as chemotherapy and surgery cause serious side effects. Among the various approaches to enhance the efficacy of breast cancer therapies, is the use of gold-coated magnetic nanoparticles, which have dual functionality acting as both magneto- and photo-thermal agents. Such nanoparticles may prove valuable in enhancing the therapeutic efficacy if synthesized as quantum-sized nanoparticles, which is still challenging. In this study, we tackle the synthesis of quantum-sized superparamagnetic (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles (~10 nm as an inner core) coated with a thin shell of gold (~14 nm) and explore their efficiency to generate heat as a result of their superparamagnetic properties and strong NIR absorption. Our findings show that gold shell formation around a core of quantum-sized nanoparticles is troublesome unless the loading density of (3-aminopropyl)triethoxysilane (APTES) onto Fe<sub>3</sub>O<sub>4</sub> nanoparticles is maximized in order to increase the number of gold nanoparticles per Fe<sub>3</sub>O<sub>4</sub> nanoparticle. Exposing Fe<sub>3</sub>O<sub>4</sub>/Au core/shell nanoparticles to an external magnetic field and NIR irradiation (~808 nm) results in complete apoptosis-mediated breast cancer death at 45°C, significantly reducing tumor growth in comparison to single mode treatments (magnetic or laser hyperthermia). Apparently, our quantum-sized core-shell nanoparticles afford greater heat efficiency when successfully applied as a dual magneto- photo-thermal therapy for breast cancer.

#### **NM02.06.33**

**pH-Controlled Dealloying Route to Hierarchical Bulk Nanoporous Zn Derived from Metastable Alloy for Hydrogen Generation by Hydrolysis of Zn in Neutral Water** Jintao Fu and Eric Detsi; University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Dealloyed nanoporous metals made of very reactive elements have rarely been reported. Instead, reactive materials are used as sacrificial components in dealloying. The high chemical reactivity of non-precious nanostructured metals makes them suitable for a broad range of applications such as splitting water into H<sub>2</sub> gas and metal hydroxide. On the other hand, the same high chemical reactivity hinders the synthesis of nanostructured metals. In this talk, I will present a nanofabrication route to hierarchical bulk nanoporous Zn and demonstrate its potential to produce hydrogen from neutral water. Typically, we used a pH-controlled dealloying strategy to fabricate bulk nanoporous Zn with bulk dimensions in the centimeter range via the selective removal of Al from metastable face-centered cubic bulk Zn<sub>20</sub>Al<sub>80</sub> at. % parent alloys. The corresponding bulk nanoporous Zn exhibits a hierarchical ligament/pore architecture characterized by primary ligaments and pores with average feature size in the sub-micrometer range. These primary structures are made of ultrafine secondary ligaments and pores with characteristic feature size in the range of 10-20 nm. I will show that the bulk nanoporous Zn can spontaneously split water into H<sub>2</sub> and Zn(OH)<sub>2</sub> at ambient temperature and pressure, and continuously produce H<sub>2</sub> at a constant rate of 0.08 mL/min per gram of Zn over several hours. It is anticipated that in this hierarchical bulk architecture, the macropores facilitate the flow of water in the bulk of the material, while the mesopores and ultrafine ligaments provide a high surface area for the reaction of water with Zn. The bulk nanoporous Zn/water system can be used for on-board or on-demand H<sub>2</sub> applications during which H<sub>2</sub> is produced when needed, without prior storage of this gas compressed in cylinders as it is currently the case. [1]

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Wednesday Morning, November 28, 2018  
Sheraton, 3rd Floor, Commonwealth

**8:30 AM \*NM02.07.01**

**Synthesizing Cooperative Metal-Support Interfaces for Catalysis** Sheng Dai<sup>1,2</sup>; <sup>1</sup>Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; <sup>2</sup>Department of Chemistry, The University of Tennessee, Knoxville, Tennessee, United States.

Understanding the cooperative interactions of metals with active supports is essential to tailoring their catalytic activities and/or control of reaction pathways. These interfacial interactions can be achieved through two mechanisms: interfacial charge redistribution (electronic interaction) and interfacial atom transport (chemical interaction). In the last two years, a number of new advances have been made by our BES team toward tuning the metal-support interactions. The success of our approach capitalizes on nanoconfined spaces (e.g., confined interface restructuring), complex oxide supports (e.g., perovskite oxides), and 2D material edge sites (e.g., boron nitride), demonstrating that uniquely strong interfacial interactions and cooperativities between nanoparticles and supports can emerge through judicious structural choices of metals and supports. This presentation will be focused on the following three synergistically linked research activities: (1) sacrificial strong metal-support interactions, (2) "intelligent" metal-support interactions, and (3) charge-flow metal-support interactions. The interconnections among the above three metal-support interactions will be also discussed.

**9:00 AM NM02.07.02**

**Understanding and Controlling Nanoparticle Entrenchment in Oxide Supports** Abha A. Gosavi, Justin Notestein and Chad A. Mirkin; Northwestern University, Evanston, Illinois, United States.

On rapid heating to high temperatures and under inert conditions, metal nanoparticles exhibit entrenchment in the SiO<sub>2</sub> layer on a silicon wafer to create nanopores. This phenomenon occurs above a critical temperature of around 1000 C, at ramp-rates above 3.3 C/sec, resulting in nanopores as deep as 250 nm or more, depending on the thickness of the SiO<sub>2</sub> layer. We have studied and characterized this entrenching behavior and subsequent nanopore formation for a wide variety of metal nanoparticles, including Au, Ag, Pt, Pd and Cu. Using Pd on SiO<sub>2</sub> as our model system for studying the behavior of nanoparticle entrenchment, we have established the critical conditions (temperature, times and ramp-rates of heating) required to observe entrenchment. The subsequent trends in this behavior with changing particle size and spacing have also been identified. We have thus tried to establish a mechanism by which nanoparticle entrenchment occurs and competes with other surface phenomenon (sintering, evaporation and diffusion) that occur for silicon dioxide supported metal nanoparticles at high temperatures.

The behavior of metal nanoparticles under entrenchment conditions was also studied for various different oxide supports (TiO<sub>2</sub>, HfO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) and compared to the nanopore formation on SiO<sub>2</sub>. We observed that while nanoparticles supported on TiO<sub>2</sub> and HfO<sub>2</sub> undergo surface coarsening under high temperature treatment, Al<sub>2</sub>O<sub>3</sub> acts a barrier to nanoparticle entrenchment and subsequent pore formation. This behavior inspired a novel tri-layer approach for immobilizing Au nanoparticles in SiO<sub>2</sub> supports. By creating a tri-layer architecture consisting of SiO<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub> on silicon wafers, we could control the depth to which nanoparticles entrench between 3-5 nm. This small range enabled us to sufficiently entrench particles for the purpose of immobilization but still maintain access to the nanoparticle surface to allow for catalytic activity studies. The two advances of moving into the sub-15 nm nanoparticle size regime and of controlled particle immobilization through entrenchment have important implications in studying site-isolated and stabilized metal nanoparticles for applications in sensing, separations, and catalysis. As proof-of-concept, we evaluated the reduction of 4-nitrophenol by NaBH<sub>4</sub> catalyzed by Au nanoparticles buried 3 nm into the trilayer substrate.

While the nanoparticles immobilized in the tri-layer supports can be used for catalysis, the nanopores formed in the course of the entrenchment could have a wide range of applications on their own. These linear, high-aspect ratio nanopores have diameters comparable to those of the starting nanoparticles (<15 nm) and can be hundreds of nanometers long. The size and surface density of the nanopores can be tuned by changing the particle sizes and distribution of the nanoparticles being heated. The resulting porous, planar materials could have applications in sensing and separation of large molecules.

**9:15 AM NM02.07.03**

**Size-Controlled Synthesis of CuNi Nano-Octahedra and Their Catalytic Performance Towards 4-Nitrophenol Reduction Reaction** Can Li<sup>1</sup>, Yiliang Luan<sup>1</sup>, Bo Zhao<sup>2</sup>, Amar Kumbhar<sup>3</sup> and Jiye Fang<sup>1</sup>; <sup>1</sup>SUNY Binghamton, Binghamton, New York, United States; <sup>2</sup>Texas Tech University, Lubbock, Texas, United States; <sup>3</sup>University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

Compared with noble metal catalysts, non-noble metallic nanocrystals (NCs) as a new class of catalysts have attracted increasing attention due to their low cost, abundant content in the Earth's crust, and outstanding catalytic performance in some reaction such as oxidation, hydrogenation, and electrocatalysis. It is well-known that some specific crystal facets on the catalysts can promote the catalytic activity. However, most reported NCs with some exclusive facets are noble metal or metal oxide based catalysts. There are limited studies on the synthesis of facet- (or shape-) controlled non-noble metallic NCs. As standard reduction potentials of the non-noble metals are much lower than those of the noble metals, the relatively high sensitivity and instability of the non-noble metal NCs, especially when they expose to air or aqueous solution, make it hard to harvest non-noble metal NCs in controlled shape and size.

Herein, we demonstrate a size-controlled synthesis of CuNi nano-octahedra using a hot colloidal solution approach. Borane morpholine was used as a reducing agent to promote a rapid nuclei formation. The as-synthesized CuNi NCs could be stably dispersed into an organic solvent such as hexane with capping ligands anchored on their surface. Two different sizes of CuNi nano-octahedra were chosen and investigated in this report. A number of synthetic factors such as the ratio of oleic acid and oleyamine were identified and optimized in order to efficiently control the size and shape. It was further determined that the concentration remarkably played a key role in the size-control of the CuNi nano-octahedra. In terms of the catalytic evaluation, the size effect of CuNi nanocatalysts on 4-nitrophenol reduction activity was carried out. Our study indicates that the obtained CuNi nano-octahedra exhibited higher catalytic activity compared with those CuNi NCs reported previously, and their performance was strongly size- and shape- dependent due to the surface area and the specific atomic arrangement of the {111} surfaces.

**9:30 AM NM02.07.04**

**Room Temperature Electrodeposition of Palladium Based Intermetallic Electrocatalyst** Yunfei Wang, Du Sun, Justine Wagner, Tomojit Chowdhury, Thomas J. Kempa and Shoji Hall; The Johns Hopkins University, Baltimore, Maryland, United States.

Recently, ordered intermetallic compounds have become emerging materials for catalysis. The synthesis of ordered intermetallic compounds usually requires annealing at temperatures > 700 C. Here we present a method of preparing ordered intermetallic Pd<sub>31</sub>Bi<sub>12</sub> at room temperature via electrochemical deposition. According to the phase diagram, this system is thermodynamically stable at temperatures between 550 C to 605 C, indicating that the deposited material is metastable. The Pd<sub>31</sub>Bi<sub>12</sub> morphology consists of a compact nanoparticulate film, the particles sizes range from 30nm to 100nm. We assessed the catalytic activity of this material for the oxygen reduction reaction, Pd<sub>31</sub>Bi<sub>12</sub> exhibits 60 times higher specific activity than Pd

and Pt at 0.85V. The half wave potential of Pd<sub>31</sub>Bi<sub>12</sub> is 0.93V, 43mV higher than Pd and 69mV higher than Pt. Pd<sub>31</sub>Bi<sub>12</sub> also displays high stability under accelerated durability cycling, after 10K cycles a 4 mV shift of its half wave potential, and 40% decay in specific activity is observed. Ultraviolet photoelectron spectroscopy is applied to explore the valence band of Pd<sub>31</sub>Bi<sub>12</sub>. The results show that alloying Bi with Pd drastically lower the center of valence band compared with Pd, thus reduce adsorption energy of intermediate in oxygen reduction reaction. In conclusion, we have demonstrated that electrodeposition can be used to prepare thin films of ordered intermetallic Pd<sub>31</sub>Bi<sub>12</sub> on glassy carbon electrodes. Pd<sub>31</sub>Bi<sub>12</sub> is a highly active and stable material for performing the reduction of O<sub>2</sub> to H<sub>2</sub>O.

#### 9:45 AM NM02.07.05

**A General Route to Synthesize Core@Shell ORR Nanocatalysts** Jocelyn T. Gamler, Hannah M. Ashberry and Sara E. Skrabalak; Indiana University, Bloomington, Indiana, United States.

The need for sustainable energy platforms drives catalyst design and synthesis. In the case of organic liquid fuel cells, improvements in terms of activity, durability, and cost are needed for oxygen reduction reaction (ORR) catalysts, which are largely Pt-based. Typical routes to overcome the high cost and unfavorable surface-adsorbate interactions are to incorporate a secondary transition metal, either through a core@shell architecture or alloy formation; this addition decreases expensive metal loadings and tunes the surface-adsorbate interaction in accordance with the Sabatier principle. The present work demonstrates the versatility of seed-mediated co-reduction (SMCR) to deposit PtM (M = Ni, Co, Cu, Fe) random alloyed shells on PdCu B2 intermetallic seeds, integrating the concepts of a core@shell architecture and alloyed surfaces into one nanostructure. Control of both shell thickness and Pt:M ratio are also demonstrated. The catalytic activity as a function of shell thickness for a model system, B2@PtNi, was evaluated for the ORR. The series of B2@PtM catalysts are also evaluated for the ORR to determine the role surface composition plays in activity and durability. Collectively, this work aims to develop synthetic techniques to achieve complex nanocatalyst compositions.

#### 10:00 AM BREAK

#### 10:30 AM \*NM02.07.06

**Efficient Generation of Hot Electrons in 'Quantum-Sized' Metal Nanoparticles for Selective Oxidation of Alcohols** Yugang Sun; Temple University, Philadelphia, Pennsylvania, United States.

Selective oxidation of alcohols to aldehydes rather than ketones/acids represents a class of important chemical reactions for many industrial processes (e.g., esterification). Current practices primarily rely on the use of strong oxidants (e.g., permanganate and dichromate), which are usually toxic and have to be removed from the products. The strong oxidizing power of the traditional oxidants easily leads to overoxidation of alcohols to ketones, lowering the selectivity and yield of aldehydes. In contrast, using ambient oxygen as oxidant is promising to develop an environmentally friendly synthesis strategy that does not require additional separation. However, ambient oxygen is lack of the power to oxidize alcohols at mild temperatures. Therefore, precisely controlling the oxidizing power of the oxidants becomes crucial to promote the selective oxidation of alcohols to aldehydes. We focus on the use of appropriate metal catalysts (i.e., quantum-sized metal nanoparticles) to improve the selective oxidation with ambient oxygen by converting the molecular oxygen adsorbed on the catalyst to more active species. The change of adsorption states of oxygen relies on the efficient generation of hot electrons in the quantum-sized metal nanoparticle catalysts that are under illumination of visible light. Selective aerobic oxidation of benzyl alcohol to benzaldehyde represents an example to demonstrate the feasibility of enhancing reaction kinetics on quantum-sized platinum group metal (PGM) nanoparticle catalysts with the assistance of simulated solar irradiation.

#### 11:00 AM NM02.07.07

**Synthesis of New Nanoparticle Catalysts for Application in Direct Methanol Fuel Cells** Jil Rüter, Hauke Heller and Horst Weller; University Hamburg, Hamburg, Germany.

Direct methanol fuel cells (DMFCs) show great potential for applications in portable power sources or hybrid vehicles.<sup>[1]</sup> One key challenge for the commercialization is to reduce the high costs of fuel cells due to expensive catalyst materials. The electrocatalysts, mostly based on platinum, are dispersed on a high surface area supporting material. Therefore, a reduced and effective use of the costly platinum is essential. In this context, multimetallic nanoparticles with controllable size and composition are interesting materials to reduce the amount of utilized catalyst material and simultaneously enrich the accessible catalytic metals on the surface.

The size, composition and structure of the nanoparticles have a high influence on the efficiency. An increase of the catalytic activity has been proved, by combining platinum with various transition metals (e.g. nickel, cobalt, ruthenium)<sup>[2]</sup> as alloy or core-shell structure, while reducing the cost at the same time. The combination of specific transition metals with platinum increases the activity of oxygen reduction reaction (ORR) due to ligand and strain effects.<sup>[3]</sup> Moreover, it is advantageous to use core-shell-nanoparticle (CSN) systems, as the platinum amount can be further reduced by using it only on the outer shell.

The investigated Ni@Au@NiPt<sup>[4]</sup> and Ni@Pd@NiPt CSNs exhibit a great potential for application as DMFC catalysts due to their high catalytic activity, low platinum amount, high surface area and stability. Here, we demonstrate nanoparticles with an average diameter of 5 nm and a narrow standard deviation. The gold interlayer enhances the durability of platinum due to the prevention of oxidation and dissolution of platinum during the cycling process. Besides platinum, palladium is an attractive material as it has a positive effect on the stability and activation and a lot of different combinations of platinum and palladium or a substitution of platinum may be possible as well.

Furthermore, the carbon source for supporting the catalyst material is of great interest. Carbon nanotubes (CNTs) may be an alternative to conventional carbon materials due to their high surface area as well as remarkable mechanical and electric properties.<sup>[5]</sup> CNTs consist of (multiple) graphene layers in cylindrical form with a closed fullerene end cap. We show that nanoparticles and CSNs were successfully supported on hierarchically ordered CNTs, which are synthesized by chemical vapor deposition and grown on steel meshes.

Combining the multimetallic CSNs with CNTs could induce an enhanced catalytic activity. In future, further combinations of palladium and platinum will be investigated.

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#### 11:15 AM NM02.07.08

**Development of New Solid-Solution Alloy Nanoparticles for Catalytic Applications on the Basis of Density-of-States Engineering** Kohei Kusada<sup>1</sup>, Dongshuang Wu<sup>1</sup>, Tomokazu Yamamoto<sup>2</sup>, Syo Matsumura<sup>2</sup>, Wei Xie<sup>2</sup>, Michihisa Koyama<sup>3</sup>, Katsutoshi Sato<sup>4</sup>, Katsutoshi Nagaoka<sup>4</sup> and Hiroshi

Kitagawa<sup>1</sup>; <sup>1</sup>Kyoto University, Kyoto, Japan; <sup>2</sup>Kyushu University, Fukuoka, Japan; <sup>3</sup>National Institute for Materials Science, Tsukuba, Japan; <sup>4</sup>Oita University, Oita, Japan.

The properties of elements are correlated directly with their electronic states. If we can realize a concept of “density-of-states (DOS) engineering”<sup>1</sup> for the design of materials having the most suitable electronic structure for the target properties, we will be able to make full use of available elements and relieve the resource problems. To freely control an electronic state of a material, the solid-solution alloy is advantageous because its electronic state can be continuously controlled by tuning the compositions and/or combinations of the constituent elements. However, the majority of bulk alloy systems are the phase-separated type under ambient conditions. Recently, we demonstrated that the nanosize effect offers a chance to find a way out of this metallurgical difficulty; that is, we can obtain metal nanoparticles (NPs) having new phases that do not exist in bulk states<sup>2-7</sup>. In general, a nanoparticle with the same crystal structure as the corresponding bulk material can be obtained. However, if we find appropriate synthetic conditions, it allows us to develop novel NPs adopting new phases including solid-solution alloy NPs consisting of immiscible combinations.

In this work, we discuss the structural and chemical properties of PdRu<sup>5</sup> and AuIr<sup>9</sup> alloy NPs as the examples of DOS engineering. Both of binary alloy systems are immiscible and solid-solution alloys of these systems have not been obtained so far. We first succeeded in synthesizing the solid-solution alloy NPs and characterized the alloy structures by synchrotron X-ray powder diffraction technique and scanning transmission electron microscopy coupled with energy dispersive X-ray spectroscopy. It is noted that obtained PdRu and AuIr solid-solution alloy NPs showed very enhanced catalytic properties for three-way catalysis and oxygen reduction reactions, which are comparable to Rh and Pt, respectively<sup>8,9</sup>. The calculation results indicated that the formation of solid-solution alloy realized new electronic states and provided enhanced properties.

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### 11:30 AM NM02.07.09

**Investigating Subnanometer Transition Metal Catalysts for Methane Activation from First Principles** Victor Fung<sup>1</sup>, Zili Wu<sup>2</sup> and De-en Jiang<sup>1</sup>; <sup>1</sup>University of California, Riverside, Riverside, California, United States; <sup>2</sup>Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Subnanometer transition metal clusters have received significant attention as promising materials for catalysis, particularly over their bulk counterparts. The electronic structure of the exposed metal sites can vary significantly with atomic size and geometry, which presents the opportunity to design metal clusters of a specific atomic size and composition for the desired catalytic application. One such application is towards methane conversion, which requires suitable catalysts to promote the activation of its strong C-H bond. Using density functional theory, we investigate a selection of promising transition metal clusters and identify promising candidates based on strong methane adsorption and low C-H activation barriers. Our results conclude that facile C-H activation is closely related to the ability of the metal sites to complex with the methane molecule. We further show that these methane activation properties are extremely size, geometry and composition dependent, with significant implications for eventual experimental applications. These studies provide the first step in designing realistic metal cluster catalysts for methane conversion.

### 11:45 AM NM02.07.10

**Determining Metallic Nanoparticle Core Structures from Atomic Pair Distribution Function (PDF) Data** Soham Banerjee<sup>1</sup>, Chia-Hao Liu<sup>1</sup>, Jennifer Lee<sup>2</sup>, Anton Kovyakh<sup>3</sup>, Viktoria Grasmik<sup>4</sup>, Oleg Prymak<sup>4</sup>, Christopher Koenigsman<sup>5,6</sup>, Haiqing Liu<sup>5</sup>, Lei Wang<sup>5,7</sup>, Milinda Abeykoon<sup>8</sup>, Stanislaus S. Wong<sup>5</sup>, Matthias Epple<sup>4</sup>, Christopher B. Murray<sup>2,9</sup> and Simon J. Billinge<sup>1,8</sup>; <sup>1</sup>Department Applied Physics and Mathematics, Columbia University, New York, New York, United States; <sup>2</sup>Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States; <sup>3</sup>Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark; <sup>4</sup>Inorganic Chemistry and Center for NanoIntegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Essen, Germany; <sup>5</sup>Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York, United States; <sup>6</sup>Department of Chemistry, Fordham University, Bronx, New York, United States; <sup>7</sup>Department of Materials Science and Chemical Engineering, State University of New York at Stony Brook, Stony Brook, New York, United States; <sup>8</sup>Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York, United States; <sup>9</sup>Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Accurate determination of the structure of noble metallic nanomaterials is a key step towards understanding and controlling their properties. This is especially challenging for small particles, below 10 nm, where x-ray diffraction data is often broad and diffuse and not amenable to quantitative crystallographic analysis. In these cases a better approach is the use of atomic pair distribution function (PDF) analysis of synchrotron x-ray total scattering data. Even in this case, extracting detailed models of nanoparticle cores is notoriously difficult.

Nanoparticle models based on close packed crystallographic cores, often simple but at times elaborate, lead to characteristically poor or unreliable fits. We collected PDF data for 12 metallic nanostructured samples, both elemental and alloyed, prepared using different synthesis methods, with significantly different shapes and sizes as disparate as 2 nm wires and 40 nm particles, using different synchrotron sources and beamlines. We found that previously ignored signals in residuals (difference curves) from PDF fits of close-packed models can be explained as originating from well defined domain structures in the nanoparticle cores, and that most of the materials studied were significantly better described using small multiply-twinned clusters. The methodology holds the promise of providing rapid screening of non-crystallographic cluster motifs when modelling PDF data from metallic nanomaterials.

SESSION NM02.08: Expanding Chemical Space  
Session Chairs: De-en Jiang and Grant Johnson  
Wednesday Afternoon, November 28, 2018  
Sheraton, 3rd Floor, Commonwealth

### 1:30 PM NM02.08.01

**Carbothermal Shock Synthesis of High-Entropy-Alloy Nanoparticles** Yonggang Yao; University of Maryland, College Park, Maryland, United States.

The controllable incorporation of multiple immiscible elements into a single nanoparticle merits untold scientific and technological potential, yet remains a challenge using conventional synthetic techniques. We present a general route for alloying up to eight dissimilar elements into single-phase solid-solution nanoparticles, referred to as high-entropy-alloy nanoparticles (HEA-NPs), by thermally shocking precursor metal salt mixtures loaded onto carbon supports [temperature ~2000 K, 55-ms duration, rate of ~10<sup>5</sup> K/s]. We synthesized a wide range of multicomponent nanoparticles with a desired chemistry

(composition), size, and phase (solid solution, phase-separated) by controlling the carbothermal shock (CTS) parameters (substrate, temperature, shock duration, and heating/cooling rate). To prove utility, we synthesized quinary HEA-NPs as ammonia oxidation catalysts with ~100% conversion and >99% nitrogen oxide selectivity over prolonged operations.

#### 1:45 PM \*NM02.08.02

**Megalibraries—Changing the Pace of Materials Discovery** [Chad A. Mirkin](#); Northwestern University, Evanston, Illinois, United States.

Nobel metal catalysts are crucial for many energy, materials, and environmental applications. To date, we have relied heavily on the use of precious metal particle catalysts for many of these applications. However, in certain cases, the high cost and scarcity of such elements, significantly limit their wide-spread use and pose major challenges for future adoption and scaling. Alloying precious metals with earth abundant transition metal elements is recognized as a promising method for reducing cost and improving catalytic activity, selectivity, and catalyst stability, however, the selection of appropriate element combinations remains largely empirical, posing significant challenges in designing and synthesizing high-performance, low-cost catalysts. The problem is daunting. Indeed, when one considers the 91 metal elements in the periodic table, and all possible combinations, including stoichiometric ratios and particle size, a nearly infinite number of possible materials exist. Being able to rapidly synthesize and subsequently screen materials for activity remain limiting steps. In this presentation, an approach to combinatorial nanoscience relying on “megalibraries” consisting of as many as 5 billion positionally encoded nanoparticle features will be described. Methods to use megalibraries to identify new materials and catalysts (comprised of as many as 8 different elements) for important chemical transformations will be presented. Importantly, one megalibrary contains more new inorganic materials than scientists cumulatively have produced and characterized to date. Therefore, this novel approach lays the foundation for dramatically changing the pace at which we both explore the breadth and discover the capabilities of the materials genome.

#### 2:15 PM NM02.08.03

**Fabrication and Characterization of Multinary Transition Metal Alloy Nanoparticle Libraries** [Alfred Ludwig](#)<sup>1</sup>, [Hajo Meyer](#)<sup>1</sup>, [Dario Grochla](#)<sup>1</sup>, [Alan Savan](#)<sup>1</sup>, [Michael Meischein](#)<sup>1</sup>, [Tobias Loeffler](#)<sup>2</sup>, [Alba Garzon-Manjon](#)<sup>3</sup>, [Christina Scheu](#)<sup>3</sup> and [Wolfgang Schuhmann](#)<sup>2</sup>; <sup>1</sup>Institute for Materials, Ruhr-University Bochum, Bochum, Germany; <sup>2</sup>Analytical Chemistry-Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, Bochum, Germany; <sup>3</sup>Max-Planck-Institut für Eisenforschung GmbH, Duesseldorf, Germany.

Multinary transition metal nanoparticles (NPs) are of interest for energy applications, e.g. as catalysts in fuel cells. As an immense composition space exists for multinary NPs, efficient experimental strategies are necessary to identify which particular compositions have new or highly-optimized properties. Here, combinatorial co-sputtering (1) from up to five elemental targets (e.g. Cr-Mn-Fe-Co-Ni) was used to synthesize multinary NP libraries into ionic liquids. Due to their low vapor pressure, ionic liquids can be used as substrates that are able to stabilize NP dispersions. The suitability of different ionic liquids for different metal combinations can be tested with high-throughput by using arrays of ionic liquids which are sputtered with one material system (2). The multinary NPs were characterized using atomic-scale characterization methods such as Cs-corrected high-resolution transmission electron microscopy, (scanning) transmission electron microscopy and energy dispersive X-ray spectroscopy. With these techniques the chemical composition as well as size, shape, crystallinity and defects of the NPs are obtained. Effects on the resulting crystallinity of the NPs were found by using either direct current or high-power impulse magnetron sputtering. Furthermore, catalytic properties of the NPs were measured by potential-assisted immobilization of the NPs at a microelectrode which allows the evaluation of their intrinsic electrocatalytic activity in alkaline media. The obtained results indicate that the multinary nature of the NPs affects their catalytic activity: e.g. quinary NPs were found to be more active than all of the respective quaternary subsystems.

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#### 2:30 PM BREAK

SESSION NM02.09: Biological Applications  
Session Chairs: De-en Jiang and Grant Johnson  
Wednesday Afternoon, November 28, 2018  
Sheraton, 3rd Floor, Commonwealth

#### 3:30 PM NM02.09.01

**Antimicrobial Peptide-Based Platform with Fluorescent Gold Nanoclusters for Selective Detection of *Listeria monocytogenes*** [Kamaljit Kaur](#); Chapman University, Irvine, California, United States.

*Listeria monocytogenes* is a Gram-positive foodborne pathogen that causes infections such as listeriosis and meningitis. The mortality rate from such infections exceeds 20 percent, which designates this microbe as a high threat to humans (1). Highly sensitive and selective detection of pathogenic bacteria from various samples ranging from human specimens to food samples is a major challenge in industry and medical fields (2, 3). Here we have developed a novel peptide-based biosensor platform utilizing fluorescent gold nanoclusters for quick and easy detection of *L. monocytogenes* species from different samples. Leucocin A, a potent antimicrobial peptide from class IIa bacteriocins, is used to selectively bind specific receptor present on *Listeria monocytogenes*, namely, mannose phosphotransferase system permease. A self-assembled monolayer (SAM) of peptide on glass surface is exposed to contaminated sample allowing target bacteria to bind to the immobilized peptide on the surface. The peptide-bound bacteria are then labeled with highly fluorescent gold nanoclusters directly on the glass surface allowing quick detection of bacteria with a limit of detection (LOD) of 2000 cfu in each 10 microliter sample (4). The gold nanoclusters are made by mixing and spotting aqueous tetrachloroauric acid and 3-mercaptopropionic acid (MPA) on top of bacteria on the glass slide. The gold nanoclusters thus formed label the bacteria, and absorb in the UV range and emit fluorescence in the visible to near infrared region (~ 612 nm) where other biomolecules do not fluoresce and interfere. The biosensor assay developed here is unique as it allows detection of *L. monocytogenes* in < 1 hour and does not require trained personnel. Compared to other techniques for the detection of *L. monocytogenes*, this method is simple, fast, and requires no sample preparation.

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### 3:45 PM NM02.09.02

**Renal Clearable Catalytic Gold Nanoclusters for *In Vivo* Disease Monitoring** Colleen Loynachan<sup>1</sup>, Ava Soleimany<sup>2</sup>, Sangeeta Bhatia<sup>2</sup> and Molly Stevens<sup>1</sup>; <sup>1</sup>Imperial College London, London, United Kingdom; <sup>2</sup>Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Recent advances in the synthesis and characterization of ultra-small gold nanoclusters (AuNCs) have enabled their use as sensitive probes for fluorescence and x-ray contrast bioimaging applications.<sup>1</sup> However, their intrinsic catalytic activity has yet to be explored for biosensing *in vivo*. Employing peroxidase-mimicking catalytic AuNCs as reporter probes in sensing applications may enable rapid and facile disease diagnosis at the point-of-care.<sup>2</sup> We propose to address this need by leveraging both the catalytic activity of AuNCs and the precise size filtration of the kidney to develop a nanocatalyst amplification platform that produces a direct colorimetric urinary readout of disease state. Here we have engineered AuNC-functionalized protease nanosensors that are disassembled in response to dysregulated protease activity at the disease site. Liberated AuNCs are then efficiently filtered into the urine, where a colorimetric urinary assay enables rapid disease detection in mouse models of cancer and pulmonary embolism.

Renal clearable AuNCs were synthesized via a versatile bio-templated process which introduces protease cleavable peptide sequences on the particle surface with orthogonal functional handles for further site selective modification. The resulting *ca.* 1.5 nm noble metal nanoclusters exhibited both luminescence and robust catalytic activity. Renal clearance studies *in vivo* showed that *ca.* 60% of the injected dose of functionalized AuNCs leave the body via this route and retain their catalytic activity in urine. Peptide functionalized AuNCs were tethered to a protein carrier to form nanosensor complexes, and specific proteolytic cleavage of AuNC complexes was demonstrated *in vitro* by gel filtration chromatography. Finally, disease detection was demonstrated *in vivo* in a mouse model of colorectal cancer by monitoring catalytic activity of cleared AuNCs in collected urine. After injection with tumor-specific AuNC nanosensors, urine from tumor-bearing mice showed a 20-fold increase in colorimetric signal compared to healthy mice in our assay.

We developed a library of catalytic AuNC probe complexes which can be efficiently excreted into urine in response to specific enzymatic levels *in vivo*. This simple and sensitive colorimetric urinary assay can be read by the naked eye in < 1 h and has enabled non-invasive disease detection in mouse models of cancer and pulmonary embolism. We envision that this approach will be applicable for rapid detection of a diverse range of disease-associated proteases.

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### 4:00 PM \*NM02.09.03

**Gold Nanoparticles in Biology—Delivery of Proteins and CRISPR Machinery** Vincent M. Rotello; University of Massachusetts, Amherst, Massachusetts, United States.

A key issue in the use of nanomaterials is controlling how they interact with themselves and with the outer world. Our research program focuses on the tailoring of nanoparticles of surfaces for a variety of applications, coupling the atomic-level control provided by organic synthesis with the fundamental principles of supramolecular chemistry. Using these nanoparticles, we are developing new strategies for biological applications. This talk will focus on the interfacing of nanoparticles with biosystems, and will discuss the application of self-assembled nanoparticles as delivery vehicles. We will demonstrate the delivery of proteins and nucleic acids directly into the cytosol, including functional CRISPR systems. We will also show how this efficient cellular delivery translates into effective systemic CRISPR editing *in vivo*.

### 4:30 PM NM02.09.04

**Gold Nanoprisms as Optical Coherence Tomography Contrast Agents for Contrast Enhanced Imaging of Tumor Microvasculatures *In Vivo*** Peng Si, Edwin Yuan, Orly Liba, Yonatan Winetraub, Siavash Yousefi, Elliott SoRelle, Derek Yecies, Rebecca Dutta and Adam de la Zerda; Stanford University, Palo Alto, California, United States.

Angiogenic tumor vessels are hallmarks of cancer and critical sites for drug delivery, angiogenic therapy, chemotherapy, and immunotherapy. Better characterization of tumor microvasculatures *in vivo* could lead to better understanding of the tumor microenvironment, improved monitoring of tumor progression and therapeutic responses, and more accurate patient prognosis. Optical coherence tomography angiography (OCTA) provides three-dimensional microvasculature image of the imaged tissue by detecting the dynamic scattering produced by flowing red blood cells (RBCs), and becomes an emerging tool for *in vivo* microvascular imaging due to its micrometer spatial resolution and millimeter tissue penetration depth. However, due to the abnormal blood flow in the angiogenic tumor vessels and strong light attenuation by the tumor tissue, it is challenging to image the complete tumor microvasculature with traditional OCTA. In this work, we demonstrate that gold nanoprisms (GNPRs) can be used as intravascular OCT contrast agents for significantly improved imaging of tumor microvasculatures in the second near infrared window (1100–1400 nm). With the injection of incremental concentrations of PEGylated GNPRs in the mouse blood, higher density of microvasculature can be observed in the tumor tissue of melanoma mice models on the OCT angiograms. After the GNPR concentration reached 2 nM in the bloodstream, OCTA showed an increase of tumor vascular density by 136 % compared to the baseline angiogram image. Longitudinal OCTA study shows that the highest vascular density was achieved at 5 min post-injection. Two photon microscopic imaging validated that there is no extravasation of GNPRs within 5 min of injection.

### 4:45 PM NM02.09.05

**DNA Modified Gold Nanoparticles for Drug Delivery in Cells** Maria-Eleni Kyriazi and Antonios G. Kanaras; Physics and Astronomy, Institute for Life Sciences, University of Southampton, Southampton, United Kingdom.

Nanoparticulate systems are of great interest for applications in biomedicine due to the ability to design their properties. The ligand coating of the nanoparticles is critical for nanoparticle stability and function while the morphology and chemical composition of the nanoparticle core is important in defining optoelectronic and magnetic and other properties of the particles. In recent years, advances in nanoparticle chemical synthesis and surface functionalization rendered available a library of functional nanomaterials. The next step of evolution is to synthesize nanomaterials that perform multitasking roles triggered by external stimuli. Such designs will be of high importance in biomedicine, especially for targeted and efficient drug delivery. In this presentation I will discuss recent progress in our group concerning the design of nanoparticle assemblies and their incorporation in biological systems to facilitate sensing, drug delivery and accurate manipulation. My talk will focus on a new class of nanoparticle dimers that can accommodate multiplexed synergistic actions of sensing and drug delivery in cells.<sup>1-3</sup> These multitasking particle assemblies are able to selectively release anticancer drugs in response to specific messenger RNA signatures and selectively kill model cancerous cells as opposed to healthy cells.

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SESSION NM02.10: Poster Session III  
Session Chairs: Mika Pettersson and Jianping Xie  
Wednesday Afternoon, November 28, 2018  
8:00 PM - 10:00 PM  
Hynes, Level 1, Hall B

#### NM02.10.01

**Core Metal in MAu<sub>24</sub>(SR)<sub>18</sub> Nanocluster (M=Au, Pt) Controls the Products Selectivity in Electrocatalytic CO<sub>2</sub> Conversion** Yongjin Lee, Woojun Choi, SangHyeok Im, Hyeon Seong and Dongil Lee; Department of Chemistry, Yonsei University, Seoul, Korea (the Republic of).

Gold nanoparticles have been studied extensively as an efficient electrocatalyst for CO<sub>2</sub> conversion. However, the electrochemical CO<sub>2</sub> conversion on gold nanoparticles typically requires large overpotentials and the reaction products are a mix of major and minor products, including CO and hydrogen. In this poster, we report that the product selectivity can be controlled by the core dopant of MAu<sub>24</sub>(SR)<sub>18</sub> (M= Au, Pt), where SR is 1-hexanethiol. Linear Sweep Voltammetry studies show that the onset potential of CO<sub>2</sub> reduction catalyzed by Au<sub>25</sub>(SR)<sub>18</sub> is significantly different from that by PtAu<sub>24</sub>(SR)<sub>18</sub>. Furthermore, constant potential electrolysis on electrodes modified with these clusters exhibits drastically different product selectivity. That is, whereas CO is predominantly produced on Au<sub>25</sub>(SR)<sub>18</sub> with a selectivity higher than 90 %, nearly 75 % H<sub>2</sub> is produced on PtAu<sub>24</sub>(SR)<sub>18</sub>. Density functional theory (DFT) calculations show that the product selectivity appears to be closely related with the adsorption energies of the reactants, i.e., CO<sub>2</sub> and proton on the cluster catalyst.

#### NM02.10.02

**The Effect of the Tip Radius on Dislocation Nucleation in [0 0 1] Tungsten Single Crystal Under Spherical Nanoindentation** Seok-Woo Lee and Hetal Patel; University of Connecticut, Storrs, Connecticut, United States.

Mechanical behaviors of nanometals, such as metallic nanowires and nanoparticles, are usually controlled by dislocation nucleation due to the absence of pre-existing glide dislocations in such a small volume. Dislocation theory suggests that a significantly high stress needs to be applied to nucleate a dislocation, leading to an ultrahigh strength of nanometals. Thus, nanometals has drawn a great attention as the candidate of advanced structural materials. In order to understand the mechanical behavior of nanometals, thus, it is critical to understand the dislocation nucleation behavior in detail. Spherical nanoindentation has been widely used to study the dislocation nucleation phenomena. Upon loading on the flat surface of low dislocation density material, the Hertzian contact of spherical tip can induce the maximum load at the inside of material, leading to the dislocation nucleation. This nano-scale volume plasticity is nearly identical to the plasticity of nanometals. So, spherical nanoindentation is a great method to study the plasticity at small length scales. Tungsten is an excellent model system to investigate dislocation nucleation. Its strong hardness allows the low dislocation density at the underneath of the free surface after the fabrication of flat surface. In this study, therefore, we studied the dislocation nucleation behavior of [0 0 1] tungsten single crystal using spherical nanoindentation with different indenter tip radii. The surface of tungsten single crystal was chemo-mechanically polished. The spherical nanoindentation was performed with the tip radii, 0.2, 2, 4, and 20 micrometers, and the critical stress of dislocation nucleation were measured using the Hertzian contact mechanics. Our results show that the critical stress of dislocation nucleation is a strong function of the tip radius. The dislocation theory suggests that the critical stress of dislocation nucleation must be constant regardless of loading condition, but this is inconsistent with our results. We found that stress gradient on the potential site of dislocation nucleation could be different according to the tip curvature, leading to the different critical stress of dislocation nucleation. Therefore, we combined the stress gradient theory with the Hertzian contact mechanics and confirmed that our model explains the dependence of the tip radius on the critical stress of dislocation nucleation very well. Our new model can be applied in any general cases when the inhomogeneous stress field is available in the nanoscale volume of metals such as the bending of nanowires or the compression/tension on nanoparticles. We confirmed that the same phenomenon is observed in uni-axial compression of dislocation-free gold nanoparticles, and the size effect of its yield strength can be understood by our stress gradient model. In sum, our spherical indentation study can shed a light into a fundamental understanding on the plasticity of nanometals.

#### NM02.10.03

**Effect of Synthetic Parameter on the Cytotoxicity of CdTe/CdSe Nanoparticles Against Osteosarcoma Cell Line** Vuyelwa Ncapayi<sup>1, 2, 3</sup>, Sandile P. Songca<sup>4</sup> and Samuel O. Oluwafemi<sup>1, 2</sup>; <sup>1</sup>Applied Chemistry, University of Johannesburg, Johannesburg, South Africa; <sup>2</sup>Centre for Nanomaterials Science Research, University of Johannesburg, Johannesburg, South Africa; <sup>3</sup>Applied Science, Walter Sisulu University, East-London, South Africa; <sup>4</sup>Chemistry, Walter Sisulu University, Kwadlangezwa, South Africa.

LM-8 is a murine osteosarcoma cell line associated with bone tumor and is commonly found in young adult and children. The LM-8 cell line has Nuclear factor (NF)- $\kappa$ B which make them high resistance to irradiation thus limiting their treatment only to chemotherapy and surgery and this has become a source of concern for cancer therapy. In addressing this problem, quantum dots (QDs), which has high potential application in cancer treatment not only as imaging tool but also as a drug transport agent have been proposed as a possible agent to address this problem. Thus, in this study, we herein report the synthesis of CdTe/CdSe QDs core/shell NPs via a simple, economical and green method in the absence of inert atmosphere. The temporal evolution of the CdTe/CdSe QDs cytotoxicity against osteosarcoma cell line was investigated by varying the pH and reaction time. The optical properties of the as-synthesised quantum dots were monitored by UV-Vis and photoluminescence spectrophotometer, while electron microscope was used for structural properties. Prolonging the reaction time and increasing the pH resulted in highly monodispersed CdTe/CdSe core-shell NPs with good optical properties in the near infrared region and high cell viability. The high fluorescence intensity and improved cell viability against the osteosarcoma cell line confirm QDs great potential for imaging and drug delivery applications.

#### NM02.10.04

**Synthesis and Processing of Polymer-Nanoparticle Hybrid Materials for H<sub>2</sub> Sensing** Alicja Stolas, Ida Holm, Iwan Darmadi, Christoph Langhammer, Christian Muller and Kasper Moth-Poulsen; Chalmers University of Technology, Göteborg, Sweden.

Nanoparticles bearing Surface Plasmon (SPR) and Localized Surface Plasmon Resonance (LSPR) phenomena are excellent tools for novel concepts and

technologies such as the creation of bio- and chemosensors<sup>1-6</sup>, plasmonic lasers, optical metamaterials, photovoltaic devices and metal photocatalysts. However, there is a number of challenges related to the use of nanoplasmonic systems related to stability, composition and the large-scale incorporation in real devices. To address the above, we have used wet-chemical synthesis of palladium based plasmonic nanoparticles with tunable optical properties, and implemented these into suitable polymer matrixes, in order to invent cheap, easy and robust nanocomposites. Subsequently the nanocomposites will be applied to realize the creation of an optical hydrogen sensor.

In this project Pd NCs for H<sub>2</sub> sensing have been synthesized and successfully implemented into a PMMA matrix resulting in a H<sub>2</sub> active nanocomposite. The synthesis of nanoparticles is mainly surfactant based which has series of disadvantages that need to be mitigated such as the disruption of H<sub>2</sub> absorption onto the Pd surface, therefore demonstration of surfactant effect on Pd Nanoplasmonic Hydrogen Sensing and removal strategies were tested.

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#### NM02.10.05

**Magneto-Optically Active Mn-Doped 2D Quantum Structures** Chi Li<sup>1</sup>, Sheng-Chih Hsu<sup>1</sup>, Tom Lin<sup>2</sup> and Yihsin Liu<sup>1</sup>; <sup>1</sup>National Taiwan Normal University, Taipei City, Taiwan; <sup>2</sup>Chemistry, Washington University, St. Louis, Missouri, United States.

Mn-doped 2D quantum structures are potential diluted magnetic semiconductors (DMS) for spintronic applications, showing strong coupling of spin states with electronic states. 2D CdSe(ethylenediamine)<sub>0.5</sub> containing Mn<sup>2+</sup> of various concentrations (0.5-7.7%) were successively introduced to explore optical, magnetic and spin interactive properties within single atomic layers. Giant magneto-optical effects and exciton dynamics are revealed by multiple internal transitions (*e.g.* <sup>4</sup>T<sub>1</sub> to <sup>6</sup>A<sub>1</sub>) phosphorescence between 580-660 nm and magneto-optic Kerr effect (MOKE). Strong *sp-d* exchange interaction of nearly isolated Mn<sup>2+</sup> in 2D regimes suggests giant Zeeman effect in magnetic circular dichroism (MCD). Additionally, three anisotropic *g*-values are characterized in orientation-dependent electron paramagnetic resonance (EPR) experiments. Magnetic properties ( $C=2.62 \times 10^{-3}$  emu K/G,  $\mu=1.32 \mu_B$ ) from superconducting quantum interference devices (SQUID) with the magneto-optical studies above suggest effective chemical doping of magnetic ions and possibilities of spintronic applications for 2D semiconductors.

#### NM02.10.06

**Development of Multifunctional ZnO Nanocarriers for Controlled and Enhanced Biofilm Dispersion** Zakiya Skeete, Sara Row, Dickson Kirui and Nancy Millenbaugh; Craniofacial Health and Restorative Medicine, NAMRU-SA, JBSA Fort Sam Houston, Texas, United States.

**Background:** Zinc Oxide (ZnO) nanoparticles (NPs) are utilized in a myriad of biomedical applications, such as drug delivery and infection control, due to their unique material properties, ease of tunability, and multifunctional capabilities. The goal of this study is to design carriers capable of enhanced delivery of dispersal agents and antibacterial Zn<sup>2+</sup> in acidic microenvironments typically present within biofilms.

**Methods:** A sonochemical method for the synthesis of ZnO nanoshells (NSs) via self-assembly of ZnO NPs into hollow NSs was adapted to allow the encapsulation of the enzymatic dispersal agent papain. Size and morphology of bare and papain-loaded ZnO NSs were characterized over 14 days using dynamic light scattering (DLS) and scanning electron microscopy (SEM), respectively. Incorporation of papain into ZnO NSs was assessed via Fourier transform infrared spectroscopy (FTIR) and the crystallinity of the NSs was studied by x-ray diffraction (XRD). The stability of papain encapsulated in ZnO NSs was also monitored over 14 days via an enzyme activity assay. Dissolution of ZnO NSs at pH 5 and 6 was assessed over 24 hours via spectrophotometry.

**Results:** Syntheses resulted in bare and papain-loaded ZnO NSs with hydrodynamic diameters of 401.0±64.3 nm and 529.1±112.5 nm, respectively. In contrast, SEM analyses of the dried samples showed diameters of 180.0±77.3 nm for bare ZnO NSs and 177.4±50.2 nm for papain-loaded ZnO NSs, a decrease associated with loss of the hydration layers. FTIR analyses showed vibrational bands associated with amine and alkane groups in enzyme-loaded ZnO NSs, confirming papain incorporation. XRD analyses confirmed that bare and papain-loaded ZnO NSs maintained the wurtzite structure attributed to ZnO materials, indicating that papain did not alter the crystal structure of the NSs. Papain-loaded ZnO NSs (2 mg/mL) retained an enzymatic activity of 0.343±0.060 U/mL the day after synthesis (Day 2). At 7 days of storage under vacuum at room temperature, the Z-average particle size varied by >3 standard deviations beyond the mean particle size at Day 2, and papain activity decreased by 25%. However, SEM analyses revealed structural stability of particles up to 14 days. Acid-induced dissolution over 5 hours at pH 5 and 6 led to a reduction in ZnO absorbance of 91% and 88% for bare ZnO NSs, respectively, and 68% and 61% for papain-loaded ZnO NSs, respectively, relative to controls (time 0).

**Conclusion:** Results showed reproducible syntheses of bare and papain-loaded ZnO NSs, which were structurally stable up to 14 days. Data also confirmed effective acid-induced dissolution of ZnO NSs. Future work will optimize the amount and rate of papain release and evaluate the efficacy of papain-loaded ZnO NSs against bacterial biofilms. These results are a first step toward developing a novel drug delivery system for the controlled disruption of biofilms that will aid in the treatment of multidrug resistant bacterial infections.

#### NM02.10.07

**Ambient Pressure Particle Mass Spectrometry for Inline Detection of Nanoparticle Growth in Spray-Flame Reactors** Samer Suleiman<sup>2,1</sup>, Christof Schulz<sup>2,3,1</sup> and Hartmut Wiggers<sup>2,3,1</sup>; <sup>1</sup>University of Duisburg, Duisburg, Germany; <sup>2</sup>Reactive Fluids, Combustion and Gas Dynamics, Duisburg, Germany; <sup>3</sup>Center for Nanointegration Duisburg-Essen, Duisburg, Germany.

Inline characterization of nanoparticle formation with particle mass spectrometry (PMS) is well established to investigate the evolution of particle size distributions during the nanoparticle synthesis in low-pressure gas-phase reactors. It is commonly used to investigate the synthesis of metal and metal oxide nanoparticles to determine the influence of process conditions (temperature, precursor concentration, pressure, fuel/oxygen equivalence ratio) on the particle growth. The method is based on molecular-beam sampling by vacuum expansion of the particle-laden gas at variable locations in the reaction chamber through a nozzle/skimmer system. The vacuum conditions immediately suppress further reactions and particle growth. The system is equipped with an electrostatic deflection unit and a Faraday cup detector to measure potential-energy-filtered currents of charged particles. Due to limitations in the achievable pumping rates and (too high) particle loading, conventional PMS systems with a two-step skimmer/nozzle arrangement are limited to sampling from low-pressure (< 100 mbar) environments at low particle number concentrations. There are only few reports on molecular-beam mass spectrometry (MBMS) of particles from atmospheric-pressure systems, mostly used for the investigation of sooting flames.

In this study, we present a newly designed PMS that can be operated at atmospheric pressure. It is based on a three-stage system that consists of the conventional nozzle/skimmer system combined with an additional expansion chamber in front of the PMS nozzle between reactor and PMS. The PMS is connected to the reactor via a thin pipe (1.7 mm inner diameter). Fluid-dynamic calculations as well as Schlieren measurements show that a supersonic

expansion develops in the first chamber. Dependent on the length of the pipe, the supersonic expansion moves upstream. This enables the determination of the best skimmer position that ensures the charge preservation of the sampled particles by extracting them before interacting with the shock wave. Thus, the sampled aerosol is directly transferred into a particle-laden molecular beam, which then passes the nozzle and the skimmer of the PMS. The additional expansion chamber enables sampling with the PMS within a wide pressure range between 5 mbar and atmospheric pressure. Results concerning Schlieren measurements and spatially resolved investigation of nanoparticles from sooting flames as well as from a spray-flame nanoparticle reactor, both operated at ambient pressure, will be discussed.

#### NM02.10.08

**Study the Synthesis and Characterization of Silver Nanocrystals by Two Methods with Four Solvents** Elizabeth Chavira, [Daphne Meixueiro](#), Karla Eriseth Morales Reyes, Josué Esaú Romero-Ibarra and Adriana Tejada; Universidad Nacional Autónoma de México, México, México.

In this work, there are fabricated silver (*Ag*) nanocrystals by two-step methods, with low-cost. Using the following four different solvents: acetone, distilled water, ammonium hydroxide and methanol. Our interest on creating *Ag* nanocrystals relies on its unexpected properties; they have exceptional optical, electrical, thermal and antibacterial ones. Its possible applications like medical devices, electronics, textiles, sensors, among others.

The purpose of this work is to obtain *Ag* nanocrystals with techniques never reported, at a short price. And to make a comparison among the obtained morphologies depending on employed solutions and the two wet nanomaterials techniques (by either a magnetic stirrer or an ultrasound equipment). All the samples were under the same room conditions of temperature (20-24 °C) and humidity (40-60 %).

The most unexpected result we obtained, seen via an optical microscopy, was the detection of a circular *Ag* sponge, when the used technique was with acetone in an ultrasound equipment for 4 hours; it conserved the same crystal structure. As for the acetone solution via a magnetic stirrer, we obtained a silver nanocluster.

By Powder X-Ray Diffraction (XRD), we acquired the *Ag* reagent purity (Powder Diffraction file, PDF 01-089-3722), a cubic unit cell with  $a = 4.0861$ . Through High-Resolution Transmission Electron Microscopy (HRTEM), we acquired the crystals sizes between 10-30 nm and the diverse morphologies of the four dissolutions by the two different synthesis methods. In order to complete the nanocrystals analysis, we used Differential Scanning Calorimetry and Thermogravimetric Analysis (TGA/DSC) on a simultaneous technique, in which we observed the thermal behavior of *Ag* nanocrystals, in function of temperature, giving as result the thermal degradation and the melting point of *Ag*.

#### NM02.10.09

**Silver Nanoparticles and Ion Silver in the Antimicrobial Activity** [Luiz F. Gorup](#), Francisco N. Souza Neto, Andressa M. Kubo and Emerson R. Camargo; Federal University of Sao Carlos, Sao Carlos, Brazil.

For decades colloids of silver nanoparticles have been studied due to their use as antimicrobial agents. There is an increasingly common application is the use of silver nanoparticles for antimicrobial coatings<sup>1</sup>, and biomedical devices that contain silver nanoparticles to provide protection against bacteria. After preparing the silver nanoparticles, the most commonly laboratory measurement of the activity against a bacterial and fungal is the minimum inhibitory concentration (MIC) is the lowest concentration of an antimicrobial that will inhibit the visible growth of a microorganism after overnight incubation. Minimum inhibitory concentrations are important in diagnostic laboratories to confirm resistance of microorganisms to an antimicrobial agent and also to determine the potency of new antimicrobial agents.

In many these work there are divergence in the results of MIC in the same method, the most widely used explanation is that shape, particle size, method of synthesis, stabilizing agent, and size distribution play an important role in antibacterial and antifungal properties.

In this work, we will show that the Mic test, commonly used, needs to undergo modifications that it is possible to accurately determine the antimicrobial activity of silver nanoparticles. Therefore, of the way it has been done only determines the bactericidal activity of silver ion. This result opens a long discussion about accuracy of the results to determine the bactericidal activity of silver colloids.

Thus, this work the turkevich. Initially, the samples were diluted in deionized water in a geometric progression, from 2 to 1024 times. The final concentrations of NPs/ions silver in the dispersion ranged from 5 mg/mL to 0.01 mg/mL. The MIC test was performed

The colloidal solution with 100% to 90% of silver nanoparticle did not show any effect antimicrobial activity against *C. albicans*

The mixing of colloidal silver nanoparticle and ion silver solution containing more 10% to of ion silver show effect antimicrobial activity. The samples with 10% to 100% of ion silver showed the growing antimicrobial activity varying between 0,100 to 0,01 mmol/L. If the results are normalized as a function of the ion silver concentration, the MIC values will all n the concentration less than 0,010 mmol/L. The results showed that the MIC values were dependent on the ion silver concentration in the samples

In this work, we showed that the Mic test, commonly used, needs to undergo modifications for to accurately determine the antimicrobial activity of silver nanoparticles. Because in the current procedure only determines the bactericidal activity of silver ion. This results opens a long discussion about accuracy of the results to determine the bactericidal activity of silver colloids.

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#### NM02.10.10

**Gamma Radiation Induced Synthesis of Metal Nanoparticles** [Luiz F. Gorup](#)<sup>1,2</sup>, Francisco N. Souza Neto<sup>1</sup>, Andressa M. Kubo<sup>1</sup> and Emerson R. Camargo<sup>1</sup>; <sup>1</sup>Federal University of Sao Carlos, Sao Carlos, Brazil; <sup>2</sup>Chemistry, Federal University of Grandes Dourados, Dourados, Brazil.

Nano-scaled materials has been largely synthesized along the years. Different methods were developed, since complexes to green reactions. One alternative that has been emerging is the use of gamma radiation applied to syntheses of nanoparticles [1]. However, a simple synthesis promoted by gamma radiation is still a challenge. In this context, this work aims the synthesis of gold, silver and platinum nanoparticles using different combinations of the precursors such as sodium citrate (Na<sub>3</sub>Cit) and polyvinylpyrrolidone (PVP), ammonium hydroxide. A multipurpose irradiator of Cobalt-60 were used to emit gamma radiation, responsible to provide the necessary energy for the reaction. A 8 KGy-intensity was chosen to irradiate the flasks containing the precursors.

Three reactions were prepared in Erlenmeyer flasks containing 100 mL of deionized water combining of metal salt (1.0 mM), PVP (102g/L), Na<sub>3</sub>Cit (3.0 mM). The reactants were added shortly before the beginning of the emission. The metal colloidal dispersions were characterized by Scanning Electron Microscopy (SEM) to verify the formation of the nanoparticles. Images of SEM clearly showed the metal nanoparticles synthesized by the different synthetic routes with a size around 15-80 nm and different shapes. Using the gamma radiator, it was possible to synthesize metal nanoparticles with control of size and shape by combination of stabilizer agent.

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#### NM02.10.11

**Plasmonically Enhanced Virus Inactivation in a Flow Cell Geometry** Mina Nazari<sup>1</sup>, Min Xi<sup>2</sup>, Rahm Gummuluru<sup>3</sup>, Mi Hong<sup>4</sup>, Björn Reinhard<sup>2,5</sup> and Shyamsunder Erramilli<sup>4,5</sup>; <sup>1</sup>Department of Electrical and Computer Engineering, Boston University, Boston, Massachusetts, United States; <sup>2</sup>Chemistry Department, Boston University, Boston, Massachusetts, United States; <sup>3</sup>Department of Microbiology, Boston University, Boston, Massachusetts, United States; <sup>4</sup>Physics Department, Boston University, Boston, Massachusetts, United States; <sup>5</sup>Department of Materials Science and Engineering, Boston University, Boston, Massachusetts, United States.

Nanomaterials designed for plasmonically enhanced pathogen inactivation have the potential for larger scale treatment in biopharmaceutical processing and manufacture where traditional sterilization methods cannot be readily used. Recently, it has been demonstrated that plasmon excitation in gold nanoparticle can be used as an effective technique for selective inactivation of viruses. In this study, we test the scalability of plasmonically enhanced inactivation of viruses for larger-scale processing by investigating virus inactivation in a flow chamber connected to a syringe pump. A femtosecond laser beam is transversely incident on a flow cell made of Quartz through which the viral load samples are driven in laminar flow. The laser based upon a Legend Elite Duo (Coherent Inc.) Ti-sapphire regenerative amplifier which produced a continuous train of 35 fs pulses centered at 805 nm with a repetition rate of 1 kHz is used to excite plasmon in the nanoparticles. Our experimental findings indicate the presence of plasmonic gold nanoparticle in the virus solution can dramatically increase the efficiency of 805 nm laser induced inactivation which leads to > 4-log viral reduction measured by virus infectivity assays. The findings confirm the potential for plasmonically enhanced viral inactivation by femtosecond lasers, and propose a path for additional larger scale studies.

#### NM02.10.12

**Gadolinium Oxide Nanoparticles as Magnetic Resonance Imaging Contrast Agents** Edward P. Esposito; Brown University, Johnston, Rhode Island, United States.

Magnetic Resonance Imaging (MRI) allows for early detection of diseases that normally present once treatment is futile (e.g. cancer, cardiovascular dysfunction, neuropathology). With such an important role, any increase to its functionality will have a great impact in medicine. The MRI can be improved – MRI contrast agents (CAs) can increase signal intensity, enhancing the contrast between healthy and abnormal tissues to allow for clearer diagnoses. MRI CAs provide an opportunity to target specific cells, leading to novel detection methods.

The principle underlying MRI is Nuclear Magnetic Resonance (NMR). NMR is observed as an absorption and emission of electromagnetic radiation by spinning nuclei in an external magnetic field. CAs enhance the MRI quality by affecting the amount of time it takes for the nucleus to relax after excitation. There are two relaxation times,  $T_1$  and  $T_2$ , that affect the quality of the image. Gadolinium (Gd) chelates, a currently used CA, offer increased  $T_1$  relaxation times. Radiologists prefer this type of CA because increases in  $T_1$  relaxation result in increased positive, white contrast in the image. A  $T_2$  CA enhances the negative, black contrast of the image which can easily be misidentified as an internal hemorrhage.

Despite being a  $T_1$  CA, Gd chelates can have harmful side effects in humans. Deposition of Gd can cause nephrogenic systemic fibrosis in patients with kidney disease. Gd chelates are small and therefore tumble in the bloodstream which reduces  $T_1$  relaxation rates. With decreased amplification of the image, a higher dosage is required which further contributes to a long-term deposition of Gd in the brain.

The nanoscale alternative is the gadolinium oxide ( $Gd_2O_3$ ) nanoplate (NP) system. Using these NPs will evade the toxic and tumbling faults of the Gd chelates while maintaining the  $T_1$  CA properties of Gd. Gd in NPs is thermodynamically stable, preventing any metal deposition or adverse renal effects. This allows NP CAs to be used on the 14% of the total population that has preexisting kidney disease. The larger size of the NPs reduces tumbling in the bloodstream. NPs have a larger Gd to volume ratio which concentrates the part of the system that directly affects  $T_1$  relaxation. Encapsulation of the oleic acid coated  $Gd_2O_3$  NPs with an amphiphilic sulfonic acid copolymer allows for successful phase transfer. Functionalized polyethylene glycol (PEG) derivatives added to this system can enhance its biocompatibility and its targeting properties.

$Gd_2O_3$  NPs offer a novel method for detecting non-alcoholic fatty liver disease (NAFLD). Kupffer cells in the liver are found at elevated concentrations with NAFLD. These cells uptake NPs at a high rate in the body.  $Gd_2O_3$  NPs will accumulate in these cells when NAFLD is present, appearing bright white on MRI. Currently, there doesn't exist a method to detect NAFLD early enough to treat it but the  $Gd_2O_3$  nanometal system offers a promising approach.

#### NM02.10.13

**The Synthesis of Copper Nanoparticles from Thermal Decomposition of Amino Carboxylate Copper Complexes** Thamer Alraddadi<sup>1</sup>, Grace Kinunda<sup>3</sup>, Ali Bakly<sup>2</sup>, Egid Mubofu<sup>3</sup>, David J. Lewis<sup>2</sup> and Paul O'Brien<sup>1,2</sup>; <sup>1</sup>School of Chemistry, University of Manchester, Manchester, United Kingdom; <sup>2</sup>School of Materials, The University of Manchester, Manchester, United Kingdom; <sup>3</sup>Chemistry Department, University of Dar es Salaam, Dar es Salaam, Tanzania, United Republic of.

This paper reports the synthesis of copper complexes with four different ligands; glycine (gly) alanine (ala) valine (val) and picolinic acid (pic). The products were characterized by Fourier Transform Infrared (FT-IR) Spectroscopy, Thermogravimetric analysis (TGA) and Elemental Analysis (EA). The potential use of these complexes as precursor to prepare nanoparticles has been investigated. Two different methods have been applied to produce nanomaterials, the thermal decomposition method and hot injection utilizing oleylamine as capping agent. The prepared copper nanoparticles were characterized by XRD and SEM.

#### NM02.10.14

**Structural and Magnetic Properties of TM Doped ZnO Films Produced by Growing ZnO/MT/ZnO Arrays by RF-Magnetron Sputtering at Different Power** Lucía I. Juárez Amador<sup>1</sup>, Miguel I. Galván Arellano<sup>2</sup>, Gabriel I. Romero Paredes<sup>2</sup>, José Alberto Andraca Adame<sup>3</sup> and Ramón Peña<sup>2</sup>; <sup>1</sup>Programa de Doctorado en Nanociencias y Nanotecnología, CINVESTAV-IPN, México, Mexico; <sup>2</sup>Sección de Electrónica del Estado Sólido. Departamento de Ingeniería Eléctrica, CINVESTAV, México, Mexico; <sup>3</sup>Instituto Politécnico Nacional, UPIIH, Hidalgo, Mexico.

Diluted magnetic oxide semiconductors (DMOS) show ferromagnetic behavior that can be used to produce spin-based devices as light-emitting diodes, sensors or transistors. ZnO is an oxide semiconductor with remarkable optical and electrical properties that progressively gains relevance due to the continuous advances in the doping technology with transition metal (TM) ions, such as Ni, Cu, Mn, Cr and Fe, or rare earth ions, particularly as nanostructured films. Both types of ions have partially filled d and f shells, respectively, causing unpaired electrons of the TM ions into the ZnO nanocrystalline films, but changing the carrier density and the ZnO film structural features. Distinct studies demonstrate the influence of the nanostructure particularities on the film magnetic behavior, as the increase on the Curie temperature or the magnetoresistive behavior. With the aim to analyze the influence of the TM dopant and the nanostructure issues on the magnetic characteristics, this study was directed to clarify the origin of the magnetoresistance on TM doped ZnO nanostructured films (ZnO:TM) grown by the non-equilibrium RF-sputtering method at distinct RF-power regimes. n-type ZnO:TM films with homogeneous and reproducible characteristics were produced by forming ZnO/TM/ZnO arrays with ZnO and TM films grown by RF- and DC-sputtering technique at room temperature, respectively. The structural characteristics of the films can be further controlled with additional

annealing stages at 400 °C in N<sub>2</sub> atmosphere by 30 min until the samples reach the usual electrical insulating character of separated ZnO films. The required annealing period to get insulating layers varies with the thickness of the intermediate TM film and the film nanostructure. The ZnO:TM films are formed by nanocrystallites of 15 to 20 nm in size with (002) preferred orientation, and are stressed along the c-parameter according to X-ray diffraction measurements. The electrical resistivity of the films was varied from 0.01 to 100 Ω-cm, the electron concentration from 1021 to 1017 cm<sup>-3</sup>, for a range of carrier mobility from 0.367 to 2.8 cm<sup>2</sup>/V-s. The band gap energy of the films was of ~ 3.3 eV with transmittance of 83 % to 72 % of in the visible region.

#### NM02.10.15

**Effect of the Surface in the Amorphous Ga<sub>2</sub>O<sub>3</sub> Thin Films by Metals of Group IB** Lucía I. Juárez Amador<sup>1</sup>, Miguel I. Galván Arellano<sup>2</sup>, Yazmin M. Hernández Rodríguez<sup>1</sup>, Gabriel I. Romero Paredes<sup>2</sup>, José Alberto Andraca Adame<sup>3</sup> and Ramón Peña<sup>2</sup>; <sup>1</sup>Programa de Doctorado en Nanociencias y Nanotecnología, CINVESTAV-IPN, México, Mexico; <sup>2</sup>Departamento de Ingeniería Eléctrica, sección de electrónica del estado sólido, CINVESTAV-IPN, México, Mexico; <sup>3</sup>Instituto Politécnico Nacional, UPIIH, Hidalgo, Mexico.

Gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) is a metal oxide material with  $\alpha$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$  and  $\beta$  polymorphs; among these polymorphs, the compound  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> with monoclinic structure is the only thermodynamically stable. There are many reports on the effect on the surface modification caused by doping of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> doping with metals of group IB as Au, Ag and Cu. In this work a procedure to control the surface morphological of Ga<sub>2</sub>O<sub>3</sub> nanometric films using Au, Ag and Cu. The procedure is based in the growth of nanometric multilayers Ga<sub>2</sub>O<sub>3</sub>/metal/Ga<sub>2</sub>O<sub>3</sub> by RF sputtering and DC-sputtering at room temperature conditions. To study of surface morphology and structural characteristics the amorphous-Ga<sub>2</sub>O<sub>3</sub>:M arrays were annealed in dry N<sub>2</sub> atmosphere at temperature 600 °C by 30, 60 and 120 min. The morphological results can be related to the evolution of the amorphous character of the films towards the nanocrystalline phase driven by the nature of the intermediate Metal.

The optical, Structural and morphological properties of the Ga<sub>2</sub>O<sub>3</sub>: M arrays were evaluated using transmittance, X-ray diffraction, scanning electron microscopy and Raman spectroscopy. A relationship between the growth procedure and the resultant microstructure and optical properties is proposed.

#### NM02.10.16

**Magnetic Properties of Al Nanoparticles and Al/Ag Nanoparticles Composites** Ryo Yonezawa<sup>2</sup>, Taku Saiki<sup>3</sup>, Akira Matsuo<sup>1</sup>, Tadashi Saitoh<sup>2</sup> and Mitsuru Inada<sup>2</sup>; <sup>1</sup>ISSP, The University of Tokyo, Kashiwa, Japan; <sup>2</sup>Department of Pure and Applied Physics, Kansai University, Osaka, Japan; <sup>3</sup>Department of Electrical Engineering, Kansai University, Osaka, Japan.

We report the magnetic properties of aluminum nanoparticles (AlNPs) and composites of AlNP and silver nanoparticles (AgNPs). The AlNP powder was prepared by reducing aluminum oxide beads in pure water using high-repetition pulsed ablation method. An Nd:YAG pulsed laser with a wavelength of 1064 nm and a receptivity of 20 kHz was used for the ablation. From the results of SEM image and XRD measurements, the average particle diameter of the AlNP was 19 nm. The magnetic properties of the AlNP powder were measured by SQUID. The M-H curve showed superparamagnetism. But Pauli paramagnetic component was not found from M-T curve.

In order to apply this AlNP powder as a solid material, it was mixed with silver paste and solidified by heat treatment. Note that it was confirmed that the AgNP obtained by drying the silver paste was weakly diamagnetic. The magnetic properties of the composite of AlNP and AgNP ((AlNP)<sub>x</sub>(AgNP)<sub>1-x</sub>) showed interesting properties. Here, the number ratio of AlNPs and AgNPs in the composite material is expressed as (AlNP)<sub>x</sub>(AgNP)<sub>1-x</sub>. Basically, the magnetic properties of the composite material were superparamagnetic. Although the magnitude of its saturation magnetization increased with the value of x, it did not increase monotonically but reached a maximum when x = 0.8. In the M-T curves of the composites, there was a paramagnetic component independent of the temperature. The value of this paramagnetic component was also not proportional to the value of x, and it was the maximum when x = 0.4. This result suggests that the paramagnetic component is not due to defects but Pauli paramagnetism. Even more surprisingly, hysteresis was observed in the M-H curve for the samples with x = 0.6 and 0.8, indicating that the samples are ferromagnetic material. Although the origin and mechanisms of the magnetic properties of these composite materials are under investigation, the experimental results show that the unique magnetic moment is induced in the composites and the existence of the magnetic exchange interaction inside the composites.

#### NM02.10.17

**Bulk Nanoporous Aluminum for On-Board Hydrogen Generation by Metal Hydrolysis** John Corsi and Eric Detsi; Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Hydrogen gas technology is a promising replacement for fossil fuels as a next generation mobile energy solution because of its high gravimetric energy density and minimal environmental impact. However, there are still many scientific and engineering challenges that must be addressed before a true "hydrogen economy" can be realized. Although hydrogen gas has a very high gravimetric energy density, it has a low volumetric energy density. One solution that avoids the safety concerns of transporting and storing pressurized flammable gases is the on demand production of hydrogen from water-reactive nanostructured materials. This has been demonstrated for materials such as silicon nanoparticles. It is difficult to produce reactive nanomaterials that are oxide free, high yield and allow for morphological tuning. One technique for producing metallic nanostructures is dealloying, a process in which the less noble component of an alloy is selectively chemically removed, leaving behind a bicontinuous structure of nanoscale metal ligaments and voids. Two types of dealloying include chemical dealloying, in which an acid is used as an etchant, and electrochemical dealloying, in which an external voltage or current is used to etch the material. In this work, we propose a scalable fabrication method of nanostructured aluminum through electrochemical dealloying and demonstrate the ability to use of this material for hydrogen production through water splitting [1,2].

References:

[1] Eric Detsi and John S. Corsi: "Bulk Nanoporous Aluminum for On-board Hydrogen Generation by Hydrolysis". Patent Application, #18-8558-104377.000203

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#### NM02.10.18

**Metallic AsSb Nano-inclusions Strongly Enriched by Sb in AlGaAsSb Metamaterials** Vladimir V. Chaldyshev<sup>1</sup>, Nikolay Bert<sup>1</sup>, Vladimir Nevedomskii<sup>1</sup>, Vitalii Ushanov<sup>1</sup>, Maria Yagovkina<sup>1</sup>, Nikolay Cherkashin<sup>2</sup>, Valerii Preobrazhenskii<sup>3</sup>, Mikhail Putyato<sup>3</sup> and Boris Semyagin<sup>3</sup>; <sup>1</sup>Ioffe Institute, Saint Petersburg, Russian Federation; <sup>2</sup>CEMES-CNRS, Toulouse, France; <sup>3</sup>Institute of Semiconductor Physics, Novosibirsk, Russian Federation.

Motivated by the recent experimental discovery of localized plasmon resonance in the infrared optical spectra of AlGaAsSb metamaterials, we have studied the microstructure of AsSb nano-inclusions embedded in the AlGaAsSb matrix by low-temperature molecular-beam epitaxy followed by high-temperature annealing. Measurements of the interplanar spacings in the nano-inclusion lattice by transmission electron microscopy in both diffraction and high-resolution (HRTEM) modes as well as high-resolution x-ray diffraction showed that the AsSb nano-inclusions possess the rhombohedral A7 structure characteristic of bulk As and Sb. The nano-inclusions appeared to be strongly enriched by antimony (over atomic 90%) even when the Sb content in the matrix is as small as 2.8 atomic %. Our analysis of the Al-Ga-As-Sb phase diagram showed that the observed strong enrichment should happen just above

the AsSb alloy melting point as prescribed by the local thermodynamic equilibrium in the system.

The determined composition of the AsSb nano-inclusions causes a substantial lattice mismatch with the AlGaAsSb matrix. By comprehensive structural investigations we determined the orientation relationships between the atomic lattices. The c-axes of the nano-inclusion lattice, which can be described as hexagonal, is oriented along one of the  $\langle 111 \rangle$  directions of the matrix, which possesses the zinc-blende structure. The  $[-2110]$  direction in the inclusion is parallel to one of the corresponding  $\langle 110 \rangle$  directions in the matrix.

As a result of the lattice mismatch, large AsSb nano-inclusions are accompanied by satellite dislocation loops. In order to determine strain components inside and outside the nano-inclusions we performed geometric phase analysis (GPA) of a HRTEM image with the reference to a known undistorted and quasi-similar lattice. By GPA we also determined the Burgers vector of the dislocation loops, which appeared to be perfect prismatic with  $b = a[001]$ . We considered the corresponding problem of elasticity and show that the dislocation loop formation reduces the total elastic energy in the system.

The established composition and microstructure of AsSb inclusions in AlGaAsSb laid a solid basis for deeper insight into plasmonic properties of the metal-semiconductor metamaterial.

#### NM02.10.19

##### **Monodisperse Dual Plasmonic Au@Cu<sub>2</sub>-xE (E=S, Se) core@shell Supraparticles—Aqueous Fabrication, Multimodal Imaging and Tumor Therapy at *In Vivo* Level Yunsheng Xia; Anhui Normal University, Wuhu, China.**

We herein report aqueous fabrication of well-defined Au@Cu<sub>2</sub>-xE (E = S, Se) core@shell dual plasmonic supraparticles (SPs) for multimodal imaging and tumor therapy at the *in vivo* level. By means of a modified self-limiting self-assembly based strategy, monodisperse core@shell dual plasmonic SPs, including spherical Au@Cu<sub>2</sub>-xS SPs, Au@Cu<sub>2</sub>-xSe SPs, and rod-like Au@Cu<sub>2</sub>-xS SPs, are reliably and eco-friendly fabricated in aqueous solution. Due to plasmonic coupling from the core and shell materials, the as-prepared hybrid products possess an extremely large extinction coefficient (9.32 L g<sup>-1</sup> cm<sup>-1</sup> for spherical Au@Cu<sub>2</sub>-xS SPs) at 808 nm, which endows their excellent photothermal effect. Furthermore, the hybrid core@shell SPs possess the properties of good biocompatibility, low nonspecific interactions, and high photothermal stability. So, they show favorable performances for photoacoustic imaging and X-ray computed tomography imaging as well as photothermal therapy of tumors, indicating their application potentials in biological field.

#### NM02.10.20

##### **High Activity Heterogeneous Catalysts by Plasma-Enhanced Chemical Vapor Deposition of Volatile Palladium Complexes on Biomorphic Carbon Lasse Jürgensen, Michael Frank, Lisa Czympiel and Sanjay Mathur; Inorganic Chemistry, University of Cologne, Cologne, Germany.**

New palladium complexes based on allyl and alkenolate ligands were synthesized and structurally characterized. Combination of delocalized allylic sp<sup>2</sup>-hybridized carbon centers and a strongly binding N<sup>∞</sup>O chelating unit (e.g. 3,3,3-trifluoro(pyridin-2-yl)propen-2-ol) offered a promising combination of high volatility and thermal lability not commonly observed in noble metal precursors. Application of the new Pd compounds in thermal metal organic and plasma-enhanced chemical vapor deposition demonstrated their clean and efficient decomposition pathways, which in conjunction with their intriguing air stability made them efficient precursors for Pd films and clusters. Plasma-enhanced chemical vapor deposition of the palladium compounds on biomorphic carbon used as a porous substrate with high surface area and interconnected channels delivered recyclable carbon-supported Pd catalysts (Pd@BioC), which showed excellent selectivity, stability, and recyclability in C-C coupling reactions.

#### NM02.10.21

##### **Directed and Self-Assembly of Elemental and Bimetallic Thin Films in the Au-Ag-Ni System via Pulsed Laser Dewetting David A. Garfinkel<sup>1</sup>, Philip D. Rack<sup>1,2</sup>, Ryan Allaire<sup>3</sup>, Jason Fowlkes<sup>2,1</sup>, Lou Kondic<sup>3</sup>, Miguel Fuentes-Cabrera<sup>2</sup> and Reece Emery<sup>1</sup>; <sup>1</sup>University of Tennessee, Knoxville, Knoxville, Tennessee, United States; <sup>2</sup>CNMS, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; <sup>3</sup>New Jersey Institute of Technology, Newark, New Jersey, United States.**

Both directed and self-assembly of metallic thin films via pulsed laser induced dewetting have been demonstrated as viable techniques for generating ordered arrays of metallic nanoparticles. The liquid phase dewetting of single component materials has been the subject of much study, and thus the relevant instabilities in 2d films and 1d filaments, and competing fluid forces of surface energy, viscosity, and inertia, are relatively well understood. The addition of a second component, however, creates intriguing and complementary chemical instabilities and free energy landscapes that can facilitate or compete with the hydrodynamics. For instance, phase instabilities at high temperatures can compete with the dewetting dynamics, and provide an avenue to create unique particle morphologies. Here we will examine both patterned and continuous thin film dewetting of elemental and bimetallic films in the Au-Ag-Ni system. Beyond promising bifunctional magneto-plasmonic properties and applications, the chosen material system also features three unique bimetallic phase behaviors: near complete immiscibility in the solid and liquid phase (Ag-Ni), complete miscibility (Au-Ag), and liquid miscibility with a miscibility gap in the solid phase (Au-Ni). The Primary focus is devoted to Au-Ni and Ag-Ni due to the presence of immiscibility in both systems. In this presentation we will briefly overview some of the previous work on single component pulsed laser dewetting, and in particular on the 1d breakup of lithographically patterned thin film strips. We will then compare the Rayleigh Plateau instability and hydrodynamic transport in Ag-Ni and Au-Ni, and illustrate how phase separation affects the dewetting dynamics. We will show complementary molecular dynamics simulations as well as continuum simulations, which will demonstrate how the relevant timescales of the hydrodynamic/chemical instabilities and transport affect the resultant nanoparticle morphology.

#### NM02.10.22

##### **Nanoporous Metallic Aluminium-Covered Polyimide Nanopaper as Carbon-Free Cathode for Lithium-Air Batteries Jiwon Jung<sup>1</sup>, Su-Ho Jung<sup>2</sup>, Tae Gwang Yun<sup>1</sup>, Ki Ro Yoon<sup>1</sup>, Chanhon Kim<sup>1</sup>, Jun-Young Cheong<sup>1</sup>, Su-Ho Cho<sup>1</sup>, Hye Moon Lee<sup>2</sup> and Il Doo Kim<sup>1</sup>; <sup>1</sup>KAIST, Yuseong-gu, Korea (the Republic of); <sup>2</sup>Korea Institute of Materials Science, Chanwon, Korea (the Republic of).**

Although conductive and cheap aluminum (Al), common cathode current collector in Li-ion batteries, is well known to be stable at high voltage, its active use in Li-air batteries has been limited because of a lack of synthetic method for porous, metallic Al layer with high surface area. Herein, we first developed nanoporous metallic aluminum (Al)-coated polyimide nanopaper (PI@nAl Np) as carbon-free air cathode for flexible Li-air batteries: First, self-standing PI Np was synthesized via electrospinning of PAA solution (pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) in *N,N*-dimethylformamide (DMF)) followed by imidization. Then, using our own Al ink developed by our group (patented in USA), the nAl overlayers were conformally coated on entire surfaces of the PI Np; thickness of Al coating layer was precisely optimized in terms of electronic conductivity ( $\approx 1$  ohms/square), flexibility and pore blockage in controllable manner. The finely designed PI@nAl Np showed greatly important features as porous cathode: (1) Mechanically durable PI Np without reactive carbon in electrolyte provides flexible, porous and light-weight matrix for diffusing O<sub>2</sub> and accommodating Li<sub>2</sub>O<sub>2</sub> in large void reservoirs. (2) nanoporous metallic Al coating layers serve as sufficient reaction sites and facile pathway for electron transport. The PI@nAl Np exhibits a highly stable capacity at a fixed capacity of 1000 mAh g<sup>-1</sup> for over 300 cycles at a current density of 400 mA g<sup>-1</sup>. We conducted close-investigation of reaction products in light of morphology, parasitic side reactions in carbon-free air cathode. Flexible pouch- and cable-type Li-air battery cells with the PI@nAl Np were successfully fabricated and applied as power sources for flexible electronics (5.0 V LED and 6.0 V 'Otto Bot' operating). Our synthetic strategy will open new opportunities to invent nanostructured Al materials for diverse applications.

#### NM02.10.23

**Silver Core/Silicon Nanocrystal Shell Hybrid Nanoparticle as Antimicrobial Agent** [Asuka Inoue](#)<sup>1</sup>, Hiroshi Sugimoto<sup>1</sup>, Byungji Kim<sup>2</sup>, Michael J. Sailor<sup>3</sup> and Minoru Fujii<sup>1</sup>; <sup>1</sup>Department of Electrical and Electronic Engineering, Kobe University, Kobe, Japan; <sup>2</sup>Materials Science and Engineering Program, University of California, San Diego, San Diego, California, United States; <sup>3</sup>Department of Chemistry and Biochemistry, University of California, San Diego, San Diego, California, United States.

Silver nanoparticles (AgNPs) are often used for antimicrobial applications, especially against Gram-negative bacteria, such as *E. coli*. Upon dissolution, AgNPs release Ag ions that bind to nucleic acids and thiol-containing compounds (i.e. amino acids in enzymes and proteins) to inhibit bacterial growth. However, AgNPs suffer from agglomeration and oxidation, which both degrade antimicrobial activity. To overcome this challenge, AgNPs are often coated with polymers. Recently, we developed a hybrid nanoparticle that is composed of an Ag core and a monolayer shell made of silicon (Si) nanocrystals. [1] With a hydrophilic shell formed by Si nanocrystals, the hybrid nanoparticle is able to disperse in water without agglomeration. Moreover, the size of AgNPs and the thickness of their shells can be tuned by adjusting concentration of Ag ions and Si nanocrystals. A major advantage of the hybrid nanoparticle is that it can be formed into a smooth and flexible film of antimicrobial nanoparticles by simply drop-casting the solution onto a substrate. Herein, we present the potential of the hybrid nanoparticle as an antimicrobial agent against *E. coli*, as a model Gram negative bacterium. The antimicrobial action of the hybrid nanoparticle is similar to bare AgNPs, in that Ag ions are released from the hybrid nanoparticle core through the Si nanocrystal shell to inhibit bacterial growth. Furthermore, use of the drop-cast films as antimicrobial coatings were studied as a function of structural parameters (i.e., diameter of the Ag core, diameter of Si nanocrystals forming the shell), and antimicrobial efficacy was tested in an agar diffusion assay. The results demonstrate a strong antimicrobial activity by the hybrid nanoparticle film, compared to the bare AgNP film. Moreover, the extent of bacterial growth inhibition depended strongly on the structure of the hybrid nanoparticle. Quantitative analyses reveal that hybrid nanoparticles diffuse on agar by releasing Ag ions, and that the area of the growth inhibition is determined by the diffusion rate which is in turn determined by the structural parameters of the hybrid nanoparticle. The hybrid nanoparticle remains effective when stored in aqueous solution or in air.

[1] H. Sugimoto, et al., *Nanoscale*, 8, 21, 10956 (2016)

#### NM02.10.24

**2D Single-Crystalline Copper Nanoplates as a Conductive Filler for Electronic Applications** [Tae-Wook Kim](#); Korea Institute of Science and Technology, Wanju, Korea (the Republic of).

Metal nanoparticles have received much attention due to their versatile use in catalysis, optoelectronics, magnetics, biotechnology and microelectronics applications. Because the nanoparticle size is known to be an important factor to enhance the activity or functionality for practical applications, various synthetic methods have been introduced, and a potential growth mechanism has been proposed to explain the relationship between the crystal structure and the optical, physical and electrical functionalities.

In this study, we synthesize copper nanowires (Cu NWs) and copper nanoplates (Cu NPLs) using a hydrothermal process. The combination of a mild reductant, stabilizer, and shape modifier allow the dimensional control of the Cu nanocrystals from one-dimensional (1D) nanowires to two-dimensional (2D) nanoplates. HR-TEM reveals that the prepared Cu NPLs had a single-crystalline structure. From the XPS analysis, we found that iodine plays an important role in the modification of the copper nanocrystals through the formation of an adlayer on the basal plane of the nanoplates. We successfully synthesized Cu NPLs with an average edge length of 10  $\mu\text{m}$ , and these Cu NPLs are the largest copper 2D crystals synthesized by a solution-based process so far. The application of the metallic 2D crystals as a semi-transparent electrode prove their feasibility as a conductive filler, exhibiting very low sheet resistance (0.4  $\Omega/\text{sq.}$ ). The efficient charge transport is due to the increased contact area between each Cu NPL, i.e., so-called plane contact (2D electrical contact).

#### NM02.10.25

**Synthesis and Size Analysis of DNA Conjugated Bio-Hybrid Nanostructures** [Soubantika Palchoudhury](#)<sup>1</sup>, Abdollah Arabshahi<sup>2</sup>, Yasmin Foster<sup>1</sup>, Uday Gharje<sup>1</sup> and Arnel Boutchuen<sup>1</sup>; <sup>1</sup>Civil and Chemical Engineering, University of Tennessee at Chattanooga, Chattanooga, Tennessee, United States; <sup>2</sup>SimCenter, The University of Tennessee at Chattanooga, Chattanooga, Tennessee, United States.

The remarkable advances in synthesis techniques has led to a wide variety of complex nanostructures in recent years. The hybrid nanostructures essentially integrate multiple nanoparticles into one unit to facilitate tailored material properties. Synthesis of bio-hybrid nanostructures integrating biological moieties with inorganic nanoparticles has been of particular interest due to their novel material properties and applications in bio-imaging and drug delivery, but these structures are synthetically challenging to achieve. These hybrid nanostructures are also increasingly complex in terms of metrology.

We report the synthesis of a novel hybrid nanostructure containing shape-controlled iron oxide nanoparticles conjugated to metal nanoparticles (e.g., Au) via DNA linkers. The synthesized bio-hybrid nanoparticles are stable in the aqueous phase and are characterized via a transmission electron microscope. The size and surface charge of a nanoparticle is an important metric for several biomedical applications such as targeted drug delivery as it affects the nanoparticle's circulation *in vivo*. However, it is challenging to establish a metric to accurately assess the size of these bio-hybrid nanoparticles due to their complex structure and morphology. In this study, size and zeta potential of the different bio-hybrid nanostructures synthesized have been investigated in detail on a Litesizer particle analyzer to develop a reliable material characterization method to assess the size of complex nanostructures. The study will be highly useful for biomedical applications like imaging and drug delivery.

#### NM02.10.26

**Facile Signal Amplification of Colorimetric DNA Detection Using “Nano-to-Ion” Processes for High Sensitivity** [Hye In Cho](#) and Jae-Seung Lee; Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of).

A number of signal amplification methods have been investigated to achieve high sensitivity of DNA detection schemes. In general, the signal amplification of DNA detection can be classified largely into two categories, depending on the type of the amplification target: DNA targets themselves, and artificially designed surrogate targets. These approaches have been widely taken advantage of in industry and academia owing to the high selectivity and sensitivity of the detection results. However, the amplification of target DNA, such as the polymerase chain reaction (PCR) and the rolling circle amplification (RCA), are limited with their cumbersome, time-consuming enzymatic reactions. To overcome such obstacles, the surrogate target amplification has been developed and employed in various DNA detection schemes, such as bio-barcode assays, with advantages including short detection time, no need for enzymatic reactions, and high sensitivity. Unfortunately, however, the design and incorporation of surrogate targets are accompanied with undesired expenses and labor.

In this work, we developed a DNA detection assay based on the conventional sandwich schemes using magnetic microparticles (MMPs) and silver nanoprobe, each functionalized with probe DNA strands, but with highly reliable and facile amplification technology. Importantly, we took advantage of the presence of nanoparticle probes without amplifying any targets or surrogate targets. Instead, a single nanoparticle probe can be transformed into numerous ions via a “nano-to-ion” process. This numeric enhancement can be directly correlated with the signal enhancement and eventually the improved limit of detection (LOD). To obtain the colorimetric signals, the tremendous number of silver ions is quantitatively analyzed using the  $\text{C-Ag}^+\text{-C}$

coordination chemistry in assistance with DNA-modified gold nanoparticles. Furthermore, for the better sensitivity of DNA detection, we obtained the photoluminescence of semiconductor quantum dots, which was another quantitative correlation parameter as a function of the silver ion concentration.

#### NM02.10.27

**Investigation of (WO<sub>3</sub>)<sub>x</sub> Cluster and Tungsten Oxide Nanoparticle Formation Using Time-of-Flight Mass Spectrometry** Stefan Kuns<sup>1</sup>, Christof Schulz<sup>1,2</sup> and Hartmut Wiggers<sup>1,2</sup>; <sup>1</sup>IVG, Institute for Combustion and Gas Dynamics, University of Duisburg-Essen, Duisburg, Germany; <sup>2</sup>CENIDE, Center for Nanointegration Duisburg-Essen, Duisburg, Germany.

Tungsten oxide (WO<sub>3</sub>) is an important gas sensing material due to its sensitivity to, e.g., acetone, toluene, and hydrogen sulfide. The detectability of these gases and the insensitivity to high humidity makes WO<sub>3</sub> interesting for non-invasive breath diagnostics [1]. The acetone concentration in the breath is an indication of diabetes, the concentration of toluene can indicate lung cancer. All these applications require high surface area and thus small particles. Time-of-flight mass spectrometry (TOF-MS) in combination with molecular-beam sampling enables the inline investigation of nanoparticle formation in the gas phase. Molecular-beam sampling instantaneously interrupts all reactive gas-phase processes and thus allows a spatially resolved measurement of gas-phase and particle-phase. TOF-MS can be used to identify the composition as well as intermediate species (clusters) at various locations in a reactor. To gain insight in the tungsten oxide nanoparticle formation process, respective measurements were performed in low-pressure flat-flame reactor.

WO<sub>3</sub> nanoparticles are synthesized by the decomposition of tungsten hexafluoride (WF<sub>6</sub>) in a premixed hydrogen/oxygen flame. Due to low pressure (20–30 mbar), an almost one-dimensional, spatially extended flat flame is formed enabling spatially-resolved measurements. A small sample of the aerosol is expanded through a nozzle and a skimmer into high vacuum to form a particle-laden molecular beam. The progress from the initial decomposition of the gaseous precursor to the formation and growth of (WO<sub>3</sub>)<sub>x</sub> clusters and nanoparticles can be studied by varying the distance between the burner head and the nozzle position. The distance between the sampling nozzle and the burner (height above burner, HAB), represents the residence time within the reactor. As previous investigations indicate fragmentation of tungsten oxide clusters [2] during TOF-MS measurements, electron ionization was substituted with soft ionization with a vacuum UV (VUV) lamp avoiding fragmentation.

The results show sequential cluster formation and particle nucleation. The number concentrations of differently sized clusters strongly vary indicating “magic” cluster sizes during the nucleation process. The fuel-to-oxygen ratio affects cluster growth and phase composition and low oxygen concentrations cause the formation of sub-stoichiometric clusters. Substituting a small part of hydrogen with methane changes the flame chemistry due to additional charges resulting in a significant decrease of smaller cluster sizes and a shift to larger cluster sizes.

#### NM02.10.28

**Universal Template-Synthesis Method for Three-Component Nanostructures** Han-Jung Ryu, Jang Ho Joo and Jae-Seung Lee; Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of).

Trimetallic nanoparticles have attracted growing interest recently because of their superior chemical and physical properties. They show excellent catalytic properties which belongs to their synergistic effects based on electronic charge transfers between multiple metal atoms. Despite of these unique properties, however, trimetallic nanoparticles have to suffer from high reaction temperatures, harsh reductants and multistep procedures during their synthesis. To overcome these obstacles, nanosized templates can be used as one of promising solutions. Template methods are widely used for nanomaterial synthesis, because they can provide nucleation sites to facilitate the reduction process of metal precursors. After the removal of the templates, the resultant hollow nanoparticles can obtain high surface area, which is one of the most important virtues for catalyst. In this work, we demonstrate a universal template-assisted room-temperature synthetic method for trimetallic noble metal nanoparticles which were replications of silver halide nanotemplates. As a proof of concept, we demonstrate two types of trimetallic nanoparticles, each composed of Pd-Au-Ag and Pt-Au-Ag, which were synthesized using the universal synthetic method. Importantly, the shape of the trimetallic nanoparticles was able to be controlled by adjusting the shape of the templates. The structural properties and composition of the trimetallic nanoparticles were thoroughly analyzed by transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), elemental mapping, and X-ray diffraction (XRD). Finally, the outstanding catalytic performance of the trimetallic nanoparticles for reduction of harmful toxic Cr (VI) ions were monitored by UV-vis spectroscopy. They exhibited great catalytic performances for the reduction process because of their synergistic effects owing to multiple types of metals and high surface area derived from hollow structures.

#### NM02.10.29

**Fabrication of Transparent Nanostructural Iridium/Iridium Oxide Film for Biomedical and Electrochemical Applications** Ming-Ting Hsieh and Pochun Chen; National Taipei University of Technology, Taipei, Taiwan.

Ir and iridium oxide are attractive materials for biomedical and electrochemical applications due to their desirable stability, electrochemical performance, and biocompatibility. Nanostructured iridium/iridium oxide possesses several advantageous properties including large surface-to-volume ratio, light weight, optical transmittance, and desirable electrical and electrochemical capability. However, controlling film morphology and inter-connectivity of nanostructural iridium/iridium oxide is very difficult. Nanoporous iridium/iridium oxide has excellent properties, and it can also provide extremely high surface area in applications for catalysis, sensors, and bioelectrodes. In addition, the transparency of the nanoporous iridium/iridium oxide can provide a great benefit for biomedical devices such as electronic skin and implantable optogenetic probes

In this study, we employed a facile process to fabricate a transparent and uniform iridium/iridium oxide film by chemical bath deposition with proper heat and electrochemical treatments. Besides, the formation mechanism of the nanoporous iridium/iridium oxide film was illustrated by a detail thermodynamic calculation. In addition, we carried out a transfer printing process to attach the nanostructural iridium/iridium oxide film on transparent substrates including ITO and polyimide. We characterized and evaluated the deposited films. The surface morphology, roughness, hydrophilicity, crystallinity, oxidation state, and electrochemical performances of the iridium/iridium oxide film were analyzed.

#### NM02.10.30

**Metal-Curcumin Nanoparticles—Synthesis, Characterization and Therapeutic Potential** Apoorva Singh<sup>1</sup>, Pooja Ghosh<sup>2</sup>, Suranjana Mukherjee<sup>1</sup>, Sunita Sharma<sup>3</sup>, Swagata Dasgupta<sup>2</sup>, Gayatri Mukherjee<sup>1</sup> and Koel Chaudhury<sup>1</sup>; <sup>1</sup>School of Medical Science and Technology, Indian Institute of Technology Kharagpur, Kharagpur, India; <sup>2</sup>Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur, India; <sup>3</sup>Institute of Reproductive Medicine, Kolkata, India.

In recent years, highly promising and innovative approaches involving complex formation of the curcumin molecule with transition metals has proven effective in overcoming the limitations associated with clinical translation of curcumin, i.e. low systemic bioavailability and hydrolytic instability. Owing to the significant role played by transition metals in pathological processes, these metal-curcumin complexes can act as a double-edged sword due to increased specificity and cytotoxicity. Though the complexes exhibit enhanced therapeutic potential, the low aqueous solubility still remains a challenge in achieving targeted drug delivery. Herein, we propose that nanoformulation of metal-curcumin complexes may pave a new way towards drug delivery and therapeutics due to high stability, bioavailability that may result in longer circulation time

The objective of the present study is to synthesize metal-curcumin nanoparticles (NPs) with high stability, solubility and long-term sustained drug delivery. For this purpose, the biocompatible and degradable FDA approved poly (lactic-co-glycolic) acid polymer was used as the vehicle along with poloxamer-

407 to increase the stability of NPs. Two transition metals, Copper (Cu), and Zinc (Zn) were respectively complexed with curcumin in the ratio 1:1 and characterized using spectroscopic techniques. A nanoprecipitation technique was used to prepare NPs and the formulations evaluated in terms of particle size, zeta potential, surface morphology, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), entrapment efficiency (EE) and *in-vitro* release kinetics. In addition to chemical characterization, the therapeutic potential of the NPs was investigated in different cancer cell lines and primary endometrial stromal cells isolated from endometriotic lesions. It was found that the prepared NPs were in the size range of 180-220 nm with EE of  $77\pm 2.43$  to  $82\pm 4.43\%$ . The low polydispersity index and high negative zeta potential indicated monodisperse and stable nature of NPs. FTIR and XRD confirmed the entrapment of respective compounds within NPs without any major structural alterations, while release kinetics indicated a sustained release pattern exhibited by Cu- and Zn-Cur NPs as compared to Cur NPs over a period of time. The enhanced anti-proliferative activity of metal-Curcumin NPs was evident in all the cancer cells lines and primary endometriotic cells as compared to Cur NPs. In conclusion, for the first time metal-Cur NPs with high aqueous solubility, bioavailability and diverse potential benefits were successfully prepared and characterized.

#### NM02.10.31

**Masking Strategies for DNA Detection—What can Mask Catalytic Nanoparticle Surfaces for DNA Targets?** Won Kyu Lee, Yoon Hyuck Kim and Jae-Seung Lee; Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of).

DNA-functionalized gold nanoparticles (DNA-AuNPs) have been widely used for sensitive and selective colorimetric detection of nucleic acids, because they exhibit excellent chemical and physical properties such as sharp melting profiles, cooperative binding properties, reversible assembly properties, and intense optical properties based upon the surface plasmon resonance (SPR). In particular, the conventional nanoparticle-based “litmus” test schemes proved the DNA-AuNPs to be powerful and efficient diagnostic tools in various diagnostic applications for DNA targets. The color changes were determined by the [target] and the presence of mismatches, which were correlated with the interparticle distance of the DNA-AuNPs. While simple and rapid, however, this detection scheme had to suffer from low sensitivity, and often low signal intensity, especially at lower [DNA-AuNP]s. As a result, this assembly-based colorimetric detection scheme is practically of little interest in the community. Considering its fundamental reliability and simplicity, however, it would be a significant advance if a modification could improve its sensitivity and signal intensity.

We previously demonstrated a conceptually advanced detection scheme, where the protein target binding leads to the masking of catalytic nanoparticle surfaces. Eventually, the catalytic activity of the particles can be systemically controlled, which can be quantitatively correlated with the color signals. In case of DNA targets, however, they are not sufficiently large enough to “mask” the nanoparticle surfaces. Instead, the DNA targets can “assemble” the DNA-AuNP probes as described in the conventional assembly-based schemes, which ultimately results in masking DNA-AuNP surfaces using other DNA-AuNPs. Taking advantage of this masking strategy, where the concentration of the target DNA controls the exposed surface area of AuNPs, the detection scheme in this work could be highly sensitive and selective for the colorimetric detection of DNA targets. In order to characterize and elucidate the processes controlling the exposed surface area of DNA-AuNPs, we analyzed the structure of DNA-AuNPs using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and dynamic light scattering (DLS). Melting transitions were also obtained as a function of temperature by monitoring the extinction change at 525 nm using UV-visible spectroscopy. Furthermore, we investigated the catalytic properties of the assembled DNA-AuNPs for the oxidation of *o*-phenylenediamine (OPD) and the reduction of 4-nitrophenol (4-NP). Our masking strategy studies of the DNA-AuNP assembly process will play a significant role in demonstrating colorimetric detection of the target DNA based on the self-assembly of gold nanoparticles.

#### NM02.10.32

**Effect of Hydrogen on the Mechanical Properties of Nanocrystalline  $\alpha$ -iron Using Atomistic Simulations** Mohamed A. Hendy<sup>1</sup>, Tarek Hatem<sup>1</sup> and Jaafar A. El-Awady<sup>2</sup>; <sup>1</sup>The British University in Egypt, Cairo, Egypt; <sup>2</sup>Department of Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland, United States.

Hydrogen embrittlement is a persistent problem causing premature failure for steels. Nanocrystalline metals have unique mechanical properties compared to coarse grain counterpart which makes them suitable for future structural applications. In order to assess the effect of hydrogen on nanocrystalline  $\alpha$ -iron, 3D Molecular dynamics (MD) simulations have been performed for bulk random-oriented nanocrystalline  $\alpha$ -iron. The simulation cells are of size  $76\text{nm} \times 76\text{nm} \times 76\text{nm}$  composed of 40 grains of different size with periodic boundary conditions. The simulation cells are deformed by applying strain along the x-axis with strain rate of . The effect of hydrogen on the deformation mechanism and fracture have been investigated through simulating a hydrogen-free nanocrystalline iron cell and hydrogen charged one with hydrogen concentration of 100 appm. In both cases, intergranular failure has occurred, however, the results showed a significant reduction in fracture strain for hydrogen-charged simulation cell compared to the hydrogen-free one. Moreover, hydrogen accelerated intergranular crack propagation. The hydrogen charged simulation cell experienced different deformation activities compared to hydrogen free one. For both cases, many deformation modes interact and co-exist (twinning, partial dislocation emission and grain boundary sliding).

#### NM02.10.33

**Flame Inspired Nanostructuring—Flexible Ceramic Hybrids for Advanced 3D Nanotechnologies** Yogendra K. Mishra; University of Kiel, Kiel, Germany.

Recently introduced flame based approach offers unique opportunities for advanced metal oxide nanostructuring, ranging from quasi 1D nanowires to macroscopic 3D porous interconnected tetrapodal networks.<sup>[1]</sup> The present strategy offers direct integration of ZnO nano- and microstructures and their networks on the desired substrates for various applications, e.g., whispering gallery modes, photocatalysis or nanosensing (UV/gases) applications.<sup>[1-4]</sup> The flame grown ZnO tetrapods ZnO nano- and microstructures exhibit very low cytotoxicity and they have shown strong potentials against antiviral applications.<sup>[5]</sup> The unique 3D shape of the ZnO tetrapods facilitates them to be used as efficient fillers for fabricating advanced composites, e.g., self-reporting composites<sup>[6]</sup> and many others. The 3D porous, flexible and conducting network from ceramic materials are now-a-days very important because of their technological relevance and the developed flame method offers desired synthesis of various ZnO and SnO<sub>2</sub> nanonetworks.<sup>[1]</sup> These 3D porous networks can be decorated with other nanostructures for designing hybrid multifunctional materials<sup>[7]</sup> and can also be used as sacrificial templates to grow new nanomaterials.<sup>[8,9]</sup> Additionally, polymers can also infiltrated within the network to make different polymer based composites and template can be removed later on, if needed, to develop porous polymers.<sup>[10]</sup> An overview about the possible nanostructuring opportunities by the flame method will be presented and few application examples will be discussed.

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#### NM02.10.34

**Reversible Magnetic Agglomeration—A Mechanism for Thermodynamic Control Over Nanoparticle Size** Dale L. Huber<sup>1</sup>, Grant Bleier<sup>1</sup>, John Watt<sup>1</sup>, Simocko K. Chester<sup>2</sup> and Judith Lavin<sup>1</sup>; <sup>1</sup>Sandia National Laboratories, Albuquerque, New Mexico, United States; <sup>2</sup>San Jose State University, San Jose, California, United States.

We present a method for the synthesis and precise size control of magnetic nanoparticles in a reversible magnetic agglomeration mechanism. In this approach, nanoparticles nucleate and grow until a critical susceptibility is reached, in which magnetic attraction overcomes dispersive forces, leading to agglomeration and precipitation. This phase change in the system arrests nanoparticle growth and gives true thermodynamic control over the size of nanoparticles. We then show that increasing the alkyl chain length of the surfactant, and hence increasing steric stabilization, allows nanoparticles to grow to larger sizes before agglomeration occurs. Therefore, simply by choosing the correct surfactant, the size and magnetic properties of iron nanoparticles can be tailored for a particular application. With the continuous addition of the precursor solution, we can repeat the steps of nucleation, growth, and magnetic agglomeration indefinitely, making the approach suitable for large scale syntheses.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.

#### NM02.10.35

**Engineering Nanoscale Selenium Surface Functionalization for Clinical Antibacterial Applications** James W. Moxley, Paria Ghannadian and Thomas Webster; Northeastern University, Boston, Massachusetts, United States.

Antibiotic resistance (ABR) is rapidly gaining attention within the scientific community as an escalating threat to the global health care infrastructure. The increasing frequency of occurrence of resistant bacterial strains, specifically multidrug resistant (MDR), extensively drug resistant (XDR), and totally drug resistant (TDR) phenotypes, would seemingly necessitate demand for a new generation of small-molecule drugs for clinical implementation. Unfortunately, the compounded effects of administrative barriers, technical complications, and selective economic pressures has significantly reduced the rate of discovery for new antibiotic species. Novel approaches for the management of bacterial growth in clinical settings are clearly desirable. One such approach is the development of nanoscale selenium surface functionalization for medical materials and instrumentation.

Selenium nanoparticle functionalization was achieved by heterogeneous nucleation along a range of solid supports provided by academic and federal collaborators. These materials were coated in small-batch processes, in which the supports (2 mm x 2 mm x 0.5 mm) were immersed in a reaction solution (100  $\mu$ M glutathione, 25  $\mu$ M sodium selenite, and 80  $\mu$ M sodium hydroxide) for 60 seconds, followed by several washing stages with deionized water. Nanoparticle coatings were characterized with atomic force microscopy (AFM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and contact angle measurement. Functionalized surfaces were assessed for antibacterial properties by means of colony forming unit (CFU) assay with gram-positive (*Staphylococcus aureus*, ATCC 25923) and gram-negative (*Escherichia coli*, ATCC 25922) bacterial strains.

Physical characterization demonstrated that treatment yielded heterogeneous surface coverage, with average particle interspacing smaller than the dimensions of both *S. aureus* and *E. coli*. Chemical characterization verified that observed nanoparticles were composed of elemental selenium. CFU assay demonstrated a statistically significant reduction in *S. aureus* bacteria over a 12 hour interval for the two current test materials, carbon-microfiber sheets and basalt-epoxy blocks. For carbon-microfiber sheets, treatment resulted in a 32 % and 63 % reduction in CFU at the targeted operational temperatures of 50 °C and 40 °C, respectively. For basalt-epoxy blocks, treatment resulted in a 77 % and 82 % reduction in CFU at the targeted operational temperatures of 60 °C and 50 °C, respectively. A trend of reduced bacterial colonization has also been observed for *E. coli* in preliminary studies.

Nanoscale selenium surface functionalization has demonstrated antibacterial efficacy along clinical surfaces *in vitro*. Future studies will focus on elucidating the mechanism of antibacterial activity, assessing mammalian cell biocompatibility, and determining antibacterial efficacy under biofouling conditions.

#### NM02.10.36

**Colloidal ReO<sub>3</sub> Nanocrystals—Extra Rhenium d-electron Instigating a Metallic Optical Behavior** Sandeep Ghosh; The University of Texas at Austin, Austin, Texas, United States.

Plasmonics exhibited by nanocrystalline metals has been an active area of research, mostly due to interest in exploring their unique optical response. Although elemental metals like gold and silver have been the major focus in these studies, other materials have also been shown to exhibit a metallic optical response. In this presentation, we will describe a solution based synthesis of nanocrystals (NCs) of rhenium (VI) oxide (ReO<sub>3</sub>) which exhibit localized surface plasmon resonance (LSPR) typical of metals and/or degenerately doped semiconductors. Metal oxides are often semiconductors with moderate to wide band gaps and one way of introducing charge carriers is through extensive doping. However, the inherent metallic nature of ReO<sub>3</sub> arises due to its unique electronic band structure. The presence of an extra d-electron in the outer electron shell of the rhenium (VI) ion leads to partial filling of the conduction band and manifests in its characteristic metallic conductivity and optical properties. The colloidal synthesis of these NCs follow an ether based reduction of Re(VII) precursor to the Re(VI) oxidation state. This is different from the usual chemical mechanism that a majority of the metal oxide NC syntheses follow, that of lysis of the metal alkylcarboxylate precursor by means of a suitable nucleophile like water, alkylamines or alkyl alcohols. The primary reason for this departure is the availability of a range of oxidation states for Re (+2 to +7) and a careful control of this was necessary to obtain the NCs of interest, coupled with unavailability of suitable Re(VI) precursors. In this presentation, these synthesis challenges and strategies employed to overcome them and design a successful chemical route will be described. The as-obtained NCs exhibit an LSPR optical response in the visible-near-infrared region, and are stabilized in solution by L-type ligand coordination. The advantage of such ligand coordination is demonstrated by the ease of switching between solvents of choice without having to go through the cumbersome ligand exchange procedure, most prevalent otherwise in case of X-type ligation in colloidal NCs. These NC solutions were then spin-coated on appropriate substrates and further characterized by means of electrical transport and spectroelectrochemical measurements.

#### NM02.10.37

**Polyelemental Nanopatterns via Low-Energy Plasma Bombardment for High Performance Gas Sensor** Woo-Bin Jung and Hee-Tae Jung; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Three-dimensional nanopatterns that consist of polyelemental components are promising platform for potential applications, whereas there are no effective strategies for fabrication of polyelemental nanopatterns, in which three-dimensional architectures can be explored in a systematic and site-specific manner. Generation of high resolution (< 30 nm) nanoscale pattern with multi-components regardless types of elements is one of the biggest challenge in nanotechnology because of difficulties of nanoscale mixing and 3D nanopatterning at the same time. Recently, a few study based on precursor such as dip-pen lithography and block copolymer template have been reported, but previous approaches are limited to shape and combination depending on compatibility of elements.

In this study, we accomplished significant progress toward **developing general method for fabricating complex nanostructures with a mixture of two or more types of elements**. By simply using low-energy plasma bombardment process, followed by secondary sputtering on the sidewall surfaces of the pre-pattern, the polyelemental components with diverse shapes and high resolution were generated. Unlike previous approaches, this discovery is significant in terms of the fabrication of a wide range of polyelemental complex nanostructures: **Firstly**, this method is not restricted to the selection of elements and their combination, and a wide range of combination of metals and semiconductors can be generated by the simple deposition of metals or semiconductors on a substrate. **Secondly**, nanostructures with several components of greater than three can be fabricated by simply plasma bombardment process on multi-layered films. **Thirdly**, the complex shapes and array of multi-component nanostructures with high resolution (~10 nm) and tunable inner structures can be achieved. **Finally**, this approach can be applied to hydrogen gas sensing, with the highest sensing speed observed using Pd–Au bimetallic nanopatterns. **Notably**, only one Pd-based bimetallic line-shaped nanostructure was examined in this study; this may not even be the best one, but its performance exceeds that of conventional materials. This study is expected to open the door for a large family of multi-component metals for use in a wide range of applications.

#### NM02.10.38

**Intermetallic L1<sub>0</sub>-MPt (M=Fe, Co) Nanoparticles Advance Pt Catalysis in Fuel Cells** Junrui Li and Shouheng Sun; Brown Univ, Providence, Rhode Island, United States.

Stabilizing transition metals (M) in MPt alloy under acidic conditions is challenging, yet crucial to boost Pt catalysis towards oxygen reduction reaction (ORR) in fuel cells. ~9 nm tetragonal core/shell L1<sub>0</sub>-MPt/Pt (M=Fe, Co) nanoparticles with 2-3 atomic layers of strained Pt shell were synthesized for ORR. At 60°C in acid, the tetragonal L1<sub>0</sub>-MPt better stabilizes M than its cubic A1-MPt counterpart. L1<sub>0</sub>-FePt/Pt showed superior activity to commercial Pt/C catalyst in the membrane electrode assembly (MEA) and almost no activity drop after 30,000 voltage cycles at 80°C. L1<sub>0</sub>-CoPt/Pt achieved mass activities (MA) of 0.56 A/mg<sub>Pt</sub> before durability test and 0.45 A/mg<sub>Pt</sub> after 30,000 voltage cycles in the MEA at 80°C, exceeding the DOE 2020 targets on Pt activity and durability (0.44 A/mg<sub>Pt</sub> in MA and <40% loss in MA after 30,000 cycling). Density functional theory study suggests that the ligand effect of Co and the more compressive strain brought by Co compared to Fe better tunes the binding of oxygenated species to the 2~3 Pt shell, thus leading to enhanced ORR performance in fuel cells.

#### NM02.10.39

**Hot Carrier Generation via Surface Plasmons Polaritons for Enhanced Glycerol Electro-Oxidation Reaction** Kyungwha Chung<sup>1,2</sup>, Yu Jin Jang<sup>1,2</sup>, Akira Baba<sup>4</sup>, Jianfang Wang<sup>3</sup> and Dong Ha Kim<sup>1</sup>; <sup>1</sup>Ewha Womans University, Seoul, Korea (the Republic of); <sup>2</sup>Department of Energy Science, Sungkyunkwan University, Suwon, Korea (the Republic of); <sup>3</sup>Chinese University of Hong Kong, Hong Kong, Hong Kong; <sup>4</sup>University of Niigata, Niigata, Japan.

Surface plasmon polaritons (SPPs), which can be observed from the metal films or the metal gratings, dissipate only through non-radiative decay, whereas localized surface plasmons (LSPs) in metal nanostructures decay via either radiative or non-radiative relaxation processes. The non-radiative decay of plasmonic energy can generate hot electrons, which possess higher energy than Fermi level. Plasmonic hot carriers are promising for applications in optoelectronics, plasmonics and energy conversion. However, plasmonic hot carrier generation was mostly carried out in metal nanostructures supporting LSPR modes, while very few works were reported with SPPs. In this work, surface plasmon resonance (SPR)-enhanced hot-carrier generation was demonstrated for a model electrocatalytic reaction in Kretschmann configuration. SPR coupling was employed to overcome the low efficiency of thin film-based photon-to-carrier conversion. Arrays of Au nanobipyramids decorated with Pt nanoparticles (AuNBPs@AgPt) were introduced on Au film surfaces to form the nanoparticle-on-mirror (NPoM) geometry and the performance for the glycerol electro-oxidation reaction exhibited ~2.5 times improved photocurrent evolution under illumination of p-polarized light compared with the activity based on the neat Au film with the photon-to-hot carrier conversion efficiency of  $2.4 \times 10^{-3}$  %. The results obtained in this study may pave a way to provide new opportunities for the SPP-driven energy conversion applications for electro-/photocatalysis and redox species-mediated optical sensing.

#### NM02.10.41

**Dehydration Sensing of a Polymer Film via Plasmonic Nanoparticles** Milana Lisunova<sup>1,2</sup>; <sup>1</sup>Ralph E. Martin Department of Chemical Engineering, UARK, Fayetteville, Arkansas, United States; <sup>2</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States.

It is well known that plasmonic nanoparticles possess a high sensitivity to the refractive index sensitivity of the surrounding medium. Such capabilities already widely explored in bio-plasmonic detectors to sense adsorption events. The high refractive index sensitivity allows to utilize plasmonic nanoparticles to distinguish hazardous solvents vapor from the water vapor.

However, the hydration/dehydration sensing by plasmonic nanoparticles which detect water molecules absorption/desorption by soft matter has not been introduced yet. The dehydration sensing of the soft matter is of a particular interest due to the difficulties of the utilization standard techniques in characterization dehydration process of the ultra-thin films or their complexity and extremely high cost. Therefore the development novel approach to control water molecules desorption seems a great challenge. Moreover, the non-traditional method of the water molecules absorption/desorption studies in soft matter to simulate tissue are required.

Among prospective candidates for the refractive index sensitivity by plasmonic nanoparticles are relatively new type materials such as plasmonic nanocages (NCs) which possess the ultra-high refractive index sensitivity of ~1000 nm/RIU. Such high refractive index sensitivity by NCs allows to distinguish a minor changes in refractive index of about 0.01 RIU to 0.001 RIU.

The aim of the research is on the elucidation of the applicability of the refractive index sensitivity of the plasmonic NCs in evaluation dehydration of the ultrathin transparent polymer films, such as poly(vinyl alcohol) (PVA). The PVA has been chosen because of the wide applicability in biomedical field due to the non-toxicity and biocompatibility, better film and fiber forming, excellent chemical resistance and water solubility.

The study is the first to examine the dehydration kinetic of the free standing films based on PVA via refractive index sensitivity of the NCs. Unlike well-studied plasmonic substrates which allows to research *adsorption* molecules on the surface, the incorporation plasmonic nanoparticles between the polymer layers, polymer/NCs/polymer, allows to research water molecules *absorption* which involves whole volume of the film. The utilizing nanoparticles allows to estimate rate and time of polymer film hydration/dehydration. For instance, the NCs introduced to polymer with 2 μm thickness of each layer possess

the dehydration time of about 180 (s), dehydration rate  $\sim 0.22$  (vol% per s) and dehydration rate constant  $\sim 50 \times 10^{-4}$  ( $s^{-1}$ ).

The work was supported by the University of Arkansas Foundation. I thank Jingyi Chen and Samir V. Jenkins for synthesis of the plasmonic bimetallic nanocages and Nano Bio Photonics group (nbphotonics.uark.edu). The initial research was performed under supervision of Prof. Mostafa El'Sayed and Dr. Mahmoud Mahmoud at GATECH supported by U.S. Department of Energy, Office of Basic Energy Sciences under award # DE-FG02-09ER46604.

#### NM02.10.42

**DNA-Coated Gold Nanoparticles for the Detection of mRNA *In Vivo* Within Hydra Vulgaris Animals** Maria Elena Kyriazis<sup>1</sup>, Maria Moros<sup>4</sup>, Afaf El-Sagheer<sup>3</sup>, Tom Brown<sup>3</sup>, Claudia Tortiglione<sup>2</sup> and Antonios Kanaras<sup>1</sup>; <sup>1</sup>University of Southampton, Southampton, United Kingdom; <sup>2</sup>Istituto di Cibernetica "E Caianiello", Pozzuoli, Italy; <sup>3</sup>University of Oxford, Oxford, United Kingdom; <sup>4</sup>University of Zaragoza, Zaragoza, Spain.

The ability to detect and monitor biomolecules such as mRNA in live cells has been shown to be of great importance. For example, changes in mRNA expression levels in individual cells have been associated with the development of diseases such as cancer. Common detection strategies are often based on real-time polymerase chain reaction, microarray analysis or in situ hybridisation. However, promising developments have been made by associating nucleic acids with gold nanoparticles (AuNPs) creating a so-called spherical nucleic acid (SNA). These systems have been shown to successfully penetrate the cell membrane without the aid of transfection agents and resist nuclease degradation. When hybridised to fluorophore complements, DNA-coated AuNPs have shown great promise at visualising mRNA in living cells as they exhibit high signalling and have low background fluorescence. Nevertheless, there is less work associated with the use of such systems in a more complex *in vivo* environment.

In this study we demonstrate the targeted detection of mRNA using DNA-coated AuNPs in the freshwater polyp *Hydra vulgaris*. Hydra, an invertebrate model that has been thoroughly used in nanomedicine is found at the base of metazoan evolution and presents an intermediate complexity between cell cultures and vertebrates. We show the biocompatibility of DNA-coated AuNPs upon incubation with live animals and specifically focus on selectively imaging Hymc1 mRNA, whose downregulation is found to be associated with the progression of common cancers. We demonstrate how a precise and recognisable fluorescent pattern can be observed, which mirrors the expected Hymc1 expression pattern thus indicating high levels of specificity. However, target specificity is also demonstrated *via* the use of DNA-coated AuNPs for the detection of mRNA that is not expressed within Hydra where a fluorescent signal is significantly absent. Ultimately this research aims to expand our knowledge on the behaviour of the aforementioned systems within live animals in order to further optimise and develop it into a system that could successfully combine efficient mRNA sensing and targeted drug delivery within an *in vivo* environment.

#### NM02.10.43

**Revisiting Design of Upconverting Nanoparticles for Efficiency and Lasing** Bruce E. Cohen; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Multiphoton imaging techniques that convert low energy excitation to higher energy emission are widely used to improve signal over background, reduce scatter in subsurface imaging, and limit sample photodamage. Multiphoton imaging relies on luminescent probes able to efficiently sum the energies of 2 or more incident photons, as well as lasers powerful enough for multiphoton excitation. Lanthanide-doped upconverting nanoparticles have proven to be among the most efficient multiphoton probes, but even UCNP with optimized lanthanide dopant levels require laser intensities that may be problematic for living systems. Here, we develop protein-sized, alloyed UCNP (*aUCNPs*) that can be imaged at the single particle level at laser intensities below 300 W/cm<sup>2</sup>, over 300-fold lower than needed for comparably-sized doped UCNP. Using single UCNP characterization and kinetic models of lanthanide energy transfer, we find that addition of inert epitaxial shells radically changes optimal lanthanide content from Yb<sup>3+</sup>, Er<sup>3+</sup>-doped NaYF<sub>4</sub> nanocrystals to fully alloyed compositions. At high levels of the emitter Er<sup>3+</sup>, these ions can adopt a second role to enhance the effective *aUCNP* absorption cross-section by desaturating sensitizer Yb<sup>3+</sup> or by absorbing photons directly. Core/shell *aUCNPs* are brighter than comparably sized doped UCNP at all laser intensities tested, over 4 orders of magnitude. Core/shell *aUCNPs* 12 nm in total diameter can be imaged with strong contrast (signal:background >25) through several millimeters of tissue in live mice using a laser intensity of just 0.1 W/cm<sup>2</sup>. *aUCNPs* open up the possibility of using both low irradiance and low-energy excitation wavelengths for non-destructive bioimaging experiments. Additional recent work about dye-sensitized UCNP emission and UCNP-based micron-sized lasers will also be discussed.

New work from:

Low irradiance multiphoton imaging with alloyed lanthanide nanocrystals. *Nature Communications* **9**, 3082 (2018).

Continuous-wave upconverting nanoparticle microlasers. *Nature Nanotechnology* **13**, 572-577 (2018).

Enrichment of molecular antenna triplets amplifies upconverting nanoparticle emission. *Nature Photonics* **12**, 402-407 (2018).

#### NM02.10.44

**Highly Porous Black Metals Formed by High-Pressure Thermal Evaporation** Jun Gi Min and Sangwoo Ryu; Kyonggi University, Suwon, Korea (the Republic of).

Vacuum thermal evaporation is one of the well-known deposition processes to form dense films of metals. In conventional thermal evaporation process, heterogeneous nucleation and growth of the evaporated metal species on the substrates are key mechanisms of the dense films. The evaporation method introduced in this presentation utilizes high pressure inside the vacuum chamber during the evaporation so that it causes repeated collisions of evaporated metal atoms with each other, which is led to homogeneous nucleation and growth before arriving at the substrates. This process results in the formation of nanoporous structures composed of nanoparticle aggregates of the parent metals. The porosity and the color of the porous metals varies depending on the working pressure of the background inert gas. The porosity estimated by the dimensions determined by the electron microscopy exceeds 95% and the obtained nanoporous structures absorbs almost all visible light showing black color. Herein, we present the details of this high-pressure thermal evaporation, examples of Au, Cu, Sn, and applications to chemical sensors or Li-ion batteries.

### 8:30 AM NM02.11.01

**Fabrication of Hollow Metal Nanoshapes by Solid State Dewetting and Oxidation of Al on Sapphire Substrate** [Nimrod Gazit](#)<sup>1</sup>, Gunther Richter<sup>2</sup>, Amit Sharma<sup>1</sup>, Leonid Klinger<sup>1</sup> and Eugen Rabkin<sup>1</sup>; <sup>1</sup>Technion-Israel Institute of Technology, Haifa, Israel; <sup>2</sup>Max Planck Institute for Intelligent Systems, Stuttgart, Germany.

The Al-Au couple is a classic example of a system in which the Kirkendall effect and Kirkendall porosity represent a major reason for failure in microelectronic devices. In this work we demonstrated that the Kirkendall effect during controlled oxidation of Al in the Al-Au core-shell nanoparticles can be utilized for the synthesis of hollow particles of the intermetallic phase.

We produced metallic nanoshapes by performing a solid state dewetting treatment of Al thin film deposited on sapphire substrate, followed by the deposition of thin Au layer on the top of dewetted sample. Annealing of the core-shell nanoparticles in air resulted in outdiffusion of Al from the particles, formation of pores, and growth of the AlAu<sub>2</sub> intermetallic phase in the particles. We demonstrated that the driving force for hollowing is the oxidation reaction of the Al atoms at the Au-sapphire interface, leading to the homoepitaxial growth of newly formed alumina at the interface. We developed a kinetic model of hollowing controlled by diffusion of oxygen through the Au thin film, and estimated the solubility of oxygen in solid Au.

### 8:45 AM NM02.11.02

**Nanoparticle Megalibraries—Expanding the Materials Genome Through Size** [Edward J. Kluender](#)<sup>1</sup>, James L. Hedrick<sup>3</sup>, Rahul Rao<sup>2</sup>, Benji Maruyama<sup>2</sup> and Chad A. Mirkin<sup>4</sup>; <sup>1</sup>Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States; <sup>2</sup>Air Force Research Laboratory, WPAFB, Ohio, United States; <sup>3</sup>Chemical Engineering, Northwestern University, Evanston, Illinois, United States; <sup>4</sup>Chemistry, Northwestern University, Evanston, Illinois, United States.

The nanomaterial landscape is so vast that a combinatorial approach, with complex parameter inputs, is required to fully understand the underlying structure-function relationships. To address this challenge, a new approach for the synthesis and screening of megalibraries of unique nanoscale features (>10 million features) with tailorable location, size, and composition has been developed. Polymer pen lithography, a massively parallel scanning probe lithographic technique, is combined with a novel method for spray-coating the pen array with gradients of inks such that each pen in the array has a different, but deliberately chosen, quantity and composition of ink. With this technique, gradients of Au-Cu bimetallic nanoparticles have been synthesized on SiO<sub>2</sub> micropillars, and then screened for activity by *in situ* Raman spectroscopy with respect to single-walled carbon nanotube growth (SWNT) via chemical vapor deposition. Through this methodology, Au<sub>3</sub>Cu, a structure not previously known to catalyze SWNT growth, has been identified as the most active composition.

### 9:00 AM NM02.11.03

**High Density Ag Nanoparticle Clusters for High Sensitive SERS Substrate** [Han Lu](#) and Mingliang Jin; South China Academy of Advanced Optoelectronics, South China Normal University, GuangZhou, China.

Surface-enhanced Raman scattering (SERS) is a powerful analytical tool for sensitive detection of chemical[1] and biological molecules[2] even allowing the single-molecule detection[3]. The nanoparticle clusters (paired, trimers, tetramers and linear chains) has emerged as one of the most efficient and widely used configurations in studies involving surface-enhanced phenomena, producing intense electromagnetic fields in the interstices of a reasonably simple structure. Numerous methods have been developed to fabricate nanoparticle clusters in the past few decades, including evaporative self-assembly[4], surface modification[5], template-guided assembly[6] and light-directed assembly[7]. However, these methods are time-consuming and expensive. Thus, it is a challenge to fabricate a simple and cheap nanoparticle clusters for a surface enhance Raman spectroscopy (SERS) substrate with high sensitivity to detect single-molecules and excellent reproducibility and stability of signal. In this work, we introduce a simple method that generates Ag nanoparticle clusters for SERS substrate with high sensitivity and excellent reproducibility based on galvanic reaction in one step without any additional assembly steps. We systematically investigated the effect of the concentration of cetyltrimethylammonium bromide (CTAB), reaction time and temperature on the morphologies of Ag nanostructure. Fig.1a shows the SEM images of Ag nanoparticle clusters. Fig.1b-c shows the SERS spectra of  $1 \times 10^{-16}$  M R6G aqueous solution and  $1 \times 10^{-10}$  M L-Phenylalanine solution respectively, in which the main vibrational features of R6G molecules and L-Phenylalanine molecules are clearly observed, which reveals excellent Raman sensitivity in the Ag nanoclusters SERS substrate. The Ag nanoparticle clusters may serve as high sensitivity SERS substrate for wide-ranging applications in single-molecule detection and molecule diagnostics.

### 9:15 AM NM02.11.04

**Holistic Structural Hierarchy in Metal Nanoparticle Composite Superlattices** [Robert J. Macfarlane](#); Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Structural hierarchy is a powerful design concept where specific geometric motifs are used to influence material structure across multiple size regimes. These complex levels of organization are typically achieved in the laboratory by conceptually breaking a material down into the smallest components that can be manipulated (e.g. individual molecules, macromolecules, or nanoparticles), and using the geometric information in those components to control how they build up into larger length scale patterns. Conversely, complex assemblies in natural systems are commonly achieved through a more holistic approach where assembly behaviors at the molecular, nano, and macroscopic scales are interlinked. This means that not only does structural information contained in molecular building blocks filter upwards to dictate material form at the nano to macroscopic levels, but also that the environment created by the larger length scale features can affect the behavior of individual components. Despite the potential of such a method of materials design, our ability to mimic these natural processes and holistically program structural hierarchy in artificial materials is still severely underdeveloped. Here, we demonstrate a metal nanoparticle-based building block that enables nanoscale geometry to function as a design handle to directly modulate the assembly behavior of a collection of supramolecular binding groups. The ability to use nanoscale geometry to modify molecular behavior allows a single set of nanoparticles to access different nanoscale bonding valencies, resulting in different mesoscale particle arrangements and different supramolecular bond strengths. The formation of distinct hierarchical structures at the nano and mesoscale is therefore both a consequence of and a direct influence on the molecular binding events that drive assembly. The use of nanoscale geometry to dictate supramolecular binding provides a major step forward in understanding how the assembly of hierarchically ordered artificial materials can be done in a holistic manner across multiple size regimes.

### 9:30 AM NM02.11.05

**Nanostructured Hybrid Metal-Polymer Nanoparticle Systems and Continuous Flow Chemistry Synthesis** [Rigoberto C. Advincula](#); Case Western Reserve University, Cleveland, Ohio, United States.

The synthesis of various hybrid metal-polymer nanomaterials pre-supposes the ability to utilize various synthetic approaches based on topologically exact dendrimers (and star copolymers) and their ability to surround the metal as stabilizing ligands. For the polymer component, the use of macroinitiators and

macromonomers enable the synthesis of the various block copolymer and miktoarm systems that can surround the metal nanoparticles core. In dendrimers, this can be based on convergent and divergent approaches of carefully designed AB<sub>2</sub> monomers to dendrons that can be linked. In this work, we outline and demonstrate the use of various dendrimer and polymer synthons to form hybrid nanoparticle systems. We also describe the use of continuous flow chemistry fabrication methods at the bench scale to produce metal nanoparticles and atomic clusters resulting in higher throughput synthesis and better distribution. We describe control of the metal nanoparticle synthesis parameters based on pressure, temperature, flow rate and mixing ratios. The grafting on surfaces and electropolymerization methods enable us to apply these nanomaterials hybrid into electron and charge transfer properties. These materials have the potential for use in catalysis. Also, a key to the analysis of such materials is the use of surface sensitive analytical methods as well as microscopy imaging methods.

#### 9:45 AM NM02.11.06

**Fabricating Ultra-Low-Density Nanoporous Metals by Freeze-Casting Nanowire Suspensions** Alyssa L. Troksa, Tyler M. Fears, Fang Qian, Tom Braun, Anna Ringuette, Joshua A. Hammons, Michael Nielsen, Jean-Baptiste Forien, Theodore Baumann, T. Yong Han, Sergei Kucheyev and Michael Bagge-Hansen; Lawrence Livermore National Laboratory, Livermore, California, United States.

Ultra-low-density (1-30 mg/cm<sup>3</sup>) nanowire aerogels are a new class of monolithic nanoporous materials with potential applications in energy storage, generation, and utilization. These materials can be fabricated by freezing suspensions of metal nanowires and gently removing the solidified matrix, e.g., via freeze-drying, to prevent collapse of the porous nanowire network. As such, the macroscopic properties of the final aerogels are intrinsically linked to the composition of the feedstock suspensions, namely solvent composition, nanowire dimensions, and surface ligands. Herein will be discussed recent developments at Lawrence Livermore National Laboratory to produce high-quality ultra-low-density metal (Cu, Ag, Au) aerogels with ligaments of controlled diameter between 5 and 30 nm via a facile freeze-casting approach. We will demonstrate how the modification of suspension characteristics can be used to tune the final mechanical, electrical, and chemical properties of the aerogels. This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

#### 10:00 AM BREAK

#### 10:30 AM NM02.11.07

**Bias-Dependent Chemical Enhancement and Non-Classical Stark Effect in Tip-Enhanced Raman Spectromicroscopy of CO-Terminated Ag Tips** Rebecca Gieseking<sup>1,2</sup>, Joonhee Lee<sup>3</sup>, Vartkess Apkarian<sup>3</sup> and George Schatz<sup>2</sup>; <sup>1</sup>Department of Chemistry, Brandeis University, Waltham, Massachusetts, United States; <sup>2</sup>Department of Chemistry, Northwestern University, Evanston, Illinois, United States; <sup>3</sup>University of California, Irvine, Irvine, California, United States.

Tip-enhanced Raman spectromicroscopy (TERS) with CO-terminated plasmonic tips can probe Ångstrom-scale features of molecules on surfaces. The development of this technique requires understanding of how chemical environments affect the CO vibrational frequency and TERS intensity. At the scanning tunneling microscope junction of a CO-terminated Ag tip, we show that rather than the classical vibrational Stark effect, the large bias dependence of the CO frequency shift is due to ground-state charge transfer from the Ag tip into the CO  $\pi^*$  orbital softening the C-O bond at more positive biases. The associated increase in Raman intensity is attributed to a bias-dependent chemical enhancement effect, where a positive bias tunes a charge-transfer excited state close to resonance with the Ag plasmon. This change in Raman intensity is contrary to what would be expected based on changes in the tilt angle of the CO molecule with bias, demonstrating that the Raman intensity is dominated by electronic rather than geometric effects.

#### 10:45 AM NM02.11.08

**Ion-Implanted Silver Nanoparticles for Metal-Enhanced Fluorescence** Shahid Iqbal, Masoud Shabaninezhad, Mohammad Hatshan, Prashant Niraula, Ramakrishna Guda and Asghar Kayani; Western Michigan University, Kalamazoo, Michigan, United States.

Metal Enhanced Fluorescence (MEF) has promising applications in the field of optical displays, bio-sensing and photodynamic therapy. In this work, we exploit the plasmons of embedded silver nanoparticles (Ag-NPs) fabricated by ion implantation to enhance the fluorescence of Coumarin 515 dye (C515) via MEF. Ion Implantation of 70 keV Ag ions in quartz matrix at different fluences was carried out to synthesize Ag-NPs inside quartz matrix. The formation of Ag-NPs is characterized by the optical absorption measurements. Rutherford Backscattering Spectrometry (RBS) measurement was used to obtain the depth profile and concentration of silver within the substrate. From the RBS results, it was determined that front edge of the layer containing Ag was formed at an average depth of 16 nm below the surface, which closely agreed with Stopping and Range of Ions in Matter (SRIM) calculations. Increase in the size of the Ag-NPs is observed as the fluence of the silver within the substrate is increased. The MEF of drop casted C515 dye was studied using steady-state emission and excitation spectra measurements. Photoluminescence (PL) enhancement factor ranging from 1.2 to 2.1 with a maximum enhancement for the largest fluence was obtained. The observed MEF was ascribed to a combination of plasmon enhancement with larger nanoparticles due to increase in fluence and to increase plasmonic hot spots.

#### 11:00 AM NM02.11.09

**Roughening Temperature of Facets in Au Electrodeposition** Nathan T. Nesbitt<sup>1</sup>, Samantha Jaszewski<sup>2</sup>, Ming Ma<sup>1</sup>, Bartek Trzesniewski<sup>1</sup>, Fazel Fallah Tafti<sup>2</sup>, Michael Burns<sup>2</sup>, Michael J. Naughton<sup>2</sup> and Wilson Smith<sup>1</sup>; <sup>1</sup>TU Delft, Delft, Netherlands; <sup>2</sup>Physics, Boston College, Chestnut Hill, Massachusetts, United States.

A theory has been established to describe the formation of facets on metal crystals grown from their melt. There exists a temperature for each crystallographic orientation below which it will form a facet, and above which the metal surface will be rounded and atomically rough. Here we have extended this theory to electrodeposition. We used potentiostatic electrochemical impedance spectroscopy to measure the approximate surface energy of Au at different applied potentials to determine the roughening temperature for each potential. From this, we grew different nanostructures with different proportions of facets and tested them as electrocatalysts for CO<sub>2</sub> reduction.

#### 11:15 AM NM02.11.10

**Modelling of Surface Atomic Arrangements of Bimetallic Nanoparticles** Kayoung Yun<sup>1</sup>, Ho-Seok Nam<sup>2</sup> and Seungchul Kim<sup>1</sup>; <sup>1</sup>Korea Institute of Science and Technology, Seoul, Korea (the Republic of); <sup>2</sup>Kookmin University, Seoul, Korea (the Republic of).

With increasing worldwide demands for green energy, catalyst engineering has rapidly developed for several decades. Noble metals such as platinum (Pt) show outstanding catalytic activity and stability in various energy production/conversion techniques. However, high cost of the noble metal catalysts disturbs growth of energy industry. Bimetallic nanoparticles are emerging as low-cost but high-efficiency catalysts. Catalytic reactions only occur on the surface of nanoparticles, therefore, it is essential to understand surface morphology and atomic arrangements of alloy nanoparticles in order to improve their catalytic properties. In this study, we predicted energetically stable atomic arrangements on the surface and shape of different bimetallic nanoparticles

such as Au-Pt, Cu-Pt, and Pd-Pt by Monte Carlo (MC) and molecular dynamics simulations. These works provide phase diagrams of the bimetallic nanoparticles in terms of size, shape, atomic composition and temperature of the system. Also, the trends in mixing patterns of alloy nanoparticles are discussed with regard to difference of binding energies between two elements.

SESSION NM02.12: Hot Topics II  
Session Chairs: De-en Jiang and Mika Pettersson  
Thursday Afternoon, November 29, 2018  
Sheraton, 2nd Floor, Constitution A

#### 1:30 PM NM02.12.01

**Controlling Nanoparticle Dimensions and Shapes Through Microreactor Flowrate Manipulations** Joshua S. Santana and Sara E. Skrabalak; Chemistry, Indiana University, Bloomington, Indiana, United States.

Droplet-based reactors for nanoparticles are receiving attention due to their ability to maintain thermal and compositional equilibrium within and between droplets, enabling flow operations for inline analyses and the scale-up of nanomaterial syntheses. This presentation will show the versatility of these microreactors by synthesizing different dimension-controlled and shape-controlled nanostructures through manipulation of the relative flow rates of reagent stock solutions. Specifically, different Pd shell thicknesses can be grown on cubic or octahedral Au seeds. In addition, Au-Pd nanocrystal shapes ranging from sharp-branched octopods to core@shell octahedra can be controlled using seed-mediated co-reduction on Au octahedral seeds. This approach allows process conditions to be modified inline, rather than from batch to batch, to achieve particles with different shell thicknesses and shapes, and this procedure should be applicable to other multicomponent systems.

#### 1:45 PM NM02.12.02

**Selective Control of Crystal Structure in Solid-Solution Alloy—fcc and hcp Phases in Au–Ru Nanoparticles** Quan Zhang<sup>1</sup>, Kohei Kusada<sup>1</sup>, Dongshuang Wu<sup>1</sup>, Tomokazu Yamamoto<sup>2</sup>, Syo Matsumura<sup>2</sup>, Yoshiki Kubota<sup>3</sup> and Hiroshi Kitagawa<sup>1</sup>; <sup>1</sup>Chemistry, Kyoto University, Kyoto, Japan; <sup>2</sup>Kyushu University, Fukuoka, Japan; <sup>3</sup>Osaka Prefecture University, Osaka, Japan.

The crystal structure is one of the most dominant factors that strongly affect the properties of an alloy because its electronic and surface structures change drastically with the crystal structure. A solid-solution alloy, in which the constituent atoms are randomly and homogeneously mixed at the atomic scale, generally adopts one of three principal crystal lattice forms: body-centred cubic (bcc), hexagonal close-packed (hcp) and face-centred cubic (fcc) structures. However, once its constituent elements and composition are fixed, the crystal structure of the alloy is uniquely determined. Therefore, it is difficult to change the crystal structure of a solid-solution alloy at a certain composition.

Here, we propose a new approach for selective control of the crystal structure in solid-solution alloys by using a chemical reduction method. By precisely tuning the reduction speed of the metal precursors, we demonstrated the first example of selective control by synthesizing fcc- and hcp-AuRu<sub>2</sub> alloy nanoparticles (NPs).<sup>1</sup> The alloy adopts an fcc structure when the Au precursor starts to be reduced slightly earlier, while it adopts an hcp structure when the reduction of Ru precursor begins slightly earlier. The structures of the obtained NPs were investigated using synchrotron powder X-ray diffraction analysis and atomic resolution scanning transmission electron microscopy (STEM). The mechanism of crystal structure control is discussed by using the results of UV-Vis spectral and electrochemical analyses. The influence of crystal structure on the catalytic performance for oxygen evolution reaction (OER) was also examined.<sup>2</sup> The alloy with hcp structure shows much improved durability in acid solution compared to the fcc one.

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#### 2:00 PM NM02.12.03

**In Situ Nucleation Mechanism of the Nanometer-Sized Precipitates of the AA7050 Aluminium Alloy** TsaiFu Chung<sup>1</sup>, Yang Yo-Lun<sup>3</sup>, Hsiao Chien-Nan<sup>2</sup>, Li Wei-Chih<sup>4</sup> and Yang Jer-Ren<sup>1</sup>; <sup>1</sup>National Taiwan University, Taipei, Taiwan; <sup>2</sup>Instrument Technology Research Center, National Applied Research Lab, Hsinchu, Taiwan; <sup>3</sup>Department of Mechanical Engineering, Imperial College London, London, United Kingdom; <sup>4</sup>E.A. Fischione Instruments, Inc., Pittsburgh, Pennsylvania, United States.

Cs-corrected high-angle-annular-dark-field scanning-transmission-electron microscopy (Cs-corrected HAADF-STEM) with nanometer-scale energy-dispersive X-ray (EDX) was employed to investigate the transformation mechanisms of the  $\eta'$   $\rightarrow$   $\eta$  precipitation sequence of AA7050, an Al-Zn-Mg-Cu alloy. Evidence from Cs-corrected HAADF-STEM coupled with EDX showed that in-situ nucleation of a new  $\eta_2$  precipitate (one form of  $\eta$ ) took place, wherein it gradually developed from the original  $\eta'$  precipitate via a similar hexagonal structure with different compositions. The in-situ transition product was composed of two distinctive regions; one was identified as  $\eta'$ , and the other, as  $\eta$ .

#### 2:15 PM NM02.12.04

**Mono- and Bimetallic Nanoparticles of Noble Metals—The Influence of the Composition and Nanostructure on Biological Effects** Alexander Rostek<sup>1</sup>, Marina Breisch<sup>2</sup>, Kateryna Loza<sup>1</sup>, Kevin Pappert<sup>1</sup>, Viktoria Grasmik<sup>1</sup>, Marc Heggen<sup>3</sup>, Manfred Köller<sup>2</sup>, Christina Sengstock<sup>2</sup> and Matthias Eppler<sup>1</sup>; <sup>1</sup>Inorganic Chemistry and Center for Nanointegration Duisburg-Essen (CeNIDE), University of Duisburg-Essen, Essen, Germany; <sup>2</sup>Bergmannsheil University Hospital/Surgical Research, Ruhr-University Bochum, Bochum, Germany; <sup>3</sup>Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich GmbH, Jülich, Germany.

Metallic nanoparticles represent a well-established field of nanoscience, medicine, catalysis, and industry. Due to the numerous applications, a contact with biological systems is unavoidable. Depending on the nanoparticles' characteristics, the biological response can be rather different. Therefore, a detailed investigation of the structure and composition of monometallic, alloyed, and core-shell nanoparticles is a decisive factor for the assessment of biological effects. In addition to colloid-chemical and spectroscopic methods for the characterisation of nanoparticle dispersions, high-resolution (HR)TEM and scanning transmission electron microscopy (STEM) are advantageous to elucidate size, crystal structure (e.g. domains), and internal composition of mono- and bimetallic nanoparticles.

Spherical Rh, Pd, Pt, Ag, Au, and bimetallic (alloy, core-shell) nanoparticles (5-10 nm) were wet-chemically prepared, stabilised with poly(N-vinylpyrrolidone) and characterised by colloid-chemical and spectroscopic methods. Particle diameters as determined by analytical disc centrifugation and

dynamic light scattering correspond very well to the results obtained by HRTEM. The overall elemental composition was determined by atomic absorption spectroscopy and X-ray powder diffraction. The nanostructure and elemental distribution was assessed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDX).

The biological studies comprised the analysis of the antimicrobial activity against gram-positive and gram-negative bacteria as well as the biocompatibility towards human mesenchymal stem cells (hMSC). Silver-containing nanoparticles with a high silver content showed a significant concentration- and time-dependent antimicrobial effect against *S. aureus* and *E. coli* as well as a toxicity towards hMSC. The other metals showed neither an antimicrobial effect nor a toxicity against hMSC. Interestingly, Rh, Pt and AgPt ( $\geq 50\%$  Pt) nanoparticles led to a nodule-like convergence of hMSC indicating a cell activation.

### 2:30 PM NM02.12.05

**Chiro-magnetic Nanoparticles and Gels** [Jihyeon Yeom](#)<sup>3</sup>, Andre F. de Moura<sup>2</sup> and Nicholas A. Kotov<sup>1</sup>; <sup>1</sup>University of Michigan, Ann Arbor, Michigan, United States; <sup>2</sup>Federal University of São Carlos, São Carlos, Brazil; <sup>3</sup>Massachusetts Institute of Technology, Boston, Massachusetts, United States.

The manipulation of chiroptical effects using a magnetic field is one of the ubiquitous interplays of chirality and magnetism. Ceramics such as transition metal oxides are intriguing in this regard, since many useful magnetooptical properties involve electric and magnetic transitions to amplify or modulate the chiroptical activities of the system. Here we synthesized chiral magnetic nanoparticles (NPs) using cobalt to investigate the enhancement of the rotatory optical activity and magnetic field modulations. The obtained NPs showed g-factors as high as 0.02 and strong optical rotation in the visible range that is at least 10 times higher than conventional chiral metal or semiconducting NPs. It was also possible to observe an increase of light transparency in the UV region with an external magnetic field. The chiral ceramic NPs prepared herein are versatile and fundamental experimental systems for potential application in chiroptical and magnetooptical devices, as well as for the investigation of (up to second-order) magneto-chiral and magneto-dielectric effects.

### 2:45 PM NM02.12.06

**Near-Infrared Fluorescent Metal Nanoclusters for the Gene Delivery and Bioimaging** [Yuanqing Sun](#), Yiming Ouyang, Jiaqing Luo and Jian Liu; College of Science, China University of Petroleum, Beijing, Beijing, China.

We synthesized tunable near-infrared fluorescent gold nanoclusters (AuNCs) protected by branched polyethylenimine (PEI) modified by surface segmental attachment of sulfhydryl groups (PEI-SH). The cationic polymer PEI-SH with positive charges enables AuNCs to perform gene delivery, and the gene transfection efficiency can reach 22.8%. Moreover, the fluorescence of AuNCs is tunable from visible red light (wavelength 609 nm) to NIR light (wavelength 811 nm) with high quantum yields, which is very suitable for bioimaging. To obtain nanomaterials with longer fluorescent wavelength in near-infrared region (NIR), we introduced Cu element into system to prepare Au/Cu alloy nanoclusters, which possessed the second near-infrared region (NIR-II) fluorescence emission at 1080 nm. The Au/Cu alloy nanoclusters exhibit high quantum yields (~2%), which are 5 times higher than that of the commercial carbon nanotube. More interesting, Au/Cu alloy nanoclusters show tunable luminescence from NIR-I (811 nm) to NIR-II (1130 nm) corresponding to increasing the content Cu element in the nanoclusters. The Au/Cu alloy nanoclusters with high photoluminescence intensity, good fluorescence stability and low cytotoxicity can be used as an excellent NIR-II fluorescent probe for potential applications in the field of *in vivo* NIR-II fluorescent imaging.

### 3:00 PM BREAK

### 3:30 PM NM02.12.07

**Thermomechanical Nanomolding of Crystalline Metals—The Smaller the Easier** [Jan Schroers](#)<sup>1</sup> and Ze Liu<sup>2</sup>; <sup>1</sup>Yale University, New Haven, Connecticut, United States; <sup>2</sup>Wuhan University of Technology, Wuhan, China.

Molding, associated with a materials flow-ability, becomes increasingly more difficult with decreasing mold size. The flow-ability of crystalline metals is usually much lower than that of thermoplastics, gels, and some glasses. As a consequence, attempts to mold on the nanoscale have been limited to thermoplastics, gels, and glasses, while crystalline metals have not been considered. Here, we report a thermomechanical nanomolding method for crystalline metals which becomes easier, quantified by the ratio of mold depth to mold diameter, with decreasing mold diameter. As the underlying diffusion mechanism is present in all metals and alloys, discovered nanomolding process provides a toolbox to shape essentially any metal and alloy into nanosize features. Technologically, this highly versatile and practical thermomechanical nanomolding technique offers a method to fabricate high-surface area metallic nanostructures which are impactful in diverse fields of applications including catalysts, sensors, photovoltaics, microelectronics, and plasmonics.

### 3:45 PM NM02.12.08

**3D Nano-Printing Technique Based on Ion-Assisted Aerosol Lithography** [Wooik Jung](#)<sup>1,2</sup>, Yoon-ho Jung<sup>1,2</sup>, Petro Pikhitsa<sup>2</sup> and Mansoo Choi<sup>1,2</sup>; <sup>1</sup>Seoul National University, Seoul, Korea (the Republic of); <sup>2</sup>A Global Frontier Center for Multiscale Energy Systems, Seoul, Korea (the Republic of).

On demand of miniaturization of 3D structure manufacturing following up the growth of nanodevice study, developing bottom-up based nanoparticle assembly technique has received attention. Establishing successful capability of 3D structure is closely related to precise positioning of nanoscale elements into 3D structures. We have developed Ion assisted aerosol lithography (IAAL) for charged metal nanoparticles assembly, making it possible to deposit nanoparticles to the desired location. IAAL utilizes the distorted local electric field induced by accumulated ions on a pre-patterned substrate to manipulate the trajectory of charged metal nanoparticles as they get attracted to the substrate by electrostatic attraction. The distorted electric field has brought the technique into nanoscale structures even though openings of aperture size is only a few micrometers. (Kim et al., 2006; Lee et al., 2010; Choi et al., 2015.) Based on this technique, replacing pre-patterned substrate to installing dielectric mask floated few micrometers from the substrate, it is possible to design versatile 3D nanoparticle structures shape by substrate trajectory.

Building upon this, novel 3D nano-printing technique based on IAAL is found in two different process types '3D writing' and '3D growth' depending on the horizontal substrate translation speed. To deposit nanoparticles beside the existing nanoclusters, horizontal translation speed of 3D writing mode is faster than 3D growth mode. In 3D writing mode, movement of substrate function as pen, as a meaning of writing material to the substrate in 2D form. Interestingly, repeating substrate movement along given trajectory leads to 2D form into 3D structures. In '3D growth' mode, fine-tuning of horizontal speed of substrate enables structures to have various slanted pillar shapes even over right angle. Adjusting substrate movement to the vertical growth rate of structures can assemble high aspect ratio nanowires. Furthermore, it is possible to create complex structures such as helices by precise control of substrate movement.

This direct 3D nano-printing technique, which utilizes the charged metal nanoparticles as building blocks, has an ability to depositing various materials. Manufacturing various shapes of multicomponent 3D metal nanostructures is relative ease for demanding applications.

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#### 4:00 PM NM02.12.09

**Covalent Surface Functionalization of Ultrasmall Gold Nanoparticles (2 nm) by Click Chemistry for Protein Targeting** Selina B. van der Meer<sup>1</sup>, Kateryna Loza<sup>1</sup>, Christine Beuck<sup>2</sup>, Peter Bayer<sup>2</sup> and Matthias Eppele<sup>1</sup>; <sup>1</sup>Inorganic Chemistry and Center for Nanointegration Duisburg-Essen (CeNIDE), University of Duisburg-Essen, Essen, Germany; <sup>2</sup>Department of Structural and Medicinal Biochemistry, University of Duisburg-Essen, Essen, Germany.

Ultrasmall gold nanoparticles of 2 nm diameter are smaller than most proteins and therefore should allow a specific epitope targeting on a protein surface. Thereby, the conformation and the function of a protein can be manipulated.<sup>1</sup> A surface functionalization of the gold nanoparticle with azide groups and a subsequent click reaction, i.e. a copper-catalyzed azide-alkyne (CuAAC) cycloaddition, permits an orthogonal covalent conjugation under mild conditions.<sup>2</sup> Azide-terminated ultrasmall nanoparticles were prepared by reducing tetrachloroauric acid in the presence of an azide-carrying cysteine-containing tripeptide.<sup>3</sup> Functional molecules with an alkyne function were covalently attached to the particles by CuAAC click chemistry. The hydrodynamic diameter of the functionalized gold nanoparticles was measured by diffusion ordered NMR spectroscopy (DOSY), also ensuring the absence of dissolved molecular impurities or reaction by-products.<sup>4</sup> Disc centrifugal sedimentation (DCS) and transmission electron microscopy (TEM) showed the dispersion state of the nanoparticles and the diameter of the metallic core. Atomic absorption spectroscopy (AAS) gave the gold concentration and allowed us to compute the particle number concentration. <sup>1</sup>H-<sup>1</sup>H-TOCSY NMR spectroscopy showed the binding between the gold surface and the cysteine of the tripeptide. The successful click reaction to the azide-functionalized gold nanoparticles was demonstrated by DOSY with propargylglycine as model compound clicked to the gold nanoparticle surface. This synthetic route offers a wide range for the synthesis of covalently functionalized ultrasmall gold nanoparticles for protein targeting.

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#### 4:15 PM NM02.12.11

**Role of the Internal Interface in the Equilibrium Shape of Metal Fe-Au Core-Shell Nanoclusters** Marie-Jose Casanove, Segolene Combettes, Patrizio Benzo, Beatrice Pecassou and Magali Benoit; CNRS, Centre d'Élaboration des Matériaux et d'Études Structurales, Toulouse, France.

Whereas the equilibrium shape of a metallic nanocrystal can be predicted by the Wulff construction, it can hardly be anticipated when this nanocrystal is covered by a shell formed of another metal. Different parameters are well known for their influence on the geometry of core-shell nanocrystals; these are, for instance, the size of the nanocrystals or the core / shell volume ratio. However, the construction of a metal-metal internal interface during the growth process should also play a determining role.

In order to analyze this mechanism, we choose to combine experimental and modeling approaches. Nanoclusters are experimentally grown using a ultra-high vacuum (UHV) physical vapor deposition method, magnetron sputtering, in order to limit interaction with their environment (gas, liquid, ligands...) during the growth process. This process makes it possible to use high temperatures which promote atomic diffusion during deposition or annealing steps. In addition, it is possible to proceed sequentially, by growing the shell on the previously formed core, or to proceed by co-deposition of the core and shell metals. The modeling approach combines DFT calculations with large-scale (MD) or Monte Carlo (MC) molecular dynamics simulations to study systems with size comparable to the experimentally grown nanocrystals (5-15 nm).

After a presentation of the different parameters that should be taken into account during the formation of the crystalline interface, with a particular emphasis on the concept of nanoepitaxy, we will report the results obtained on the Fe-Au system. This system is indeed of particular interest as it is likely to adopt a core-shell geometry fully compatible with applications in the biomedical field. Through our combined experimental and modeling results, we will then discuss the effects of size and composition on the equilibrium shape of the nanoclusters as well as the evolution of the iron core when coated by the gold shell.

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