SYMPOSIUM ET08

Emerging Materials and Characterization for Selective Catalysis
November 26 - November 29, 2018

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* Invited Paper

SESSION ET08.01: Catalytic Water Splitting
Session Chairs: Yugang Sun and Lianzhou Wang
Monday Morning, November 26, 2018
Hynes, Level 3, Room 306

8:30 AM *ET08.01.01
Elucidation of Electrocatalysis to Understand Photocatalytic Overall Water Splitting Kazuhiro Takanabe[1,2]; [1]The University of Tokyo, Toride, Japan; [2]King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

The climax of photocatalytic overall water splitting in powder suspension form is the simultaneous occurrence of electrocatalytic hydrogen evolution and oxygen evolution. In order for a semiconductor powder to achieve both reactions, the chemical potential at the surface should be shifted negatively and positively at the redox sites. It is however difficult to quantitatively describe such potentials of the powder suspension system. Knowledge transfer from electrocatalytic measurement to photocatalysis is effective to estimate the difficult-to-measure potentials of the photocatalytic system. This contribution discusses the effectiveness of electrocatalytic measurements to understand photocatalytic behavior, mainly focusing on hydrogen evolution catalysis and water-forming back reaction.
Successful photocatalytic overall water splitting is achievable when the water-forming back reaction from H_2 and O_2 to form H_2O does not prevail. Although decoration of hydrogen evolution catalysts on the semiconductor powder is often essential to achieve high photocatalytic efficiency, the same catalyst surfaces often introduce the thermodynamically-favorable back reaction. We show that the suppression of the back reaction is achievable when the semiconductor powder is decorated with highly dispersed noble metal catalysts, such as Pt species, with tungsten carbide nanoparticles, or with hydrogen-evolving catalysts covered with membrane-function layers, such as CrO_x, MoO_x, and SiO_x. To elucidate the catalytic rates for both forward (hydrogen evolution) and backward (water formation) reactions, electrocatalytic measurements are effectively utilized where the potential of the catalysts is determined.
In a similar way, the importance of electrolyte identity is evaluated mainly at near-neutral pH by effectively comparing electrocatalysis and photocatalysis. It is well accepted that buffering action is considered inevitable especially at high rates, but our elucidation pins down such effects quantitatively, dividing the functions into solution resistance, concentration overpotential, and kinetic contribution in a photocatalytic system. Such electrolyte engineering may lead to the discovery of new reaction environments for water electrolysis in more benign conditions and more towards membrane-less systems.

9:00 AM ET08.01.02
Comprehensive Kinetic Analysis of Photocatalytic Water Oxidation and Reduction at TiO₂ Surface Maning Liu[1] and Yasuhiro Tachibana[1,2]; [1]RMIT University, Bundoora, Victoria, Australia; [2]Osaka University, Osaka, Japan.

Solar water splitting is one of the most attractive energy generation reactions to utilize solar energy. Light generated hydrogen is clean energy source, since their consumption for energy generation produces only water. Moreover, it can be stored and used whenever required. Semiconductor TiO_2 is known as a photocatalyst and was investigated for solar water splitting reactions over the last several decades. TiO_2 has still been employed to assess the capability of photocatalysis reactions. The water splitting kinetic reaction mechanism at the TiO_2 surface has been elucidated, particularly employing transient absorption spectroscopy, however detailed understanding of the mechanism remains to be clarified.

In this presentation, we will demonstrate quantitative assessment of photocatalytic water splitting mechanism at the TiO_2 surface by employing a series of transient absorption spectroscopies covering from fs to 10 s over UV-VIS-NIR wavelength ranges. The reaction paths and their dynamics at the charge trap states will be discussed.

9:15 AM ET08.01.03
Understanding the Critical Role of P in Transition Metal Phosphide Catalysts—Achieving Pt-Like HER Performance Through Stoichiometric Variation in Co₂P, CoP and CoP₂ Dominique S. Itanze and Scott M. Geyer; Chemistry, Wake Forest University, Winston Salem, North Carolina, United States.

The developing of renewable fuel sources requires highly efficient and robust pathways to convert earth abundant resources into high energy fuels, as well

as efficient methods to convert the energy stored in chemical bonds into useable power. At each step of the fuel cycle, high performance catalysts are essential. Transition metal phosphides (TMP) have proven to be highly active and stable catalysts and are of great interest for the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR) and carbon dioxide reduction to hydrocarbon fuels. However, a detailed understanding of the role of phosphorous is still emerging, and even for the case of HER the performance has previously lagged behind that of the Pt benchmark.

We presented a detailed theoretical and experimental study in which we synthesize nanocrystalline CoP_x particles with highly uniform size, allowing a systematic comparison of performance. The phosphorous rich CoP and CoP_2 TMPs, as oppose to Co_2P, are highly effective and selective catalyst toward HER and ORR. In fact CoP_2 exhibits Pt-like performance at small overpotential of 39mV to achieve -10 mA/cm^{-2} and long term stability. The role of P in promoting catalysis must be understood by considering multiple effects: reducing the number of tightly bound multi-cobalt H adsorption sites, increasing the surface disorder, and increasing the Co-H bond length. We will present both data from our recent publication (*Adv. Mater.*2018, 30, 1705796) as well as our new results for high-performance CoP_2 HER catalysts. The conclusions drawn from this study will be highly relevant to the broader energy catalysis community, and the study of TMP catalysts in particular.

9:30 AM ET08.01.04
Defect-Engineered Interface Assembly for Efficient Electrocatalyst Kishwar Khan and Zhengtang Luo; Hong Kong University of Science & Technology, Kowloon, Hong Kong.

The expansion of economical, effective, and durable electrocatalysts for the oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER) have significant importance aimed at numerous electrochemical devices, such as fuel cells, water electrolyzer, and rechargeable metal-air batteries. Heteroatom-doped catalyst has arisen as one of the best emergent candidate to replace the metal based marketable catalyst for electrochemical reactions. But, their delicate structure parameters to optimize the catalytic capability, and atomic-level mechanistic understanding are still a challenging issue. Herein, we advocate the assembly of separate single atoms of Ni and Fe (SSAs-NiFe) dual sites, anchored in defects engineered graphene (DG) substrate prepared by a facile nitrogen (N) elimination procedure from an N-doped precursor by an adsorption-calcination strategy. The concept of defect mechanism, exhibited the topological defect (e.g. multiple pentagon—octagon—pentagon or pentagon—heptagon—pentagon rings) correspondingly appeared in carbon atoms combination that avoid dislocations and disclinations. We believe that these specific combination of carbon atom rings in defective substrate with the decoration of Ni and Fe SSAs can provide more active sites, better electrical conductivity, and lowest energy barier during catalytic reaction. We used the combination of high resolution transmission electron microscopy/high-angle annular dark field (HAADF) images established in scanning transmission electron microscopy (S/TEM) for studying the atomic structure of Ni and Fe isolated atoms on DG. At very low resolution (1nm) the individual atoms Ni and Fe in the field of view is detected through S/TEM, and resolved in graphene lattices. The electron energy loss spectroscopy (EELS) atomic spectra are used to identify the Ni/Fe SSAs in DG. The chemical insights structure of the material are examined by pre-edge peaks in X-rays absorption near edge structure (XANES) spectra. We demonstrated the electrocatalytic performance of SSAs-NiFe-DG hybrid material in acidic/alkaline mediums, and found it very active and stable trifunctional electrocatalyst for ORR, OER and HER. This work offers new prospects and underscores the importance of identifying the active species for multiple reactions catalysts and demonstrates how such knowledge can be applied to develop better multifunctional catalysts.

9:45 AM ET08.01.05
Carbon Nanodots as Efficient Photosensitizers for "Green" Solar Fuel Production Demetra S. Achilleos, Hatice Kasap and Erwin Reisner; Christian Doppler Laboratory for Sustainable SynGas Chemistry, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK., University of Cambridge, Cambridge, United Kingdom.

The accelerated consumption of fossil fuels and the emerging ecological concerns, due to the alarming concomitant rise in greenhouse gas emissions, emphasize the need for the society to move towards renewable "green" resources. Photocatalysis is a promising approach for mitigating simultaneously both the energy and environmental concerns, since it allows the storage of the abundant solar energy in high energy density fuels, such as H_2 (120 MJ/kg),[1] in benign aqueous media. However, the development of economically sustainable processes for this purpose, creates the pressing need for new photosensitizers and catalysts of low cost and toxicity, which however maintain substantial performances.

Carbon dots (CDs) can efficiently serve as photoabsorbers for this purpose since they fulfil all these requirements.[2-5] In particular, CDs are hydrophilic nanoparticles of low toxicity, which can be synthesized at low cost, are chemically and photochemically robust and show optimum photocatalytic properties upon pre-designed synthesis.[6,7] In this work, we focus on the synthesis of CDs from naturally abundant and inexpensive biopolymers of various compositions and nanoarchitectures, which bestow the derived photoabsorbers with distinctive photocatalytic performances. These light harvesters when combined with noble-metal free molecular catalysts in aqueous-based photocatalytic systems, not only allow for substantial "green" fuel synthesis but also simultaneously facilitate waste oxidation. Such substrates which originate from numerous resources and are abundantly available at no cost, serve as electron donors to quench the photogenerated holes and maintain the photocatalytic stabilities of the systems. The use of waste materials for this purpose, eliminates the need for additional sacrificial reagents,[8] traditionally used in great excess, which add to the overall cost of the processes, and often result in by-products which need to be disposed. We anticipate that this approach, could be a breakthrough in the development of scalable, economically and environmentally sustainable photocatalytic systems, which could efficiently serve the increased energy needs of our societies.

References
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10:00 AM BREAK

10:30 AM *ET08.01.06
Designing Semiconductor Photoelectrodes for Integrated Photo-Electrochemical Water Splitting Lianzhou Wang; University of Queensland, St Lucia Brisbane, Queensland, Australia.

Semiconducting materials hold the key for efficient photocatalytic and photoelectrochemical water splitting. In this talk, we will give a brief overview of our recent progresses in designing semiconductor metal oxides materials for photoelectrochemical energy conversion including photocatalytic solar fuel

generation. In more details, we have been focusing the following a few aspects; 1) band-gap engineering of layered semiconductor compounds including layered titanate, tantalate and niobate-based metal oxide compounds for visible light phtocatalysis, and 2) two-dimensional nanosheets/nanoplates of TiO_2, Fe_2O_3, WO_3, $BiVO_4$ as building blocks for new photoelectrode design, and 3) the combination of a high performance photoelectrode $BiVO_4$ with perovskite solar cells can lead to unassisted solar driven water splitting process with solar-to-hydrogen conversion efficiency of >6.5%.[1-6] The resultant material systems exhibited efficient visible light photocatalytic performance and improved power conversion efficiency in solar energy, which underpin important solar-energy conversion applications including solar fuel generation and simultaneous environmental application.

11:00 AM DISCUSSION TIME

11:15 AM ET08.01.08
Highly Dispersed Ruthenium Oxide Hydrate as an Efficient Cocatalyst for Z-Scheme Water Splitting Hajime Suzuki[1], Shinnosuke Nitta[2], Osamu Tomita[2], Masanobu Higashi[2], Akinori Saeki[1] and Ryu Abe[2, 3]; [1]Department of Applied Chemistry, Graduate school of Engineering, Osaka University, Suita, Japan; [2]Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan; [3]JST-CREST, Kyoto, Japan.

Photoinduced water splitting using semiconductor materials has attracted much attention owing to its potential for clean H_2 production from abundant solar light. To achieve practically high efficiency of H_2 production under solar light irradiation, it is indispensable to utilize a wide range of the solar light spectrum up to the visible region, as well as to achieve a high quantum efficiency in the photocatalytic process. Introducing two-step photoexcitation (*i.e.*, Z-scheme) in water splitting has been recently proven as one of the most promising strategies for harvesting a wider range of visible light. In this system, the water-splitting reaction is broken up into two stages: one for H_2-evolution, and the other for O_2-evolution. These are combined using a shuttle redox couple in solution. In Z-scheme water splitting systems with an IO_3^-/I^- redox couple, the reduction of IO_3^- on O_2-evolving photocatalysts *via* a six-electron process often represents the rate-determining step of the overall process, and therefore necessitates effective cocatalysts such as PtO_x and RuO_2. However, these cocatalysts cannot be loaded onto thermally unstable materials *via* conventional impregnation processes involving calcination. In the present study, we introduce a new Ru-based cocatalyst that can be loaded without calcination and effectively promotes the reduction of IO_3^- on various photocatalysts, including non-oxide materials. The results reveal for the first time that the Ru species adsorbed *via* simple stirring of photocatalyst particles such as WO_3 in an aqueous $RuCl_3$ solution effectively trigger O_2 generation in the presence of IO_3^- as electron acceptor; moreover, the O_2 evolution rate on the present Ru-loaded WO_3 sample was much higher than that obtained with conventional RuO_2-loaded WO_3. The structural analysis indicates that the Ru species adsorbed on WO_3 are highly dispersed and characterized by octahedral RuO_6 environments similar to those found in $RuO_2 \cdot nH_2O$. Time-resolved microwave conductivity (TRMC) measurement confirmed that the loaded Ru species (most likely analogous to $RuO_2 \cdot nH_2O$) effectively capture the photogenerated electrons. In electrochemical measurement, the Ru species exhibit higher activity in the reduction of IO_3^- than anhydrous RuO_2, whereas RuO_2 exhibits much higher activity for the oxidation of water than $RuO_2 \cdot nH_2O$. The newly developed Ru-based cocatalyst was also applicable to thermally unstable materials such as H_2WO_4 and Ta_3N_5, thus enabling them to generate O_2 in the presence of IO_3^-.

11:30 AM ET08.01.09
Photocatalytic Applications from Visible-Light Responsive Metal-Organic Framework Systems Kyriakos Stylianou; EPFL Valais , Sion, Switzerland.

Solar to hydrogen (H_2) energy conversion represents the Holy Grail of energy science and technology. For decades, numerous materials have been developed and used as photocatalysts for this purpose. However, their inadequate visible light absorbance, poor stability and fast charge recombination have prevented their wide, industrial-scale deployment. Additionally, the use of noble metal-based co-catalysts and the toxicity of the majority of electron donors employed in these photocatalytic systems limit the profitability of this technology. This study aims to tackle these issues using a two-fold strategy. Firstly, we systematically studied the impact of different transition metal-based co-catalysts towards the photocatalytic water reduction, when they are physically mixed with the visible-light active MIL-125-NH_2. All co-catalyst/MIL-125-NH_2 photocatalytic systems were found to be highly stable after photocatalysis, with some systems exhibiting high hydrogen (H_2) evolution rates of >2000 μmol h^{-1} g^{-1}. Secondly, we investigated how different electron donors affected the stability and H_2 generation rate of the best photocatlytic system and found that triethylamine fulfils both requirements. We then replaced the electron donor with dyes that are commonly used as simulant organic pollutant, with the aim of integrating the visible-light driven H_2 evolution with dye degradation in a single process. This is the first study where a metal-organic framework (MOF) system is used for this dual-photocatalytic activity under visible light illumination and our proof-of-concept approach envisions a sustainable waste-water remediation process driven by the abundant solar energy, while H_2 is produced, captured and further utilized. [1]

[1a] Kampouri, S.; Nguyen, T. N; Ireland, C. P.; Valizadeh, B.; Ebrahim, F. M.; Capano, G.; Ongari, D.; Mace, A.; Guijarro, N.; Sivula, K.; Sienkiewicz, A.; Forro, L.; Smit, B.; Stylianou, K. C.* *Photocatalytic Hydrogen Generation and Quantum Efficiency from a Visible-Light Responsive Metal-Organic Framework System: The impact of Nickel Phosphide Nanoparticles*(*J. Mater. Chem. A,* **2018**)
[1b] Kampouri, S.; Nguyen, T. N.; Spodaryk, M.; Züttel, A.; Smit, B.; Stylianou, K. C.* Concurrent Photocatalytic Hydrogen Generation and Degradation of Dyes using MOFs under Visible Light Irradiation *(under review, 2018)*
[1c] Nguyen, T. N.; Kampouri, S.;Valizadeh, B.; Luo, W.; Ongari, D.; Planes, M. O.; Züttel, A.; Severin, K.; Smit, B.; Stylianou, K. C.* Photocatalytic Hydrogen Generation from a Visible-light Responsive Metal-organic Framework System: Stability versus Activity of Transition Metal Cocatalysts *(under review 2018)*
[1d] Patent Application: Stylianou, K. C.; Smit, B.; Kampouri, K.; Ireland, C. P.; Nguyen, T. N; *Noble-Metal-Free Photocatalytic System for Hydrogen Evolution under Visible Light* - EP17180055.0

11:45 AM ET08.01.10
Inductive and Electrostatic Promotion of Carbon Dioxide Reduction at Metal Macrocycles Karthish Manthiram; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Electrochemical reduction of carbon dioxide at ambient conditions can enable local, modular synthesis of chemicals. Diverse catalysts have been explored for this process, including heterogeneous extended solids and molecular complexes. Among the molecular complexes, cobalt tetrapyrolle macrocycles are among the most active and selective for converting carbon dioxide into carbon monoxide, a critical chemical intermediate. These complexes are prone to aggregation as they are planar, leading to favorable pi-pi interactions, which can obscure their intrinsic turnover frequencies for carbon dioxide reduction. We demonstrate methods by which the intrinsic turnover frequencies of these catalysts can be measured, revealing activities that are orders of magnitude higher than when measured in their aggregated states. These kinetically-limited catalysts enable detailed mechanistic studies, which reveal the molecular-level details of how carbon dioxide is reduced through either electron transfer or concerted proton-electron transfers. We have also identified the inductive and electrostatic contributions to catalysis at the active site, providing design principles for developing more active molecular complexes for carbon dioxide reduction.

1:30 PM *ET08.02.01
Resolution of Electronic and Structural Factors Underlying Oxygen-Evolving Performance in Amorphous Cobalt Oxide Catalysts David M. Tiede[3], Gihan Kwon[1], Hoyoung Jang[2], Jun-Sik Lee[2], Anil Mane[1], Alex Martinson[1], Hacksung Kim[3] and Jungho Kim[4]; [1]Materials Science Division, Argonne National Laboratory, Argonne, Illinois, United States; [2]Stanford Synchrotron Radiation Light Source, SLAC National Accelerator Laboratory, Menlo Park, California, United States; [3]Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois, United States; [4]X-ray Science Division, Argonne National Laboratory, Argonne, Illinois, United States.

Non-noble-metal, thin-film oxides are widely investigated as promising catalysts for oxygen evolution reactions (OER). A key challenge for gaining insight into mechanisms for thin-film photo- and electro-catalytic OER function lies in resolving the interplay between intrinsic catalytic activity of catalytic sites and the electronic structure and charge transport properties of the thin-film OEC. Transition metal (oxy)hydroxides show linked electron-proton conductivity which confers a volume rather than a surface area dependent activity to the films. This is understood to arise from homogeneously distributed and accessible catalytic sites though out the film, and with the catalytic current densities determined by the product $(k_{cat}k_{H,e})^{1/2}$ of the catalytic rate, k_{cat}, and electron-proton conductivity, $k_{H,e}$. As a result, understanding OER function for transition metal (oxy)hydroxide requires the structural basis for both catalysis and electron-proton conductivity to be addressed.

We have investigated amorphous cobalt oxide films electrochemically formed in the presence of borate (CoBi) and phosphate (CoPi) as a means to resolve structural and electronic factors that underlie OER performance in cobalt (oxy)hydroxides. CoPi and CoBi share a common cobaltate domain building block, but differ significantly in OER performance that has been proposed to derive from different electron-proton charge transport properties. In this report, we provide a comparison of CoBi and CoPi OER performance and bulk electronic properties, and correlate these to the electronic and structural properties measured at the atomic scale using a combination of soft X-ray absorption (XAS), resonant X-ray emission (RXES), resonant inelastic X-ray scattering (RIXS), and resonant vibrational Raman scattering (RR) techniques. This combination of analytical approaches show CoBi and CoPi to have characteristic differences in electronic structure measured at the atomic scale that provide a basis for understanding enhanced conductivities for CoBi compared to CoPi as thin film OEC. In particular, the results show that the cobaltate domains for these OEC differ in the content of tetrahedral Co(II) "defect" sites, the extent of oxygen-mediated metal-metal delocalization, and mesoscale ordering that can be understood to combine and support enhanced electron-proton conductivity in CoBi compared to CoPi. More generally, this work demonstrates opportunities to use the combination of soft XAS, RXES, RIXS for investigating the interplay between intrinsic catalytic activity of catalytic sites and the electronic structure and charge transport properties of thin-film catalysis.

2:00 PM ET08.02.02
Dinuclear Heterogeneous Catalyst on Metal Oxides for Solar Water Oxidation Yanyan Zhao[1], Ke. R. Yang[2], Xingxu Yan[3], Zechao Wang[4], Sufeng Cao[5], Yifan Ye[6], Qi Dong[1], Xizi Zhang[1], James Thorne[1], Lei Jin[7], Kelly Materna[2], Antonios Trimpalis[5], Sirine Fakra[6], Shasha Zhu[1], Xiaoyan Zhong[4], Peng Wang[8], Xiaoqing Pan[3], Jinghua Guo[6], Maria Flytzani-Stephanopoulos[5], Gary W. Brudvig[2], Victor Batista[2] and Dunwei Wang[1]; [1]Boston College, Chestnut Hill, Massachusetts, United States; [2]Yale University, New Haven, Connecticut, United States; [3]University of California–Irvine, Irvine, California, United States; [4]Tsinghua University, Beijing, China; [5]Tufts University, Medford, Massachusetts, United States; [6]Lawrence Berkeley National Laboratory, Berkeley, California, United States; [7]Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Jülich, Germany; [8]Nanjing University, Nanjing, China.

Atomically dispersed catalysts refer to substrate-supported heterogeneous catalysts featuring one or a few active metal atoms that are separated from one another. They represent an important class of materials ranging from single atom catalysts (SACs) and nanoparticles (NPs). While SACs and NPs have been extensively reported, catalysts featuring two atoms with well-defined structures are poorly studied. The difficulty in synthesizing such structures has been a critical challenge. Here we present preparing dinuclear heterogeneous catalysts (DHCs) by a facile photochemical method that produces catalytic centers consisting of two Iridium metal cations, bridged by O and bound to a support. Direct evidence unambiguously supporting the dinuclear nature of the catalysts anchored on metal oxides is obtained by aberration-corrected scanning transmission electron microscopy. In addition, different binding modes have been achieved on two metal oxides with distinguishable surface oxygen densities and interatomic distances of binding sites. Side-on bound DHCs was demonstrated on iron oxide where both Ir atoms are affixed to the surface with similar coordination environment. The three-fold hollow binding sites on the OH-terminated surface of Fe_2O_3 anchor the catalysts to provide outstanding stability against detachment or aggregation. The competing end-on binding mode, where only one Ir atom is attached to the substrate and the other one is dangling was observed on WO_3. Evidence supporting the binding modes was obtained by *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy. The resulting catalysts exhibit high activities toward H_2O photooxidation. Density functional theory calculations provide additional support for atomic structure, binding sites modes on metal oxides, as well as insights into how DHCs may be beneficial for solar water oxidation reactions. The results have important implications for future studies of highly effective heterogeneous catalysts for complex chemical reactions.

2:15 PM ET08.02.03
Bismuth Substituted Strontium Cobalt Perovskites for Catalyzing Oxygen Evolution Jiayu Peng, Denis A. Kuznetsov, Livia Giordano, Yuriy Roman and Yang Shao-Horn; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The distribution and on-demand use of electrical energy from sustainable resources requires storage technologies that are cost effective and involving earth-abundant elements [1-2], such as storing solar energy in form of chemical bonds by water splitting or CO_2 reduction. The efficiency of these storage technologies is, however, severely limited by the catalysis of the oxygen evolution reaction (OER) [3], which is characterized by slow kinetics and the need for precious metal catalysts such as RuO_2 and IrO_2 [4]. The development of the efficient electrocatalysts for OER composed of earth-abundant materials is therefore crucial for the large-scale implementation of these technologies.
Here we employ the recently reported inductive effect [5] associated with metal substitution to examine the redox potentials and OER activity of cobalt-based perovskites, where bismuth-substituted strontium cobalt perovskite, $Bi_{0.2}Sr_{0.8}CoO_{3-\delta}$, showed a record intrinsic activity for OER in basic solution. OER kinetics of $Bi_{0.2}Sr_{0.8}CoO_{3-\delta}$ were found to have a low Tafel slope (<30 mV/decade) and pH dependence on RHE scale implying the decoupling of proton and electron transfer during one of the OER steps. The enhanced OER kinetics of $Bi_{0.2}Sr_{0.8}CoO_{3-\delta}$ relative to other active catalysts such as $SrCoO_{3-}$

$_{\delta}$ can be attributed to the presence of electronegative strong Lewis acid Bi^{3+} ions which can influence the surface charge facilitating deprotonation kinetics, and also enhance oxide stability by having lowered O p band center of $Bi_{0.2}Sr_{0.8}CoO_{3-\delta}$ relative to the Fermi level via partial Co reduction and inductive effect. This work demonstrates a novel design strategy for enhancement of the OER activity and stability of oxide catalysts by the inductive effect induced by metal substitution to enable efficient and sustainable energy storage.

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2:30 PM ET08.02.04
Ultrathin Amorphous Iron-nickel Boride Nanosheets for Highly Efficient Electrocatalytic Oxygen Production Jean Marie Vianney Nsanzimana and Xin Wang; Nanyang Technological University, Singapore, Singapore.

Electrochemical Hydrogen production has gained great interest over the past decades as a cleaner, higher purity and sustainable production technology for carbon-neutral alternative fuel sources.[1] However, poor oxygen evolution reaction (OER) thermodynamic up-hill reaction limits the efficiency of H_2 production from water electrolysis and photoelectrolysis routes to large-scale energy storage. Thus, it is crucial to develop efficient and low-cost material to boost the sluggish kinetics step of four-electron OER process. The state-of-the-art are the precious metal-based catalyst which suffers from higher cost and makes them lesser desirable for industrial applicable scale. Thus, developing low cost, durable, earth-abundant, and high-performance non-precious metal electrocatalyst for oxygen evolution reaction (OER) is a cornerstone for energy technologies. Despite a well-documented approach for synthesizing metal borides, it is recently that the application as promising OER electrocatalyst has emerged.[2,3] Furthermore, the synergic effect had been reported for multimetal borides materials which were found to be the most OER among the reported metal borides materials.[3] Additionally, an improvement in metal borides based catalyst had been reported when supported on a higher conductive substrate such as graphene.[4]
A cost-effective and efficient electrocatalyst for oxygen evolution reaction during water electrolysis is highly desired. In an effort to develop an economical material for replacing precious metal-based catalysts, a novel and self-standing, amorphous ultrathin nanosheets of bimetallic iron-nickel boride (FeNiB NSs) on Ni foam is presented, which displays better oxygen-evolving activity compared to precious metal catalyst RuO_2. In 1.0 M KOH electrolyte, it requires an overpotential of only 237 mV to reach a current density of 10 mA/cm^2 with a small Tafel slope of 38 mV/ dec^1 and shows prominent longterm electrochemical stability. The synergistic effect between highly abundant catalytically active sites on 3D porous substrate, improved electron transport arising from the presence of highly negative boron, and high conductivity of the substrate results in an outstanding electrocatalytic activity. The advanced catalytic activity, facile electrode fabrication, and low cost makes it a potential oxygen evolving material which may be extended to other energy conversion and storage technologies.

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2:45 PM ET08.02.05
$CoSb_2O_6$ as a Stable Oxygen Evolution Catalyst in Acidic Media Taylor A. Evans and Kyoung-Shin Choi; Chemistry, University of Wisconsin-Madison, Madison, Wisconsin, United States.

The electrochemical generation of hydrogen fuel via water reduction requires a counter reaction, typically the oxidation of water. This four electron, kinetically complex reaction has been intensely studied in basic media using a variety of inexpensive metal oxide materials (NiOx, FeOx, CoOx, etc). However, in acidic media these catalysts have been shown to be unstable and degrade rapidly. While noble metal oxides, such as RuO_2 and IrO_2, are able to perform water oxidation in a stable manner with relatively low overpotentials in acidic media, their scarcity and high cost leave significant room for the development of inexpensive novel catalysts. Antimony (V) oxides are expected to be stable under oxidizing conditions in acidic media on account of their high oxidation state and low solubility in acid. In this presentation, the investigation of $CoSb_2O_6$ as a stable water oxidation catalyst is reported. Synthesized through a facile electrochemical method, $CoSb_2O_6$ films are demonstrated to be stable in acidic media while applying the necessary potentials for water oxidation. $CoSb_2O_6$ opens the door as a possible replacement for noble metal oxide catalysts and encourages the investigation of other transition metal antimony oxide materials for use as water oxidation catalysts in acidic media.

3:00 PM BREAK

3:30 PM *ET08.02.06
Porous Transition Metal Oxides for Selective Oxidations Steven L. Suib[1,2,3]; [1]Chemistry, University of Connecticut, Storrs, Connecticut, United States; [2]Chemical and Biomolecular Engineering, University of Connecticut, Storrs, Connecticut, United States; [3]Institute of Materials Science, University of Connecticut, Storrs, Connecticut, United States.

This presentation will focus on synthesis, characterization, and applications of novel microporous and mesoporous materials. Such mesoporous metal oxide materials have crystalline walls, high thermal stability, and monomodal pore size distributions. These systems can be made for most elements throughout the periodic table. They have unique catalytic activity in a number of reactions including selective oxidations, total oxidations, coupling reactions, water splitting, one pot Wittig reactions, dehalogenations, and others. A key focus is on the mechanisms of these selective oxidation reactions. The role of reactive oxygen species in these reactions is of considerable interest. This presentation will focus on synthesis, characterization, and selective catalytic oxidations applications using both microporous and mesoporous materials. Reactive oxygen species can be detected with a variety of methods. *In situ* methods to observe these species have bene developed. How such reactive oxygen species are important in selective oxidation reactions will be discussed.

4:00 PM ET08.02.07

Advanced Structural Characterization of Ni-NW Catalysts Showing Enhanced OER Electroactivity Sagar Prabhudev[1], Minghui Hao[2], Sebastien Garbarino[2], Daniel Guay[2] and Gianluigi A. Botton[1]; [1]McMaster University, Hamilton, Ontario, Canada; [2]INRS, Montreal, Quebec, Canada.

Hydrogen is arguably one of the most promising energy carriers which can mirror all the appealing attributes of electricity. To answer whether it can meet the global demand for energy while at the same time also be an effective clean and sustainable energy carrier, however, requires a low-cost and environmentally friendly means of production. Although Electrolytic methods of producing Hydrogen provide an attractive pathway to producing Hydrogen renewably (e.g., from water), they further entail employing electrolyzer systems such as the Anionic Polymer Electrolyte Membrane Water Electrolyers that are yet to be optimized for their Oxygen Evolution Reaction (OER) kinetics.

In this work we discuss a new class of Ni-Nanowire Catalysts that were found to exhibit a significant decrease in the OER Overpotential (~200 mV) at 10 mA cm^{-2} current densities. With the use of advanced electron microscopy tools for structural and compositional characterization we provide insights into their entire synthetic pathway, where a template-assisted electrodeposition procedure first formed the Ni-filled Aluminium Anodic Oxide (AAO) membranes, from which the usable pristine 1D Ni nanowires were then recovered by electrochemical dissolution of the AAO in 1M KOH. A detailed analyses of their SEM and high-resolution TEM images reveals that the as-received AAO membrane bears a close resemblance to the hexagonal assembly of pore arrangement, which is still preserved even in the case of pristine Ni NWs that are recovered in the final synthetic step. More importantly, a detailed analyses of the NW micrographs post electrochemical testing using advanced image processing methods suggests that the hexagonal assembly can be further retained, thus highlighting the electrochemical stability observed in this 1D Ni-NW catalysts.

Similar to the above analyses performed with TEM-imaging, we performed a detailed investigation of the NW compositions using electron energy loss spectroscopy (EELS). For this we analyzed the variation in the Ni-L2,3 and O-K elemental edges at very high spatial resolution, sufficient to determine the local compositional variations between the NW core/shell regions. Our results indicate that the NW surfaces form an oxide layer over the metallic core, which seems to be still preserved even after exposing to extensive electrochemical characterization (29.4 at.% vs. 26.7 at.% before and after, respectively).

In order to deduce the thermodynamic phase of the oxide layer formed (i.e., NiO vs. Ni(OH)$_2$) in the two samples (NWs pre-/post- treatment in 1M KOH), we further estimated their Ni-L3/L2 white-line intensity ratios over the core- and surface- regions. Our results indicate that the L3/L2 ratio in the shell-region for the Pristine is comparable to the Ni(OH)$_2$ state, and there is no apparent changes in the chemical state of Ni following the extensive electrochemical characterization.

4:15 PM ET08.02.08

Origin of High Activity of Mn$_3$O$_4$ Nanoparticle in Oxygen Evolution Reaction—An Atomic-Resolution STEM/EELS Study Sangmoon Yoon[2], Hongmin Seo[2], Kyoungsuk Jin[2], Seung-Yong Lee[2], Young-Kyun Kwon[1], Ki Tae Nam[2] and Miyoung Kim[2]; [1]Kyung Hee University, Seoul, Korea (the Republic of); [2]Seoul National University, Seoul, Korea (the Republic of).

Catalysis is an atomic-scale phenomenon in which adsorbed molecules on the surface are reformed into new molecules. Because the reaction occurs predominately at a specific site, atomic-scale characterization of surfaces is a crucial step for understanding the reaction mechanism and proposing more active catalysts. Aberration-corrected scanning transmission electron microscopy (STEM)/electron energy loss spectroscopy (EELS) is one of the most powerful tools to unveil the origin of high activity of the catalyst and identify the active sites in the catalyst: STEM allows us to measure the local structures of solid at sub-angstrom resolution while EELS enables to investigate chemical compositions or electronic states of the local structures at high resolution.

We have explored the atomic structure and electronic structure of Mn$_3$O$_4$ nanoparticles using aberration-corrected STEM and EELS to understand its high activity in oxygen evolution reaction (OER). Mn$_3$O$_4$ nanoparticles exhibit relatively high activity (450mV@1mA/cm^3) in OER under neutral pH, which is comparable to that of the famous cobalt phosphate OER catalyst. From the high resolution STEM images, we discovered that the nanoparticles are surrounded by the (011) and (001) facets, and both of the facets undergo the surface reconstructions. In addition, the EELS analysis reveals that the surface reconstructions are accompanied with the suppression of Mn^{3+} ions on the surface. Importantly, such Mn^{3+} ions are still exposed at the edge of the nanoparticle. Currently, it is recognized that Mn^{3+} ions are deeply correlated to active sites of OER in Mn-based electrocatalysts[1]-[4]. Our results suggests that the edges are the active sites of Mn$_3$O$_4$, therefore, Mn$_3$O$_4$ nanoparticles enclosed by active edges compactly can show remarkably high activity in OER whereas its bulk counterpart which mostly has reconstructed surfaces do not have catalytic property.

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4:30 PM ET08.02.09

Multiple Coordinative of ZIFs with Transition Metal in Metal-Organic-Frameworks as Efficient Electrocatalysts for Energy Conversion Chun-Yu Lin and Zhenhai Xia; Materials Science and Engineering, University of North Texas, Denton, Texas, United States.

Clean energy technologies such as fuel cells, rechargeable metal-air batteries, and water splitting, are promising for future energy sources owning to their nature of no pollution and greenhouse gas emission. The key reactions in this technologies are the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) that generate power. The state-of-the-art electrocatalyst in OER is RuO$_2$ and in ORR is Pt, but their high cost and poor durability hindered their application in clean energy technologies. Zeolitic imidazolate frameworks (ZIFs), a subclass of metal organic frameworks (MOFs), mainly composed of a transition metal (TM) center and organic ligands, exhibits the excellent ability as electrochemical catalysts in clean energy conversion and storage. However, their ligand or coordination of metal ions must be modified to enhance their catalytic activities. To rationally design the ZIF catalysts, we have calculated the OER and ORR activities of TM-ZIFs and found an intrinsic descriptor which can describe the catalytic activities of the TM-ZIFs by density-functional theory (DFT) method. Our DFT calculations show that the unsaturated metal sites show high catalytic activities comparable to that of RuO$_2$ / Pt electrocatalyst. This theoretical result was confirmed by the experiment.

4:45 PM ET08.02.10

Mechanistic Investigations of Alkaline Hydrogen Electrocatalysis via Kinetic Modeling and Single-Crystal Voltammetry Maureen Tang, Joshua Snyder, Saad Intikhab and Luis Rebollar-Tercero; Drexel University, Philadelphia, Pennsylvania, United States.

It has long been recognized that the reaction rates of the hydrogen oxidation and hydrogen evolution reactions (HOR /HER) are up to 200 times slower in basic than acidic electrolytes, even though the surface intermediate of adsorbed hydrogen is independent of solution pH [1]. The mechanistic origins of this difference have been hotly debated in the literature. In this work, we investigate possible explanations for the effect of pH by combining single-crystal voltammetry with microkinetic modeling and electroanalytical methods. We specifically determine the viability of the proposed `bifunctional mechanism', in which slow water dissociation is overcome by mediation of adsorbed hydroxide [2].

Our previous work [3] has shown that on Pt(110) either a direct (hydroxide-as-spectator) or indirect (hydroxide-mediated) Volmer step can describe the measured reaction thermodynamics, but that only the direct Volmer step is consistent with realistic adsorption energies. Furthermore, increasing hydroxide adsorption strength via the electrolyte cation decreases kinetics, as observed by the dependence of peak-potential splitting on scan rate. Comparison with theory shows that this observation is consistent only with the direct mechanism. These results strongly suggest that adsorbed hydroxide serves as a competitive spectator in the alkaline Volmer step, and that the bifunctional HOR/HER mechanism plays only a minor role at best.

The inability of the bifunctional mechanism to describe experimental data is further reinforced by investigating a two-site model recently proposed in the literature [2], in which oxophilic ruthenium or nickel sites are responsible for facilitating water dissociation. We find that such chemical dissociation steps result in anomalous trends with potential, and that oxophilicity has no effect on hydrogen coverage or HER/HOR rates. Comparison with experiment strongly indicates that the observed bifunctional mechanism is unrelated to hydroxide binding strength [4]. Overall, our work resolves a long-standing paradox in electrocatalysis and surface science by determining that oxophilicity is not an accurate descriptor for alkaline hydrogen electrocatalysts. Other parameters, such as water orientation and non-covalent interactions, must play a greater role in overall activity. Efforts to identify and measure these parameters are ongoing.

[1] Durst et al. Energy Environ. Sci. 2014, 2255.
[2] Li et al. Angew. Chem. Int. Ed. 2017, 15594.
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SESSION ET08.03: Catalytic CO2 Reduction
Session Chairs: Yu Han and Yugang Sun
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 306

8:00 AM ET08.03.01
2D-Derived Catalysts for Efficient CO_2 Electroreduction F. Pelayo Garcia de Arquer, Oleksandr Bushuyev, Phil De Luna, Cao-Thang Dinh, Ali Seifitokaldani, Makhsud Saidaminov, Chih-Shan Tan, Li Na Quan, Andrew H. Proppe, Md. Golam Kibria, Shana Kelley, David Sinton and Edward H. Sargent; University of Toronto, TORONTO, Ontario, Canada.

The electrochemical reduction of CO_2 into fuels and chemicals is an attractive route to store renewable electricity. Efficient CO_2 reduction catalysts need to yield high activity, high selectivity, and low overpotential, simultaneously. The design of catalysts that exhibit tailored properties such as favourable facets for a given reaction, number of active sites, and oxidation state, is challenging: catalyst can undergo an extensive reconstruction under high productivity operating conditions such as high current densities, reducing potentials, and variable pH. Earth-abundant transition metals such as tin, bismuth, and lead have been proven stable and product-specific, but exhibit limited partial current densities. We present a strategy that employs bismuth oxyhalides as a template from which 2D bismuth-based catalysts are derived. The BiOBr-templated catalyst exhibits a preferential exposure of highly active Bi (110) facets, which we track in operando using grazing-incidence wide-angle X-ray scattering (GIWAXS) and X-ray absorption spectroscopy (XAS). The templated catalyst exhibit an enhanced CO_2 reduction reaction selectivity to over 90% Faradaic efficiency for formic acid that is sustained up to stable current densities of 200 mA cm^{-2} . This represents more than a twofold increase in the production of the energy-storage liquid formic acid compared to previous best Bi catalysts.

8:15 AM ET08.03.02
Synthesis and Characterization of Selenium-Doped Molybdenum/Tungsten Sulfide Catalysts for Electrochemical Carbon Dioxide Reduction Huiyang W. Liang and Peter Agbo; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Electrochemical transformation of CO_2 into energy-dense fuels may prove key towards the realization of economically viable, renewable fuels. However, the rational design of CO_2 reduction catalysts guided by well-grounded chemical intuition or first-principles computational approaches, have so far been met with limited success. To address this important question of how to activate a molecule as stable and unreactive as CO_2 and convert it into complex hydrocarbons, there may be no better place to look than biological systems capable of CO_2 activation, for crucial guidance and inspiration.

Recent findings have demonstrated the utility of MoS_2 and $MoSe_2$ edge sites in catalyzing the transformation of CO_2 to CO. Although this is a promising start, CO is not an easy product to work with industrially nor to transport due to its gaseous nature. Meanwhile, a close look of formate dehydrogenase (FDH), the key enzyme in formate metabolism which catalyzes the reversible two-electron oxidation of formate or reduction of CO_2, reveals a catalytic center that is defined by $Mo^{4+/6+}$ or $W^{4+/6+}$ coordination with sulfide ligands (from molybdopterin prosthetic groups and cysteine residues) and a selenocysteine side chain. Translation of these chemical moieties, which are recognized as integral to the FDH's architecture and functions, into solid-state semiconductor devices, would suggest that the inclusion of Se ions in Mo/WS$_2$ semiconductors as a dopant may promote the preferred generation of liquid formate, rather than gaseous CO, from CO_2. In this project, we want to explore interstitial Se doping of W/MoS$_2$ materials as potential CO_2 reduction cathodes, with the ultimate goal of generating reduced liquid hydrocarbon products.

8:30 AM *ET08.03.03
Coupling Solar Energy into Catalytic CO_2 Conversion Yujie Xiong; Department of Chemistry, University of Science and Technology of China, Hefei, China.

Considering the excessive emission of atmospheric carbon dioxide (CO_2) caused by the combustion of fossil fuels, the sunlight-driven CO_2 reduction into higher energy chemicals, such as carbon monoxide, formic acid, methanol or methane, offers a more promising approach to alleviate both global warming and energy crisis. Designing new photocatalytic materials for improving the photoconversion efficiency is a promising route to achieve this goal. Despite the invention of a large number of catalytic materials with well-defined structures, their overall efficiency in photocatalysis is still quite limited as the three key steps - light harvesting, charge generation and separation, and charge transfer to surface for redox reactions - have not been substantially improved. To improve each step in the complex process, there is a major trend to develop materials based on inorganic hybrid structures, in which surface and interface engineering holds the promise for boosting the overall efficiency. In this talk, I will demonstrate several different approaches to designing inorganic hybrid structures with improved photocatalytic performance via surface and interface engineering. It is anticipated that this series of works open a new window to rationally designing inorganic hybrid materials for photo-induced applications.

9:00 AM ET08.03.04
Development of Semiconductor-MOF Ternary Photocatalyst Toward Intensified Charge Carrier Density and Molecule Activation in Heterogeneous Photocatalysis <u>Xiang He</u> and Wei-Ning Wang; Virginia Commonwealth University, Richmond, Virginia, United States.

Heterogeneous photocatalysis, such as carbon dioxide (CO_2) photoreduction, is a promising engineering approach to reduce atmospheric CO_2 levels and simultaneously convert CO_2 into hydrocarbon fuels. Among the numerous catalysts for CO_2 photoreduction, semiconductors have been studied intensively because of their low cost, easy availability, nontoxicity, and exceptional chemical stability. However, the semiconductor-based CO_2 photoreduction still suffers from low efficiency and poor selectivity, mainly due to low charge carrier density and weak ability to activate the adsorbed CO_2 molecules. Towards addressing the aforementioned long-standing issues in CO_2 photoreduction (i.e., low charge carrier density and inefficient CO_2 activation), we herein report a rational development of MOF-based ternary nanocomposites composed of TiO_2/Cu_2O heterojunction and $Cu_3(BTC)_2$, where the roles of semiconductor heterojunction and MOF in charge transfer and CO_2activation are systematically explored. Specifically, the nanocomposites were synthesized via facile and rapid self-assembly of TiO_2/Cu_2O nanoparticles within microdroplets, followed by *in-situ* growth of $Cu_3(BTC)_2$ on the TiO_2/Cu_2O surface, where part of Cu_2O serves as the sacrificial metal source. The unique ternary $TiO_2/Cu_2O/Cu_3(BTC)_2$ composite possesses heterojunction and abundant coordinatively unsaturated copper sites, which results in not only increased charge carrier density but also efficient activation of CO_2 molecules, therefore leading to high CO_2 conversion efficiency and preferential formation of CH_4. With systematic measurements (e.g., gas chromatography, photoluminescence spectroscopy, X-ray photoelectron spectroscopy, and time-resolved *in-situ* diffuse reflectance infrared Fourier transform spectroscopy), a plausible pathway of CO_2 activation and subsequent reduction in this ternary system was proposed. The outcome of this work provides new insights in rational design of MOFs-based hybrid nanomaterials for efficient CO_2 photoreduction.

9:15 AM ET08.03.05
Photocatalytic and Optoelectronic Studies of SnS₂ Thin Film by Controlled Implantation of Carbon Ions <u>Tadesse Billo Reta</u>[1], Indrajit Shown[1], Weiyen Woon[2], Ruei-San Chen[3], Chih-Hao Lee[4], Li-Chyong Chen[5] and Kuei-Hsien Chen[1]; [1]Institute of Atomic and Molecular Sciences, Academia Sinica, Nangang, Taiwan; [2]Department of Physics, National Central University, Taoyuan, Taiwan; [3]Graduate Institute of Applied Science and Tech. National Taiwan University of Science of Technology (NTUST), Taipei, Taiwan; [4]Department of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan; [5]Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan.

Photocatalytic conversion of CO_2 into useful products using solar energy is one of promising technique to tackle both energy and global environmental challenges. Recently, several semiconductor photocatalyst including metal oxide and chalcogenide materials have been attracted enormous interest in the gas phase CO_2 reduction via artificial photosynthesis. Irrespective of versatile applications, SnS_2 is not well explored in photocatalytic CO_2 reduction applications. Recent experimental study has demonstrated that carbon doping significantly tuning the electronic properties of bulk SnS_2 and showing enhanced photocatalytic CO_2 reduction. However, the influence of different percentage of carbon doping into 2D SnS_2 layer structure together with optoelectronic behavior by a controlled process remains unaddressed. In this study, we report the synthesis and characterization of 2D SnS_2 thin film grown via chemical vapor transport method. The as grown thin film was implanted with carbon ions with the energy of 5 keV to form SnS_2-C composite films with different concentration of carbon. The 6 wt % carbon implanted SnS_2 thin film exhibits high photocatalytic activity and product selectivity towards gas phase photocatalytic CO_2 reduction under visible light. The SnS_2-C thin film has produced CH_3CHO as a major product which is 6 times higher than pristine SnS_2 thin films. The improved photocatalytic activity and selectivity can be ascribed due to band structure changes and pronounced charge-transfer taking place between SnS_2 and carbon. The mechanism of interfacial charge transfer was studied using wavelength dependent photocurrent studies under CO_2 and water vapor environments. The incorporation of carbon in SnS_2 has improved the photocurrent response by more than 100 times than the as synthesized SnS_2. The detail characterization and experimental results with the future perspective of this study will be presented.

9:30 AM *ET08.03.06
Heterogeneous Multi-Shelled Hollow Spheres for Efficient Photocatalytic Reduction of Carbon Dioxide <u>Dan Wang</u>, Feifei You and Dan Mao; State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China.

A significant increase of CO_2 in the atmosphere has a profound impact on global climate change, which has become a central challenge of the 21st century. Photocatalytic reduction of CO_2 into chemical fuel is an appealing strategy to resolve greenhouse gas emissions and alleviate the energy crisis. The efficiency of CO_2 conversion relies on the catalytic sites and microstructure of photocatalyst. In this work, we successfully synthesized SnS_2/SnO_2 heterogeneous multi-shelled hollow spheres by the sequential templating approach. Multi-shelled hollow structures not only have the characteristics of the large specific surface area and high loading capacity; more importantly, they have multiple adjustable shells and inter-shell spaces, enabling sequential light reflection and scattering, which greatly improve the light-harvest capability and light conversion efficiency. These unique features make them promising candidate for photocatalytic reduction of CO_2. The SnS_2/SnO_2 multi-shelled hollow spheres exhibited an enhanced efficiency and good stability for photocatalytic reduction of CO_2 to CO. Photocatalytic activity of SnS_2/SnO_2 multi-shelled hollow spheres is increased with the shell number significantly. As a result, the quadruple-shelled SnS_2/SnO_2 hollow spheres steadily photocatalyzed CO_2 to CO at a rate of 50 $\mu mol\ g^{-1}\ h^{-1}$ under AM 1.5 G simulated solar irradiation, and the rate can maintain 72 hours without decline. This work paves the way for enhancing photocatalytic performance by structural design of the emerging materials.

10:00 AM BREAK

10:30 AM *ET08.03.07
Designing Nanostructured Materials for Electrochemically Recycling Carbon Dioxide Michael B. Ross and <u>Peidong Yang</u>; University of California, Berkeley, Berkeley, California, United States.

Electrochemical carbon dioxide (CO_2) recycling enables the synthesis of high-value fuels and chemicals using renewable energy. Doing so requires the development of catalysts that both efficiently and selectively reduce CO_2 into desirable products. Nanomaterials are particularly powerful for doing so due to their high surface areas, tunable chemical and physical properties, and unique reactivities that can differ from the bulk. Thus the synthesis, characterization, and integration of nanostructured electrocatalysts for CO_2 reduction is a promising strategy for realizing breakthrough performance. Synthesis gas (syngas), a mixture of H_2 and CO, can be converted into a variety of fuels and chemicals using established industrial processes that require different syngas compositions. Here we will describe the synthesis, characterization, and catalytic properties of nanostructured electrocatalysts that are versatile and modular, and which also provide dynamic access to a wide variety of desirable syngas compositions. Strategies for generating multi-carbon products will also be discussed.

11:00 AM ET08.03.08
Controlled Selectivity of CO₂ Reduction via Electrochemical Potential Modulation Kevin Kimura, <u>Jin Suntivich</u> and Tobias Hanrath; Cornell University, Ithaca, New York, United States.

We present the product distribution of the CO_2 reduction reaction (CO_2RR) when the driving force is a pulse of electrochemical potential. The use of renewable electricity to convert CO_2 into energy-dense fuels and high-valued feedstocks is an enabler of many sustainable energy and chemical technologies. The CO_2RR offers a pathway to achieve this goal using electrochemistry. However, the CO_2RR suffers from poor selectivity, especially on Cu, despite its ability to produce hydrocarbons (such as methane, ethylene, etc.). In this presentation, we present a strategy for manipulating the CO_2RR selectivity by applying the CO_2RR driving force ('overpotential') as pulses. By applying pulses of overpotential with controlled duration and magnitude, we demonstrate that the CO_2RR selectivity can improve > 97% of faradaic efficiency (FE) with respect to the competing hydrogen evolution reaction, and the selectivity toward methane can be as high as 83% FE. We will discuss the possible mechanism for why the temporal control of the overpotential pulse can lead to the CO_2RR selectivity control and the possible implications on the timescale of the competing pathways in the CO_2RR.

11:15 AM ET08.03.09
Transition Metal Single Atom Electrocatalysts for Selective CO_2 Reduction in Water—From Identification to Scaling-up Haotian Wang[1,2]; [1]Harvard University, Cambridge, Massachusetts, United States; [2]Rice University, Houston, Texas, United States.

The development of highly selective and earth-abundant electrocatalysts for CO_2 reduction is becoming increasingly important for renewable energy applications. The challenge here is the strong competition from water reduction, as well as the low selectivity towards a desired product. In this talk I will introduce the rational tuning of electronic properties of catalytic materials for their significantly improved CO_2 reduction performance. By dispersing transition metals into isolated single atoms with electronic structures significantly different from their bulk counterparts, we can dramatically suppress the competing hydrogen evolution and deliver an ultra-high CO_2 reduction selectivity of more than 95% under ambient conditions in water. I will also talk about the successful scaling-up of both the catalytic materials synthesis as well as the CO_2 reduction current density while maintaining ultra-high CO selectivity.

11:30 AM ET08.03.10
Rational Design of Terrace, Step and Corner Sites of The Metal or Bimetallic Catalysts for Hydrogenation and Hydrodeoxygenation of Biomass-Derived Platform Molecules Shelaka Gupta, Tuhin Suvra Khan, Md. Imteyaz Alam and M. Ali Haider; Chemical Engineering Department, Indian Institute of Technology Delhi, New Delhi, India.

Deoxygenation and valorization of biomass-derived platform molecules was studied using ring-opening (RO), decarboxylation, hydrogenation and hydrodeoxygenation (HDO) reactions. The platform molecules studied here included cellulose–derived lactones, furans, 2-pyrones and lignin-derived phenolic compounds.
Study on the conversion of lactones was focused to understand the mechanism of RO and decarboxylation reaction. More specifically, oxocarbenium ions were proposed as an intermediate to play an important role in controlling the rate of RO step. The mechanism of RO and decarboxylation reaction in 2-pyrones formed an interesting case, wherein the reaction in partially saturated 2-pyrones followed a retro-Diels-Alder (rDA) route. Both solvents and substituents were expected to influence the rDA reaction of partially saturated 2-pyrones, which was studied using density functional theory (DFT) simulations. 6-amyl-α-pyrone (6PP) was suggested as a potential platform chemical, which may be obtained directly from the fermentation of waste lignocellulosic biomass. On RO and decarboxylation, 6PP was converted to C_9 linear ketones which are proposed as precursors for jet and diesel range fuels. All of these catalytic transformations of 6PP can be integrated with the upstream fermentation of biomass to form a unique bio- and chemo-catalytic process for providing high value fuels and chemicals.However biogenic impurities present in ppm levels (<100 ppm) along with the fermentation-derived molecules pose a detrimental effect to heterogeneous catalyst stability. Interaction of such impurities with the metal catalyst surface was studied using DFT simulations.Bimetallic alloy of NiAu was proposed as a more stable surface for hydrogenation reactions.
Catalytic hydrogenation reaction carried out on the Pd catalyst was an interesting case to further explore the influence of catalyst particle size and morphology on the selectivity of a desired product. Detailed mechanistic studies were carried out on Pd (111) and Pd (100) surfaces using DFT calculations to corroborate experimental finding. Since Pd (111) are the majority (~70%) sites, high selectivity observed towards the partially hydrogenated product (cyclohexanone) in the experiments is thought to be from the Pd (111) surface. Contrary to this prevalent thought, on using a combined theoretical and experimental approach, Pd (111) surface was demonstrated to selectively produce the cyclohexanol. Surprisingly, Pd (100), the minority(~25%) sites were selectively producing cyclohexanone. These results lead to the development of a comprehensive understanding on facet-dependent selectivity control in phenol hydrogenation on the Pd catalyst. Final reaction in this sequence was HDO of biomass-derived furan compounds, wherein the synergistic interaction of Zn with the Pd catalyst was studied using DFT simulations. Zn was shown to participate in C-O bond activation step while Pd surface participated in the hydrogenation step.

SESSION ET08.04: Novel Structures for Catalysis
Session Chairs: Hongyou Fan and Yugang Sun
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 306

1:45 PM *ET08.04.01
Self-Assembly and Formation of Nanostructured Porphyrin Photocatalysts Hongyou Fan[1,2]; [1]Sandia National Laboratories, Albuquerque, New Mexico, United States; [2]The University of New Mexico, Albuquerque, New Mexico, United States.

Design and engineering of the size, shape, and chemistry of photoactive building blocks enable the fabrication of functional nanocatalysts for applications in light harvesting, photocatalytic synthesis, water splitting, phototherapy, and photodegradation. Here, I will present our recent progress in the synthesis of such nanocatalysts through a surfactant-assisted interfacial self-assembly process using optically active porphyrin as a functional building block. The self-assembly process relies on specific interactions such as π–π stacking and ligand coordination between individual porphyrin building blocks. Depending on the kinetic conditions, resulting structures exhibit well-defined one- to three-dimensional morphologies such as nanowires, nanooctahedra, and hierarchically ordered internal architectures. At the molecular level, porphyrins with well-defined size and chemistry possess unique optical and photocatalytic properties for redox synthesis of metallic structures. On the nanoscale, controlled assembly of macrocyclic monomers leads to formation of ordered nanostructures with precisely defined size, shape, and spatial monomer arrangement so as to facilitate intermolecular mass and energy transfer or delocalization for photocatalysis. Due to the hierarchical ordering of the porphyrins, the nanoparticles exhibit collective optical properties resulted from coupling of molecular porphyrins and photocatalytic activities such as photodegradation of methyl orange pollutants and hydrogen production. The capability of exerting rational control over dimension and morphology provides new opportunities for applications in sensing, nanoelectronics, and photocatalysis.

2:15 PM *ET08.04.02
Membrane Coated Electrocatalysts for Stable, Active and Selective Electrocatalysis <u>Daniel Esposito</u>; Chemical Engineering, Columbia University, New York, New York, United States.

Conventional electrocatalysts used in fuel cells and electrolyzers are comprised of metallic nanoparticles that are attached to a conductive electrode support that allows for the transfer of electrons between an external circuit and the electrocatalyst/electrolyte interface. Typically, these nanoparticles are partially or fully exposed to a bulk liquid or gaseous phase to facilitate mass transfer of reactants and products. In contrast, this presentation describes recent studies on an emerging class of electrocatalysts for which the active metal electrocatalysts are completely encapsulated by ultrathin layers of permeable oxides that can exhibit membrane-like properties. These so-called membrane coated electrocatalysts (MCECs) offer many potential advantages over conventional electrocatalysts, including the ability to simultaneously mitigate degradation, alter reaction selectivity, and improve reaction kinetics at the buried interface between the overlayer and active catalyst.[1] This talk will describe three case studies of silicon oxide (SiO_x)-encapsulated Pt electrocatalysts that separately demonstrate the ability of the SiO_x overlayer to enhance catalyst stability,[2] activity, and selectivity.[3] Of particular interest to the last two studies are the task of developing a deeper understanding of the buried interfaces of MCECs, which represent confined environments where structure can, in principle, be tuned to alter reaction energetics and selectivity for a wide variety of electrochemical reactions.
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2:45 PM ET08.04.03
Colloidal Hexagonal Copper Phosphide (Cu₃P) Nanosheets for Selective and Low-Overpotential CO₂ Electroreduction to Ethylene <u>Hui Li</u>[1], Peng Wen[2], Dominique S. Itanze[1], Zachary D. Hood[3], Miaofang Chi[3], Lin Jiang[4], Yejun Qiu[2] and Scott M. Geyer[1]; [1]Chemistry, Wake Forest University, Winston-Salem, North Carolina, United States; [2]Department of Materials Science and Engineering, Harbin Institute of Technology, Shenzhen, China; [3]Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee, United States; [4]Institute of Functional Nano and Soft Materials (FUNSOM), Soochow University, Suzhou, China.

Electrochemical CO_2 reduction provides a fascinating pathway to produce valuable carbon-based fuels, but limited by low conversion efficiency, high overpotential for certain selectivity, and sluggish reaction rate. Herein, we report that colloidal hexagonal copper phosphide nanosheets (Cu_3P NSs) show a remarkable onset potential of -0.33 V vs. RHE and achieves a maximum Faradaic efficiency of 62% at -0.88 V vs. RHE for selective CO_2-to-C_2H_4 in a 1:1 volume ratio of $EMIM$-BF_4 ionic liquid and H_2O electrolyte. By contrast, Cu_3P and Cu nanoparticles (NPs) tend to selectively reduce CO_2 to CH_4 and CO/CH_4, respectively. DFT calculation reveals that the delocalized P atoms enhance the stabilization of CO^* intermediate and the stepped facets of (211) on nanosheets favor C-C coupling step rather than the low-index (111) facets on nanoparticle. Moreover, only 8% decay for a high partial C_2H_4 current density of 20.6 mA cm^{-2} at -1.0 V vs. RHE during 24 h stability test is observed on Cu_3P NSs.

3:00 PM ET08.04.04
2-pyridinide as an Active Catalytic Intermediate for CO₂ Reduction on p-GaP Photoelectrodes—Lifetime and Selectivity <u>Shenzhen Xu</u>[1] and Emily Carter[2]; [1]Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey, United States; [2]School of Engineering and Applied Science, Princeton University, Princeton, New Jersey, United States.

The active intermediate responsible for the highly selective reduction of CO_2 to methanol at p-GaP photoelectrodes is currently under debate. Adsorbed 2-pyridinide (2-PyH$^-$*), produced from a two-electron reduction and protonation of adsorbed pyridine (Py*), was recently proposed by Carter and coworkers to be a key intermediate that facilitates hydride transfer (HT) to CO_2 to produce formate. However, the lifetime of 2-PyH$^-$*, most likely controlled by the rate of 2-PyH$^-$* protonation to form adsorbed dihydropyridine (DHP*), is still in question. In this work, we provide evidence for the transient existence of 2-PyH$^-$* on a p-GaP surface by comparing the activation energy for HT to CO_2 to those predicted for 2-PyH$^-$* being protonated to form either DHP* or Py*+H_2 via a hydrogen evolution reaction (HER). We predict that 2-PyH$^-$* situated next to an adjacent surface hydroxide (OH$^-$*) will be the most effective intermediate leading to CO_2 reduction on p-GaP. Predicted high barriers of HER (via either 2-PyH$^-$* or H$^-$*) also explain the high selectivity toward CO_2 reduction observed in experiments.

3:15 PM BREAK

3:45 PM *ET08.04.05
Facet-Controlled Palladium Nanocrystals for Selective Catalysis <u>Younan Xia</u>; Georgia Institute of Technology, Atlanta, Georgia, United States.

For a structure-sensitive reaction, the activity and selectivity of a heterogeneous catalyst can both be enhanced by controlling the type of facet and thus the arrangement of atoms on the surface of nanocrystals. This concept, however, could not be materialized until recently when it became possible to synthesize facet-controlled nanocrystals, including those with high-index facets. In addition, the size of a facet-controlled nanocrystal determines the surface-to-bulk atomic ratio and the proportions of different types of atoms (*e.g.*, vertex, edge, vs. face) . In this talk, I will use palladium (Pd) as an example to illustrate how facet-controlled synthesis has enabled the development of catalysts with enhanced activity and selectivity toward an array of reactions, including formic acid oxidation and selective hydrogenation.

4:15 PM ET08.04.06
Morphological Effects of *In Situ* Reduction of Cuprous Oxide Interfaces for the Electrochemical CO₂ Reduction Reaction <u>Hamed Mehrabi</u>[1], James M. Lowe[2] and Robert H. Coridan[1, 2]; [1]Microelectronics-Photonics, University of Arkansas–Fayetteville, Fayetteville, Arkansas, United States; [2]Chemistry and Biochemistry, University of Arkansas–Fayetteville, Fayetteville, Arkansas, United States.

Copper-based electrodes have shown uncommon promise for catalyzing the electrochemical reduction of CO_2 to a variety of high-value products. Cuprous oxide (Cu_2O) is a particularly interesting starting material, as it can be reduced *in situ* to generate active Cu metal sites on the surface. In recent work, we have demonstrated that the electrochemical properties and nanoscale morphology of photoelectrodeposited Cu_2O can be modified by the illumination conditions during growth. Photogenerated electrons have sufficient energy to induce the formation of Cu metal nano-inclusions in a predominantly Cu_2O

matrix. The presence of Cu disrupts the micro-crystalline growth observed in Cu_2O electrodeposited without illumination. Here, we will describe the experiments that study the effects of photodoping on electrodeposited Cu_2O electrodes for the CO_2 reduction reaction. The transition from oriented microcrystals to disordered nanocrystalline films with increasing light intensity during growth has a significant effect on the reduction of the electrode surface. This alters the dynamics and electrochemical behavior of the electrode for CO_2 reduction. We will also explore how chemical modifications to the surface, such as the thermal oxidation of the Cu nano-inclusions or the addition of a co-catalyst, can affect the branching ratios and dynamics of electrocatalysis. The work outlined here helps to inform further use of electrodes prepared by the *in situ* reduction of Cu_2O for this application.

4:30 PM ET08.04.07
Controlling Proton and Electron Transfer to Molecular Electrocatalysts for Enhanced Selectivity <u>Christopher Barile</u>, Rajendra Gautam and Jason Mennel; University of Nevada, Reno, Reno, Nevada, United States.

The O_2 reduction reaction and the CO_2 reduction reaction are both central to important renewable energy devices. Since both reactions require the transfer of multiple electrons and protons, they can proceed by a variety of mechanisms depending upon the relative rates of these transfer events. We have developed electrode architectures that enable the modulation of proton and electron transfer kinetics to molecular catalysts such that the selectivity of catalysts can be improved. These electrodes are comprised of a metal-centered catalyst such as a Cu-triazole or an Fe-porphyrin attached via a self-assembled monolayer (SAM), which is then covered by a proton-permeable membrane. By altering the identity of the SAM, the kinetics of electron transfer to the bound catalyst can be tuned. Changing the proton permeability of the membrane enables control over the kinetics of proton transfer to the catalyst.

One of the major challenges in designing catalysts for both the O_2 and CO_2 reduction reactions is selectivity. Using a membrane-modified electrode, we demonstrate that the selectivity of a Cu-based O_2 reduction catalyst can be improved by controlling proton transfer rates such that the catalyst produces exclusively water. In contrast, the same Cu catalyst produces ~10% deleterious H_2O_2 side product when proton transfer is unregulated. We also explore how altering proton and electron transfer kinetics affects the selectivity of molecular CO_2 reduction catalysts.

4:45 PM ET08.04.08
Electrochemical CO_2 Reduction to CO on Au—Isolating the Intrinsic Activity of the Most Common Crystal Facets <u>Brian J. Seger</u>[1], Stefano Mezzavilla[1,2], Ifan E. Stephens[2] and Ib Chorkendorff[1]; [1]Technical University of Denmark, Kongens Lyngby, Denmark; [2]Department of Materials, Imperial College London, London, United Kingdom.

Due to the drastic drop in renewable electricity prices, electrochemical CO_2 reduction has received renewed interest. While CO_2 reduction can lead to a wide variety of products, almost all go through a CO intermediate, thus understanding the 2 electron transfer reaction of CO_2 to CO is important not just for CO production, but also for products such as ethylene, ethanol, methane and others. Au has been shown to be the most active electrocatalyst for CO production, however major fundamental knowledge on this reaction has yet to be discovered. While most works focus on highly active nanostructured Au electrodes, there has yet to be a comprehensive study on the intrinsic electrochemical activity of individual Au facets.

This talk will discuss our work on the electrochemical conversion of CO_2 to CO on single crystal Au <100>, <111>, <110>, and <211> facets as well as polycrystalline Au. Our results show a 25 fold difference between the least and most active crystal facets. All facets follow approximately the same Tafel slope between the tested potentials of -0.6 V to -0.8 V vs. RHE. Pb underpotential deposition (UPD) was used to deposit a monolayer of Pb on the Au gold surface to determine surface area. However, the potential at which Pb UPD deposits is facet dependent. By setting a correct potential we could selectively deposit lead on a given facet. While PB UPD favored depositing on the most active sites, we still could gain fundamental catalysis knowledge. On polycrystalline Au, 20% of a monolayer of Pb yielded a 50% decrease in CO production, but only a 30% decrease in H_2 production. 50% of a Pb monolayer on Au yielded a 95% decrease in CO production, but only a 50% decrease on H_2 production. The decrease in CO production as a function of Pb coverage indicated that not only could we passivate the most active sites, but also that the facet dependent activity was quite different for CO production versus the competing H_2 evolution side reaction.

To further utilize Pb UPD to isolate sites we reinvestigated one of our least active facets, Au <111>. Single crystals are never completely flat and thus there are always a small percentage of step sites. We used selective Pb UPD to deposit 4% of a monolayer in the attempt to passivate these sites. This led to a 50% decrease in CO activity, but the same H_2 evolution activity. Covering the Au <111> with 15% of a monolayer led to a 90% drop in CO activity, but the same H_2 evolution activity. These results suggest that the intrinsic activity of the least active facets is probably much lower than measured and the experimental results are actually dominated by a small number of highly active defect sites. While these results focus on Au, no single crystal is defect free. Thus these results may lead us to also question whether there are other situations where the non-optimal facets for a given reaction are actually much less active than originally thought.

SESSION ET08.05: Poster Session I: Carbon-Related Catalysis
Session Chairs: Gugang Chen, Yu Han, Yugang Sun and Lin Wang
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET08.05.02
***In Situ* Exsolution of Nickel Nanoparticles for Efficient Carbon Dioxide Splitting and Methane Conversion to Syngas in Ceramic Membrane Reactors** <u>Georgios Dimitrakopoulos</u>[1,2], Ahmed F. Ghoniem[3] and Bilge Yildiz[1,2]; [1]Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; [2]Nuclear Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; [3]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

In this research, we investigate the process of metal catalyst nano particle exsolution on perovskite oxides to catalyze efficiently the co-production of carbon dioxide (CO_2) to carbon monoxide (CO) and methane (CH_4) to syngas. Conversion of CO_2 has attracted significant interest due to the global effort for greenhouse gas emission reduction. A promising candidate for CO_2 reduction is its thermochemical splitting to CO using ceramic membrane reactors, which employ mixed ionic-electronic conducting perovskite materials. At elevated temperatures (~900C), the oxygen deficiency of perovskites allows the conversion of CO_2 to CO on one side of the material due to electrochemical surface reactions. Ionic conduction enables the transport of the incorporated oxygen ions to the other side where a fuel, such as CH_4, is oxidized to produce syngas, which serves as an intermediate for the synthesis of added-value

chemicals.

Stable materials in the presence of CO_2 and fuel exist but the performance is low. For surface reaction limited materials a catalyst must be applied on the gas-membrane interfaces to accelerate the kinetics, but catalyst agglomeration into large clusters at high temperatures reduces the long-term performance. In addition, carbon poisoning can deactivate or even detach the particles from the surface.

In this work, we use exsolution to grow Nickel (Ni) nanoparticles on the surface of a perovskite host. Exsolution has been shown to deliver well-distributed nanoparticles, while the anchored nature of the catalyst reduces agglomeration and carbon poisoning. To investigate exsolution, $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ (LCF), a stable perovskite under both oxidizing and reducing conditions, was doped with 5% Ni in the B-site, while a 5% A-site deficiency was introduced to facilitate exsolution. Compared to other exsolution studies using H_2 to trigger the metal reduction prior to the experiments, we show that exsolution on $La_{0.85}Ca_{0.1}Fe_{0.95}Ni_{0.05}O_{3-\delta}$ pellets does not require any pre-reduction of the perovskite, but can rather take place *in-situ* at the onset of the reactions using pure CO_2 on one side of the material and CH_4 on the other. The onset of exsolution at different temperatures and CH_4 concentrations was systematically examined. We show that no exsolution happens at 900C, while exsolution is triggered at 950C and 1000C using an inlet CH_4 mole fraction of 10% and 4%, respectively. At 1000C, we observe an order of magnitude increase in the CO production rate (J_{CO}), CH_4 conversion and syngas yield compared to LCF at the same conditions. Lowering the temperature to 900C after exsolving at 1000C reduces J_{CO} and the fuel conversion by 50%, however, the values are still 5 times higher compared to LCF.

Our results set the basis for extension of the concept to other energy related applications, such as solid oxide fuel/electrolysis cells and chemical looping, exsolution of other transition metals and for a broad range of different conversions of industrial interest.

ET08.05.03

Enhanced Hydrocarbon Trapping Over *C*-Oriented Array-Structured ZSM-5 Integrated on Cordierite <u>Junfei Weng</u>[1,2], Jie Chen[1,2], Avinash M. Dongare[1,2] and Puxian Gao[1,2]; [1]Materials Science and Engineering, University of Connecticut, Storrs, Connecticut, United States; [2]Institute of Material Science, University of Connecticut, Storrs, Connecticut, United States.

Compared to traditional wash-coated powder-form catalysts, array ensembles of one-dimensional (1D) nanostructures possess stronger gas-solid phase interaction, larger surface area and enhanced materials utilization efficiency [1, 2]. Unlike a layer of ZSM-5 film (MFI framework) grown on cordierite[3], array-structured ZSM-5 with *c*-orientation was synthesized by a secondary-growth hydrothermal method. Although the BET surface area and pore size distribution were similar with traditional film, the hydrocarbon trapping efficiency over as-synthesized ZSM-5 arrays was significantly improved. The higher extent of the exposed *a*- and *b*- planes to reactant molecules could facilitate the catalytic reactions and adsorptions by improving the mass transportation. The novel ZSM-5 array-structure could provide a promising class of structured devices for hydrocarbon trapping and separation. Furthermore, first-principles Density Functional Theory (DFT) calculations are performed to investigate the Al substitution site preference on the ZSM structure, as well as the adsorption energetics of the reactant molecules.

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ET08.05.04

Sulfur Segregation and Surface Site Vacancy Compensation During Methanol to Methoxy Reactions on MoS$_2$ <u>Prescott E. Evans</u>[3], Hae K. Jeong[1], Zahra Hooshmand[2], Duy Le[2], Takat B. Rawal[2], Sahar N. Alvillar[4], Ludwig Bartels[4], Talat S. Rahman[2] and Peter Dowben[3]; [1]Daegu University, Gyeongsan, Korea (the Republic of); [2]University of Central Florida, Orlando, Florida, United States; [3]University of Nebraska–Lincoln, Lincoln, Nebraska, United States; [4]University of California, Riverside, Riverside, California, United States.

Coverage dependent, sulfur vacancy defect formation on the $MoS_2(0001)$ basal plane resulting from the adsorption of methanol on MoS_2 and its subsequent conversion into methoxy, was investigated utilizing scanning tunneling microscopy, photoemission, photoluminescence, and modeled by density functional theory (DFT). The adsorption of methanol on MoS_2 at 110 K followed by annealing near 350 K or the adsorption of methanol on MoS_2 at 350 K results in the formation of numerous point defects at the MoS_2 basal plane. Larger patch defects, nominally ~2 nm in size as well as line defects on the MoS_2 sample surface become increasingly apparent with multiple cycles of methanol exposure and annealing. X-ray spectroscopy studies of the exposure of MoS_2 to methanol are consistent with a conversion to methoxy, and the production of defects, based on the reaction kinematics, and significant shifts in oxygen binding energies. Additionally, shifts in sulfur binding energy and temperature dependent sulfur to molybdenum integrated XPS intensity ratios near the critical 350 K formation temperature indicate sulfur segregation to the surface and compensation of surface vacancy sites. The experimental results indicate a small but persistent activation energy for the reaction consistent with DFT predicted energetics. The energy favorability of coinciding defect creation and methoxy formation is also suggested by DFT kinematics. A strongly bound methanol surface species is not favored on the defect free MoS_2 surface.

ET08.05.05

Developing Descriptor of Keggin Heteropolyacid for Application in Biomass Conversion Catalysis <u>Ejaz Ahmad</u>, Tuhin Suvra Khan, Md. Imteyaz Alam, Kamal K. Pant and M. Ali Haider; Indian Institute of Technology Delhi, New Delhi, India.

Bio-renewable resources have great potential to supersede conventional fossil fuel to meet energy and chemicals demands. Nevertheless, most of the processes employed for biomass conversion essentially requires the presence of an acid catalyst for sustainable production of fuel and chemicals. In this context, catalysts belonging to the family of Heteropolyacid (HPA) are extensively used owing to their excellent activity in biomass conversion reactions[1]. Albeit a wide range of HPA's have been classified based on their geometrical arrangements, Keggin HPA's represented by general formulae $[XM_{12}O_{40}]^{n-}$ have prevalence in industrial applications owing to their super acidic nature, high thermal stability at elevated temperatures in liquid phase reactions and ease of synthesis as compared to other HPA's. In general, the central atom X can be either P, Si, Ge, B, or Al whereas the heteroatom M can be either W^{6+} or Mo^{6+} or V in which 12 linked octahedra containing addenda atoms ($M_{12}O_{36}$) surrounds a central tetrahedron (XO_4^{n-}). Interestingly, the higher activity of Keggin HPA's is attributed to the combined effect arising from their stability, acidity, and structural accessibility, nevertheless no conclusive evidence has been suggested for the rational design of Keggin HPA's. Moreover, the effect of changing central atom X on the activity of Keggin HPA's is yet to be explored. Therefore, we have employed both theoretical and experimental approach to conclude deprotonation energy (DPE) as a suitable descriptor for rational design and selection of Keggin HPA's. In this regard, Density functional theory (DFT) have been employed to calculate the DPE of known Keggin HPA's with heteroatom W and Mo as well as propose the novel and futuristic catalysts by changing the central atom with elements from group 13-17 in the periodic table. Parallelly, esterification reactions have been performed with biomass-derived levulinic acid to produce additives for "green gasoline"[2] in the presence of phosphotungstic acid and phosphomolybdic acid to validate the theoretical results. Interestingly, it was found that activity of Keggin HPA's is a direct function of their DPE and difference in DPE remained constant when same elements from group 13-17 of the periodic table were put as central atom X in each of the Keggin HPA's with W^{6+} and Mo^{6+} heteroatom. Nevertheless, change in the central atom of the

Keggin HPA's with W^{6+} and Mo^{6+} heteroatom caused a significant change in individual DPE's, yet the overall difference in DPE remained constant when same central atoms were placed in both the catalysts. Interestingly, experimental results suggested similar trend and difference in activation barriers of both the catalysts with same central atom remained same even though esterification reactions were performed in different alcohols. Besides several tools and techniques such as XRD, BET, FT-IR, SEM, TEM, HPLC, GC-FID have been used for the characterization of catalysts and the product.

ET08.05.06
Deciphering Graphene Supported Metal-Nitrogen Active Center on CO_2 Reduction Reaction—Structure, Magnetic and Catalytic Properties from First Principle Simulations <u>Mingjie Liu</u>[1], Guangjin Wang[2, 1] and Qin Wu[1]; [1]Brookhaven National Laboratory, Upton, New York, United States; [2]College of Chemistry and Materials Science, Hubei Engineering University, Xiaogan, China.

The dispersing single atom catalysts have been developed recently and reveal highly catalytic activities. The materials of single transition metal embedded in nitrogen-doped graphene display great potential as the catalysts for many reactions. For example, single atomic Ru in nitrogen-doped graphene exhibits excellent activity for oxygen reduction reaction [1]; single Fe Co and Ni in MN_4C_4 moiety shows tunable electrocatalytic activity in oxygen evolution reaction [2], and Fe dispersed on nitrogen-doped graphene has been demonstrated as an efficient electrocatalyst for CO_2 reduction reaction [3]. In those systems, the single atom center contributes as the active site, while the interaction between the single atom and the substrate is crucial. In our study, we applied density functional theory (DFT) simulations to elaborate different nitrogen doping concentrations and configurations surrounding the metal center. The stability of graphene supported metal-nitrogen active center, the magnetic and catalytic properties have been explored. Take CO_2 reduced into CO on Fe-N-graphene system as an example, our results show that the chemical environment around the single atom is critical, and the metal center and nitrogen atoms nearby determine the catalytic performance synergistically. Regulating single atom coordination tunes catalytic activity which will be instrumental for designing catalysts with the desired properties.

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ET08.05.07
Pt/CeO₂-1D Catalysts for Steam Reforming of Methanol <u>Raul Perez-Hernandez</u>[1], Albina Gutiérrez Martínez[1], Arturo Claudio-Piedras[1], B.C. A. Alcántar-Vázquez[2] and R. M. Ramírez-Zamora[2]; [1]Instituto Nacional de Investigaciones Nucleares, Ocoyoacac, Mexico; [2]Instituto de Ingeniería, Universidad Nacional Autónoma de México, Mexico, Mexico.

In this work, we investigated the effect of the Pt-precursor, on the catalytic properties of the Pt/CeO_2-NR catalysts for H_2 production. The CeO_2-1D support was synthesized by the hydrothermal method, using a (NaOH) solution 10 M as precipitating agent [1,2]. The active phase Pt 0.5% (w/w) was impregnated to the catalytic support CeO_2-1D by impregnation method. The Pt/CeO_2-(X) catalysts were characterized by N_2 adsorption, XRD, TPR, TEM and EDS. Afterwards, the activity and selectivity in the SRM reaction was evaluated using a commercial system RIG-100-ISRI in a temperature range of 200 - 450 °C at atmospheric 204 Pressure. The reaction products were analyzed using a Gow-Mac 580 Gas chromatograph with a thermal conductivity detector equipped with a two column system. The characterization results showed a specific surface area of 89 and 95 m2/g respectively for the support and the best Pt/CeO_2-(Nit) catalyst. The XRD results showed the typical diffraction pattern of the fluorite cubic structure for CeO_2 and a peak associated with Pt is not detected, which confirms a small particle size and a high dispersion of the metal. TPR profiles of the Pt/CeO_2-(X) catalysts, showed peaks of H_2 consumption associated with the reduction of PtO_x to Pt^0 at low temperature as well as, a partial reduction of surface ceria from Ce^{4+} to Ce^{3+}, associated to the presence of the noble metal on the surface of the support [3]. Catalytic activity in the steam reforming methanol reaction, the Pt/CeO_2-(Nit) catalyst exhibited a higher catalytic activity reaching a conversion yield of 99% at 350 °C, as well as higher H_2 production. In addition, it exhibited a higher yield, as well as the lower production of CO and CH_4. None of the synthetized catalysts exhibited a significant deactivation over the evaluated time period.

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ET08.05.08
Tuning of Activity and Selectivity of Ni/(Al)-SBA-15 Catalysts in Hydrogenation of Naphthalene Tatiana Klimova, Haydee Vargas Villagran and <u>Mark Eugenii Martinez-Klimov</u>; Universidad Nacional Autonoma de Mexico, Ciudad de México, Mexico.

In the present work, two series of nickel catalysts with 4 wt. % of Ni loading were evaluated in the hydrogenation of naphthalene in order to elucidate the effect of surface acidity (Brønsted or Lewis) and preparation method used on the catalyst's activity and selectivity. On the one hand, two supports, SBA-15 silica and Al-SBA-15 with Si/Al molar ratio = 30, were synthesized by hydrothermal method in order to obtain 2D nanostructured supports with and without Brønsted acidity. On the other hand, Ni catalysts were prepared by the incipient wetness impregnation method using two different nickel precursors: nickel nitrate (NN) and a Ni-EDTA complex (ED). We were also interested in the effect of the preparation method on the nickel dispersion and the acidity of the prepared catalysts.
Prepared catalysts were labeled as: Ni/SBA(NN), Ni/SBA(ED), Ni/AlSBA(NN) and Ni/AlSBA(ED). Characterization of the catalysts was performed by nitrogen physisorption, powder X-ray diffraction, temperature programmed reduction, temperature programmed desorption of ammonia, infrared spectroscopy of adsorbed pyridine and high resolution transmission electron microscopy.
Characterization results showed that both SBA-15 and Al-SBA-15 supports had attractive textural properties. However, the characteristic hexagonal pore arrangement of SBA-15 was not preserved in the Al-SBA-15 support. The IR of adsorbed pyridine allowed us to confirm and quantify the Brønsted (B) and Lewis (L) acid sites present in the Ni/SBA and Ni/AlSBA catalysts prepared from both precursors used, being the Ni/SBA(ED) catalyst the most acidic one. Catalytic activity of the catalysts in hydrogenation of naphthalene increased in the following order: Ni/SBA(NN) < Ni/AlSBA(NN) < Ni/AlSBA(ED) < Ni/SBA(ED). Acidity of the catalysts and the dispersion of the reduced Ni nanoparticles also affected the selectivity of the catalysts to decalins (completely saturated products). Both catalysts prepared using a Ni-EDTA complex (Ni/SBA(ED) and Ni/AlSBA(ED)) showed high selectivity to decalins, whereas those prepared from a nickel nitrate solution (Ni/SBA(NN) and Ni/AlSBA(NN)) were selective for tetralin production. Therefore, the nickel precursor used and the support's acidity affected the activity and selectivity of the tested Ni catalysts.

ET08.05.09

Enhanced CO_2 Reduction in Lead-Free Perovskite $Cs_3Sb_2Br_9$ Nanocrystals—Performance and Selectivity <u>Chang Lu</u>, Xiao Ma, Dominique S. Itanze, Hui Li and Scott M. Geyer; Wake Forest University, Winston Salem, North Carolina, United States.

The last decade has witnessed the burgeoning development of halide perovskite materials with a significant focus on solar and light-emitting diodes applications. However, halide perovskites have received less attention as a catalyst for energy application, for example, water splitting and CO_2 reduction reaction. Moreover, the development for Pb-free perovskite is highly desired for all applications. To this end, in our work, we developed a facile synthesis method for Sb-based halide perovskite nanocrystals (NCs). These exhibit structure uniformity and high thermal stability, with only a 2 % weight drop (attributed to the ligand loss) under 200 °C annealing. For solar driven CO_2 reduction the $Cs_3Sb_2Br_9$ produces 400 umol(CO)/g, a 40-fold more improvement in CO per gram compared to $CsPbBr_3$. Interestingly, the use of Pb-based perovskite also generates CH_4, which is not observed in Sb-based reaction batch, and we will present DFT calculation results to shed further light into the differences in reaction mechanism for the Pb-based and Sb-based system. This brings new insights into the emerging field of Pb-free perovskite alternatives and perovskite materials for catalytic applications.

ET08.05.10

Development of Catalytic La-Based Perovskite Redox Materials for Solar Thermochemical Conversion of CO_2 into Syngas <u>Rahul R. Bhosale</u> and Gorakshnath Takalkar; Department of Chemical Engineering, Qatar University, Doha, Qatar.

The energy consumption of the world today is around 15TW and it is expected that it will raise up to 30TW by the year 2050. In addition to this, due to the excessive utilization of fossil fuels (for the production of required energy), the concentration of CO_2 in the environment increases rapidly. The production of syngas (which can be used as a precursor for the production of liquid transportation fuel) by using H_2O, CO_2, and solar energy provides a promising path to solve the issues associated with the utilization of fossil fuels and increase in the CO_2 concentration.
Direct production of syngas via thermolysis of H_2O and CO_2 is possible, however it needs a very high temperature and chances of forming a gaseous explosive mixture of H_2 and O_2 is also very high. Utilization of solar driven metal oxide based catalytic thermochemical H_2O and CO_2 splitting cycle reduces the requirement of higher temperatures and avoids the formation of explosive gas mixture.
Various non-volatile redox materials have been investigated towards the thermochemical production of solar fuel via H_2O and CO_2 splitting reactions. In addition to the ferrite and ceria based materials, recently the researchers are focused towards perovskite based redox materials as an active catalyst for the solar splitting process. In particular, La-based perovskite materials are of particular interest as they are capable of producing higher amounts of O_2 and H_2/CO at lower operating temperatures as compared to ceria and ferrites.
In this study, a variety of La-based perovskite materials were synthesized using combustion method and tested towards multiple H_2O/CO_2 splitting cycles using a high temperature themrogracimetric analyzer. It is very important to note that in most of the previous investigations the maximum number of cycles performed in case of La-based perovskites are 3 to 4. Hence, this study has a uniqueness that it tested the La-based perovskites in more than 50 thermochemical cycles.

ET08.05.11

Enhancement of CO_2 Reduction Activity Under Visible Light Irradiation Over Zn-Based Metal Sulfides by Combination with Ru-Complex Catalysts <u>Tomiko M. Suzuki</u>[1], Tomoaki Takayama[2], Shunsuke Sato[1], Akihide Iwase[2], Akihiko Kudo[2] and Takeshi Morikawa[1]; [1]Toyota Central R&D Labs Inc, Nagakute, Japan; [2]Tokyo University of Science, Tokyo, Japan.

The reduction of CO_2 to obtain useful energy-rich chemicals utilizing photocatalysts has attracted attention as a potential means of artificial photosynthesis operating under sunlight irradiation. Although the use of powdered systems for CO_2 reduction is challenging owing to the inherent difficulty in achieving the highly selective reaction of CO_2 in solution, the system is attractive as a practical cost-effective system to utilize sunlight [1]. In this regard, we have demonstrated visible light-induced selective reduction of CO_2 to HCOOH using metal-complex/semiconductor hybrid photocatalyst consisting of a Ru-complex and a p-type metal oxide semiconductor particles (N-doped Ta_2O_5) in acetonitrile (MeCN)/triethanolamine (TEOA) solution with quantum efficiencies of 1.9% and more [2, 3]. Among various semiconductors, Zn-based sulfide are also attractive semiconductor for the hybrid photocatalyst, because ZnS possesses a relatively negative conduction band minimum (E_{CBM}) formed by the Zn 4s4p orbitals, which facilitates the electron transfer from the CBM of the semiconductor to the metal-complex.
In the present study, the powdered Zn-based sulfides which were reported to be active for sacrificial H_2 evolution, were investigated in combination with various Ru-complex catalysts with regard to the promotion of visible light driven CO_2 reduction. Hybrid photocatalysts consisting of a Ru-complex and a semiconductor anchored by organic groups were prepared by an adsorption method. Photocatalytic CO_2 reduction was performed in MeCN/TEOA solution under visible light ($\geq$410 nm) irradiation. The photocatalytic activities were largely dependent on the basic characteristics of the Ru-complex and the metal sulfide. The results demonstrate that several of semiconductors improve the photocatalytic CO_2 reduction selectivity of the hybrid system, and that n-type $(AgIn)_{0.22}Zn_{1.56}S_2$ [4] and ZnS:Ni (Ni 0.2 mol%) [5] linked with a neutral Ru-complex containing phosphonate anchors ([Ru(dpbpy)(CO)$_2$Cl$_2$, dpbpy: 4,4'-diphosphonate-2,2'-bipyridine) exhibited highest turnover number with above 100 after 16 h irradiation. The carbon source for the HCOOH evolved in the reaction over the hybrid photocatalysts was confirmed to be CO_2 based on $^{13}CO_2$ analyses [6].
These results suggest that Zn-based metal sulfide are potential candidates for use in powdered semiconductor/metal-complex systems for active and selective CO_2 photoreduation. Our results also suggest that future success in powdered Z-scheme systems utilizing water as an electron donor and proton source.

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ET08.05.12

High Yield Preparation of Two-Dimensional Cu Nanocatalysts for Carbon Dioxides Reduction Reaction <u>Shutang Chen</u> and Gugang Chen; Honda Research Institute USA Inc., Columbus, Ohio, United States.

Cu-based nanostructures have been explored for catalyzing CO_2 electroreduction due to their lower working function and cost, and higher earth-abundancy. However, the practical application of CO_2 electroreduction reaction requires Cu catalysts hold a high percentage of exposed surface atoms, which can improve the utilization efficiency of catalysts and products selectivity. Here we reported a high temperature reduction method to prepare Cu nanosheets in hydrophobic system. The feeding molar ratio of trioctyphosphine/Cu ion precursor plays a critical role for the formation of Cu nanosheets. The shape of Cu nanosheets were controlled by adjusting the reaction interval, the types of Cu ion precursor, and the purity of trioctylphosphine. The size and thickness of Cu nanosheets are variable from 50 nm to 13 μm and 15 nm to 500 nm, respectively. Moreover, pure Cu nanosheets are stable in solution for more than three months. As a result of high percentage {111} of surface area, these nanosheets as catalysts have demonstrated the enhanced catalytic activity and selectivity to convert CO_2 to fuels.

ET08.05.13
CO₂ Activation on Defective MoS₂ Surfaces for CO₂ Photo-Reduction Applications <u>Yi-Fan Huang</u>[1], Hsiang-Ting Lien[2], He-Yun Du[2], Ying-Ren Lai[2], Ting-Li Lin[2], Yu-Chung Chang[2], Michitoshi Hayashi[2], Li-Chyong Chen[2] and Kuei-Hsien Chen[1, 2]; [1]Academia Sinica, Taipei, Taiwan; [2]National Taiwan University, Taipei,, Taiwan.

CO_2 activation on catalyst surface is the very first and critical step in CO_2 photo conversion into valuable chemicals. However, CO_2 is a thermodynamically stable and chemically inert molecule. How to select and treat the photocatalyst surface to enhance the chemisorption of CO_2 and improve its reactivity remains a scientific challenge. Photocatalyst surfaces with functional modifications, such as creating atomic vacancies on surface by H_2 plasma treatment are promising candidates for this purpose.
This report reveals the essential first step of CO_2 adsorption/activation on a defective MoS_2 surface by using near ambient pressure X-ray photoelectron spectroscopy (APXPS), scanning tunneling microscope (STM) experiments and density functional theory (DFT) calculations. These studies not only suggest the atomic sulfur defects on the MoS_2 surface particularly play a critical role in activating CO_2 to form chemisorbed CO_2, but also provide further mechanistic information for the intermediates species, thus guiding the design of better photocatalyst in the future.

ET08.05.14
Nanoscale Chemical Reactor Based on Localized Surface Plasmon Energy in Environmental Transmission Electron Microscope <u>Canhui Wang</u>[1, 2], Wei-Chang D. Yang[1, 2] and Renu Sharma[1]; [1]National Institute of Standards and Technology, Gaithersburg, Maryland, United States; [2]University of Maryland, College Park, Maryland, United States.

Miniaturizing chemical processes in a research context has many advantages, including the ability to examine the reaction at atomic resolution, the reduced usage of costly and/or hazardous chemical reagents, and the ability to be integrated into analytical devices. [1-2] However, current efforts towards miniaturizing chemical processes have been limited by the achievable minimum reaction volume and the lack of precision control over the reaction locations. Herein, we demonstrate a nanoscale chemical reactor, utilizing localized surface plasmon (LSP) resonance as the energy source, in an aberration-corrected environmental transmission electron microscope (ETEM). This approach allows us to confine the reaction within the proximity of the nanoparticle while taking advantage of the high spatial resolution measurement capability of the electron microscope to monitor the reaction.

Plasmonic nanoparticles, such as Au or Al, are placed in a reactive environment inside the ETEM. The composition and partial pressure of the gases are controlled by a gas handling system and analyzed using a residual gas analyzer. Electron energy-loss spectrum (EELS) imaging is used to acquire both elemental and LSP maps from the same nanoparticle. This allows the mapping and quantification of different gas adsorption on the nanoparticle surface. The energy required for the reaction of interest is provided by the LSP resonance excited by the high energy electron beam. The reaction location is confined within the proximity of the nanoparticle due to the local field enhancement of the LSP resonance. Using a non-negative matrix factorization machine learning algorithm, we map the energy transfer pathways from the electron beam to the nanoparticle at nanometer spatial resolution and 0.08 eV energy resolution. The temperature distribution of the nanoparticle is monitored with few-nanometer spatial resolution using time-resolved EELS. Reaction processes, including morphological changes and transitions between crystalline phases, are monitored using atomic-resolution movies. By utilizing LSP resonance to initiate the reaction, we show that chemical processes can be confined within a nanometer scale volume, and modulated by electron flux. Important parameters of the reaction, including composition of the reactants, adsorption of gases, transfer of energy, change of temperature, as well as reaction dynamics, can be monitored with nanometer or atomic resolution. Our approach paves the way to understanding a wide range of chemical reactions at the atomic scale. [3]

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ET08.05.15
Co-Based Bimetallic Nitride Flakes Grown on N-Doped Carbon Nanofibers as an Efficient Bifunctional Electrocatalysts for Oxygen Evolution and Reduction Reactions <u>Seokwon Song</u> and Il Doo Kim; Korea Institute of Science and Technology, Daejeon, Korea (the Republic of).

In recent years, oxygen electrocatalysis has attracted great attention due to the desire for many energy storage or conversion devices such as metal-air batteries, fuel cells, and water electrolyzer. However, the sluggish kinetics of oxygen-based electrochemical reactions hinder the efficiency. Although, noble metal-based electrocatalysts are widely used to reduce the energy loss, their high cost is critical limitation for broad and practical applications. Thereby, there are many trials to replace noble electrocatalysts with highly efficient and inexpensive non-noble metal-based oxygen electrocatalysts by employing transition metals such as Co, Mn, and Ni. Especially, transition metal nitrides such as Co4N are considered as a promising candidate material due to their superior electrical conductivity and chemical stability. Furthermore, bimetallic compounds can further induce oxygen-based catalytic activity by effective tuning of d-band structure.
Here, we proposed facile synthetic method for Co-based bimetallic nitride flakes grown on n-doped carbon nanofibers (Co-M-N@NCNF, M = Ni, Mn, Fe) by using Co-based bimetallic leaf like zeolite imidazole framework (ZIF-L), which is composed of cobalt and other metal ions (Ni, Mn, Fe) with organic linkers. Firstly, electrospun Polyacrylonitrile (PAN) nanofibers were treated by NaOH for smooth growth of Co-based bimetallic ZIF-L. Followed by subsequent stabilization and nitridation process under ammonia gas, it converted to Co-M-N@NCNF. The Co-M-N@NCNF electrodes showed remarkable electrochemical properties for both oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). We demonstrate enhanced catalytic activity of Co-M-N@NCNF for both OER and ORR in terms of overpotential, Tafel slope, and charge transfer. These are mainly attributed to the synergistic effects from Co-based bimetallic compounds with nitrogen atoms. Also, unique structure of active two dimensional flakes grown on one dimensional carbon nanofiber offered more exposed active sites and high surface area. The proposed strategy of ZIF-derived bifunctional nanomaterials provides prospects for developing highly active electrocatalysts in electrochemical energy devices.

SESSION ET08.06: Hot-Electron-Driven Catalysis
Session Chairs: Yuzi Liu and Yugang Sun
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 306

8:30 AM *ET08.06.01

Minimizing Energy Use for Surface Reactions by Using Both Light and Heat—Plasmonic Catalysts and Non-Plasmonic Catalysts Enabling Photoexcitation of Adsorbates Chanyeon Kim and <u>Hyunjoo Lee</u>; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Many heterogeneous catalytic reactions occur at high temperatures, which may cause a large energy cost, poor safety, and thermal degradation of catalysts. Here, we propose a "light-assisted surface reaction", which catalyze the surface reaction using both light and heat as an energy source.
Plasmonic metal nanoparticles absorb light energy and release the energy through radiative or non-radiative channels. Surface catalytic reaction would take advantage of the non-radiative energy relaxation of plasmon with enhanced activity. Particularly, binary nanoparticles are interesting because diverse integration would be possible consisting of plasmonic part and catalytic part. Herein, we demonstrated ethanol dehydrogenation under light irradiation using Ag-Ni binary nanoparticles with different shapes, snowman and core-shell, as plasmonic catalysts. The surface plasmon formed in the Ag part enhanced the surface catalytic reaction that occurred at the Ni part, and the shape of the nanoparticles affected the extent of the enhancement. The surface plasmon compensated the thermal energy required to trigger the catalytic reaction. The absorbed light energy was transferred to the catalytic part by the surface plasmon through the non-radiative hot electrons.
Non-plasmonic conventional metal catalysts such as Ru, Rh, Pt, Ni, and Cu were tested for CO_2 hydrogenation, and Ru showed the most distinct change upon light irradiation. CO_2 was strongly adsorbed onto Ru surface, forming hybrid orbitals. The energy gap between the HOMO and LUMO was reduced significantly upon hybridization. Hot electrons could be generated by jumping the shortened energy gap upon light irradiation, enhancing CO_2 dissociation. The light-assisted CO_2 hydrogenation used only 37% of the total energy with which the CO_2 hydrogenation occurred using only thermal energy. The CO_2 conversion could be turned on and off completely with a response time of only 3 min, whereas conventional thermal reaction required hours to terminate the CO_2 conversion. These unique features can be potentially used for on-demand fuel production with minimal energy input.

9:00 AM ET08.06.02

Investigating Light Enhanced Catalytic Lifetimes and Activities Over Plasmonic Au Catalysts in the CO Oxidation Reaction <u>Peter Novello</u>[1], Pani Varanasi[1, 2] and Jie Liu[1]; [1]Duke University, Durham, North Carolina, United States; [2]U.S. Army Research Office—Materials Science Division, Research Triangle Park, North Carolina, United States.

Light interacting with catalysts via surface plasmon resonances has the potential to dramatically improve catalytic reactions by photothermal heating and hot-electron transfer. This project investigates plasmonic light enhancement of the CO oxidation reaction over supported Au catalysts. Optimization of this reaction empowers removal of poisonous CO at room temperature which has the potential to improve human health. This reaction also features a negative activation energy which leads to a minimum in the temperature dependent conversion curve near 80 °C. Results show that catalytic activity around room temperature doubled under light and catalyst lifetimes increased by a factor of 5. From these results, an analysis of the relative magnitude of the photothermal catalytic enhancement and non-thermal catalytic enhancement effects were performed by utilizing the temperature dependent change from positive to negative activation energy. This demonstrated that the effect of photothermal heating is more substantial and that both effects enhance the reaction rate and improve catalytic lifetimes. From further experiments coupling light induced desorption of CO_2 to the regeneration of catalytic activity, a mechanism for light enhancement on gold catalysis is proposed. Light reactivates the catalyst by removing surface carbonates which otherwise act as poison, allowing for dramatically increased catalytic activity and lifetime to demonstrate a new path for highly active CO oxidation.

9:15 AM ET08.06.03

Revelation of Active Sites for Room Temperature CO Disproportionation on a Gold Nanoparticle Driven by Electron Beam Excited Localized Surface Plasmon Resonance <u>Wei-Chang D. Yang</u>[1, 2], Canhui Wang[1, 2], Lisa A. Fredin[3], Henri Lezec[1] and Renu Sharma[1]; [1]CNST, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; [2]Maryland NanoCenter, University of Maryland, College Park, Maryland, United States; [3]Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Recent reports of hot electron-induced dissociation of small molecules, such as hydrogen[1, 2], demonstrate the potential of using plasmonic nanostructures to convert light into chemical energy for low-temperature catalytic reactions. Theories have typically assumed that plasmonic catalysis is mediated by the optical excitation of energized electrons or holes through the dephasing of localized surface plasmon (LSP) modes on Au, Al, or Ag nanoparticle and subsequent charge transfer from the metal to the adsorbed gas molecules[3]. However, LSP-induced gas molecule dissociation at a sub-nanoparticle scale has not been resolved to date.

Here, we exploit the LSP resonance of a triangular Au nanoprism excited by an electron beam to drive CO disproportionation ($2CO \rightarrow C + CO_2$, known as the Boudouard reaction) that typically takes place between 300 °C to 600 °C, at room temperature, in an environmental scanning transmission electron microscope (ESTEM). Using *in situ* electron energy loss spectroscopy (EELS) mapping, combined with density functional theory (DFT) and electromagnetic boundary element method (BEM) calculations, we show that amorphous carbon deposits, resulting from the CO disproportionation reaction, occur only at selective sub-particle locations where preferred CO adsorption sites and plasmon modes antinodes are coincident. Low-loss and core-loss EELS are used to locate the maximum LSP resonance intensity excited by the electron beam and the adsorbed CO molecules, respectively, on a Au nanoprism. Amorphous carbon deposited on the cantilevered corner of a nanoprim, measured after CO is evacuated from the sample chamber, confirms that (a) CO molecules disproportionate at room temperature and (b) the location corresponds to where the CO adsorption probability and the intensity antinode of a dipolar LSP mode overlap. The combination of high energy and spatial resolution, along with simulations, provide an unprecedented insight in the catalytically active sites, for LSP induced chemical reactions.

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9:30 AM *ET08.06.04

Controlling Energy Flow in Plasmonic Photocatalysis Through the Design of Hybrid Plasmonic Nanostructures for Selective Catalysis <u>Suljo Linic</u>; University of Michigan, Ann Arbor, Michigan, United States.

It has been shown that photo-excitation of plasmonic metal nanoparticles (Au, Ag, and Cu) can induce direct photo-chemical reactions on the nanoparticles. However, the widespread application of this technology in catalysis has been limited by the relatively poor chemical reactivity of noble metal surfaces. In this presentation, we present our recent work in which we conceptualized and designed hybrid nanostructures in which a plasmonic metal harvests the energy of visible light photons and selectively channels that energy into catalytically active centers on the nanostructure. To accomplish this, we developed a synthetic protocol to deposit a few monolayers of Pt onto plasmonic Ag nanocubes. This model system allows us to conclusively separate the optical and catalytic functions of the hybrid nanomaterial and analyze the interaction between the two functions. Through experimental and theoretical

studies of the optical properties of these nanostructures, we show that the flow of energy is strongly biased towards absorption (i.e. excitation of energetic charge carriers) in the thin Pt shell. We demonstrate the utility of these nanostructures for photo-catalytic chemical reactions in the preferential oxidation of CO in excess H_2. The reactor studies conclusively show that photo-excitation of these nanostructures results in photo-chemical reactions on the Pt surface. We describe the fundamental physical reasons for the observed directed flow of energy and discuss how these discoveries impact the field of plasmonic catalysis.

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10:00 AM BREAK

10:30 AM *ET08.06.05
Rotational Spectroscopy for Characterization of Plasmonic Photocatalytic Reaction Products <u>Naomi J. Halas</u>[1], Philip Christopher[2] and Henry O. Everitt[3]; [1]Rice University, Houston, Texas, United States; [2]Department of Chemical Engineering, University of California, Santa Barbara, California, United States; [3]Army Aviation & Missile RD&E, Huntsville, Alabama, United States.

Rotational spectroscopy is introduced as a new *in situ* method for monitoring gas phase reactants and products during chemical reactions. Exploiting its unambiguous molecular recognition specificity and extraordinary detection sensitivity, rotational spectroscopy at terahertz frequencies was used to monitor the decomposition of carbonyl sulfide (OCS) over an aluminum nanocrystal (AlNC) plasmonic photocatalyst. The intrinsic surface oxide on AlNCs is discovered to have a large number of strongly basic sites that are effective for mediating OCS decomposition. The strength of rotational spectroscopy is witnessed through its ability to detect and distinguish isotopologues of the same mass from an unlabeled OCS precursor at concentrations <1 nanomole or partial pressures <10 mTorr. These attributes recommend rotational spectroscopy as a compelling approach for monitoring gas-phase chemical reactants and products in real time.

11:00 AM *ET08.06.06
Sustainable Nanocatalysis—Plasmonic Silver Nanocubes and Cellulose Nanocrystals as Non-Innocent Support <u>Audrey Moores</u>; McGill University, Montreal, Quebec, Canada.

We explored the use of cellulose nanocrystals as a non-innocent support to generate metal/cellulose nanohybrids.[1] We showed that, with Pd, we could afford active and enantioselective hydrogenation catalysts,[2] while with Ru, extremely active and recyclable catalysts were accessed for the difficult reduction of arenes under mild conditions.[3] These nanocrystals in suspension could allow the direct synthesis of silver nanoparticles without the use of any additional oxidizing or reducing chemical.[4]
Besides, we have employed silver nanocubes for hydrogen activation and hydrogenation of ketones and aldehydes *via* irradiation at 405 nm, corresponding to the position of the plasmon band of the nanocubes.[5] Exposure to other wavelengths, or absence of light failed to provide activity thus proving the plasmonic effect. Compared to other catalytic systems, the plasmonically activated catalyst provides access to primary and secondary alcohols using milder conditions, in a highly atom economical fashion. Plasmonic catalysis of the oxidation of aldehyde to carboxylic acid was also demonstrated.

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11:30 AM ET08.06.07
Efficient Ammonia Synthesis via Light-Driven Thermal Gradients in Fixed-Bed Catalytic Reactors <u>Xueqian Li</u>[1], Jie Liu[1] and Henry O. Everitt[3, 2]; [1]Chemistry, Duke University, Durham, North Carolina, United States; [2]Physics, Duke University, Durham, North Carolina, United States; [3]Army AMRDEC, Huntsville, Alabama, United States.

When the temperature of exothermic chemical reactions increases, thermodynamic equilibrium shifts away from producing products and towards retaining reactants. Unfortunately, for reactions with high activation barriers, the reaction rate can be extremely slow at the lower temperatures that favor products. Scalable industrial processes require both high reaction rates and high product yields and balancing these two represents the art of chemical engineering. A prominent example is the industrial Haber-Bosch process, which requires optimized catalysts, high temperatures, high pressures, and several recycling steps to achieve practical reaction rates and yields of ammonia, but at the cost of consuming up to 2% of the global energy produced annually. Here, we demonstrate how light-induced plasmonic heating can produce a controlled thermal gradient in a conventional Ru-based catalyst that simultaneously achieves both high reaction rates and high conversion yields in ammonia synthesis. Using continuous wave light emitting diodes, ammonia is copiously produced under ambient conditions without any external heating. Our results suggest that the optical control of thermal gradients in catalysts may become a universal strategy for simultaneously increasing reaction rates and conversion yields of many exothermic reactions.

11:45 AM ET08.06.08
Electrocatalytic CO₂ Reduction at Functionalized Cu Surfaces—Structure-Reactivity Relationships Between Organic Modifiers and Product Selectivity <u>Aya K. Buckley</u>[1, 2, 3], F. Dean Toste[3] and Francesca Maria Toma[1, 2]; [1]Joint Center for Artificial Photosynthesis, Berkeley, California, United States; [2]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; [3]Department of Chemistry, University of California, Berkeley, Berkeley, California, United States.

An efficient electrocatalyst for the reduction of CO_2 (CO2R) would enable the conversion of a major contributor to global warming into valuable carbon-based products. Cu surfaces are unique in that they are the only single-metal system to catalyze the formation of multicarbon products from CO_2. However, the lack of selectivity of these Cu surfaces necessitates investigation into how their catalytic behavior may be adjusted.

The complexity of the catalyst/electrolyte interface poses challenges in identifying how a change in an electrocatalyst affects the observed CO2R

selectivity. Therefore, we employ a methodical experimental approach that focuses upon identifying which parameters play an important role in determining CO2R selectivity.

First, we examined the effect of a series of organic modifiers on the CO2R selectivity of Cu. Oxide-derived Cu surfaces were functionalized with molecular and polymeric modifiers featuring a wide variety of structural characteristics, including neutral and cationic species, protic and aprotic species, and species bearing various functional groups. The product distribution of these surfaces in the CO2R reaction was characterized at -0.7 V vs. RHE, focusing upon the selectivity between CO, formic acid and H_2. This allowed classification of the organic structures based upon the promoted product. Finally, each class of modifiers was examined and key, common structural characteristics of the modifiers were identified.

Through this systematic study, we demonstrate that the CO2R selectivity of a non-precious metal catalyst may be improved for CO, formic acid or H_2 by changing the organic modifier applied. Selectivities of up to 76% CO or 62% formic acid were observed, and H_2 selectivity was tuned from 97% down to 2%. In this presentation, we describe the structural characteristics of these modifiers that are key to changing the observed selectivity. These common features offer insights into the mechanism by which organic modifiers influence CO2R selectivity at the metal surface. We expect that the identified structure-reactivity relationships will illuminate important design principles for novel, selective CO2R electrocatalysts and organic structures for CO2R devices.

SESSION ET08.07: Characterization for Catalysis
Session Chairs: Yuzi Liu and Yugang Sun
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room 306

1:30 PM *ET08.07.01
Quantitative Super-Resolution Imaging of Nanocatalysis Peng Chen; Cornell University, Ithaca, New York, United States.

This talk will present our latest efforts in developing and using single-molecule super-resolution microscopy to map catalytic reactions on single nanoparticles at nanometer resolution and under operando conditions. Depending on available time, the topics may include: 1) cooperative communications within and between single nanocatalysts; 2) visualizing bimetallic effect within single nanocatalysts; and/or 3) mapping catalytic hotspots on plasmonic nanostructures.

2:00 PM *ET08.07.02
In Situ Characterization of Metal Surface Dynamics in Reaction Gas by Atomic Scale and Millisecond Resolution Environmental TEM Seiji Takeda, Naoto Kamiuchi, Takehiro Tamaoka, Ryotaro Aso and Hideto Yoshida; Osaka Univ, Ibaraki, Japan.

Environmental transmission electron microscopy (ETEM) provides us with mostly static structural data of solid surfaces in reaction environments for a long time. However, given the recent advancement in TEM image detectors such as CMOS-based TEM cameras, the technique has started to progress in revealing the atomic dynamics that are correlated with catalytic reaction processes [1].

In this presentation, first we summarize the history of in-situ TEM in our research group briefly for the past decades. Second we show our recent time-resolved analyses with millisecond-resolution on the unexpected atomic dynamics on the surface of nanoporous gold (NPG) catalysts. The surface of NPG catalysts is structurally stabilized in pure oxygen environments, while the surface appears to be dynamically fluctuated with space and time in the reaction environment for the oxidation of CO at room temperature. Since the NPG catalysts inevitably include the residual impurity of Ag in addition to the majority of Au, it is concluded that the Ag atoms on the surface are oxidized to form stable Ag-O-Au atomic clusters in pure oxygen environment. It is also concluded that the self-activating atomic clusters are reduced and oxidized repeatedly in a reaction environment that, of course includes both oxygen and CO. Hence, the catalytically active structure in the gold catalysts (supported Au nanoparticulate catalysts and NPG catalysts) can now be experimentally unified toward elucidating the fascinating catalysis mechanism of gold. We also show some recent challenges on the oxidation and reductions processes on the surfaces of related metals.

Though a chemical reaction is an extremely fast electronic phenomenon, the present study has clarified that the atomic dynamics occurring on the catalytically active surfaces can be observable by the advanced ETEM technique. Finally, to derive clearly the intrinsic natures of a specimen in a reaction environment by atomic scale and millisecond resolution ETEM, it is still indispensable to consider the influence of electron beam. We also discuss the related topics [2].

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2:30 PM BREAK

3:30 PM *ET08.07.03
Investigation of Gas-Solid Reaction in Confined Space by _In Situ_ TEM and Synchrotron X-Ray Yuzi Liu; Argonne National Laboratory, Lemont, Illinois, United States.

The reaction between gas and solid is a great interest for material science. In more specific, materials transformation, gas molecules adsorption/desorption and chemical reaction on the surface are the most attractive topics. Here we use both transmission electron microscope (TEM) and synchrotron x-ray to study the gas-solid reaction with the material in gas environments in confined space (tween two SiN membranes with gap ~500nm) which allow the high energy electron beam and x-ray penetrating the system.
Firstly, the conventional and gas flow TEM were employed to study how the AgCl transformed to AgO_x at different O_2 partial pressure. It was found that the high energy electrons help to generate Cl vacancies which drive the AgCl reduction to Ag. The Ag was further oxidized to Ag_2O because of the high energy electrons radicalized the O_2, which is at very low partial pressure in TEM column. When AgCl particles were in the O_2 rich condition, the same reduction process took place to generate Ag. But, Ag was oxidized to AgO due to the high O_2 partial pressure. Clearly, there are two steps to transfer from AgCl to AgO_x. AgCl transfers to Ag upon the response of Cl vacancies generation through high energy electron beam. Then, the Ag will be oxidized either to Ag_2O or AgO at very low or high O_2 partial pressure respectively.

Secondly, the reaction between Cu_2O and CO_2 was studied by integrated imaging through combination of environmental TEM and synchrotron x-ray. The multi-beam and detectors were employed to study the same object at different length scales. A cross-platform holder was used to guarantee the same nanoparticle was investigated by electron beam and hard x-ray nanoprobe to ensure that we get the complimentary information. In addition to the study on the single particles, the investigation on the assembly of Cu2O particles by high resolution synchrotron x-ray powder diffraction (HRXRD) also indicates the charge transfer between Cu_2O and gas molecules adsorbed on certain facets.

4:00 PM ET08.07.04
Resolving the Atomic Details of Gas-solid Interfaces in Catalytic Materials Through *In Situ* Neutron Total Scattering Daniel Olds, Jue Liu and Kate Page; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Nanostructured and porous materials have widespread industrial applications in adsorption and catalysis, but experimental studies providing atomistic data regarding gas-sorbent interactions under application-relevant conditions are limited. Current analytical methods give information about either the crystal structure or the macroscopic kinetics involved in these processes, but not their interplay.

We present a new sample environment for interrogating materials under precise gas-flow conditions using time-of-flight neutron scattering. This capability allows for simultaneous measurements of stroboscopic, isotope-contrasted neutron total scattering and Steady-State Isotopic Transient Kinetic Analysis (SSITKA), thus providing material insight into both structural and kinetic details. We anticipate this sample environment will be useful in studies of gas-solid interfaces, hierarchical structure, molecular sieves, nanomaterials catalysis, and more.

The results of a commissioning study on nitrogen adsorption in calcium exchanged zeolite X will be presented. Together with theoretical considerations from Grand Canonical Monte Carlo simulation, we identify the location of a heterogeneous distribution of adsorption sites under operational conditions (1 atm, 30° C). We also highlight recent upgrades to the sample environment allowing for high-temperature studies (up to 800° C) of materials under gas flow, which is demonstrated with an *in situ* redox reaction study on ceria nanorods. This sample environment is presently available in the general user program on the NOMAD beamline at the Spallation Neutron Source (ORNL).

4:15 PM ET08.07.05
Mechanisms of Photocatalytic H_2 Evolution on Co-Catalyst Loaded Semiconductors in the UHV Constantin A. Walenta[1,2], Sebastian Kollmannsberger[1], Carla Courtois[1], Rui Nuno Pereira[3], Martin Stutzmann[3], Martin Tschurl[1] and Ueli Heiz[1]; [1]Chemistry Department & Catalysis Research Center, Technische Universität München, Garching, Germany; [2]Department of Chemistry & Chemical Biology, Harvard University, Cambridge, Massachusetts, United States; [3]Walter Schottky Institute & Physics Department, Technische Universität München, Garching, Germany.

Despite of intense research efforts in the last decade, photocatalytic processes for the generation of renewable fuels are still lacking the requirements for successful application on industrial scale. Research strategies have so far been focused on material screening due to the complexity of the underlying processes. However, a deep fundamental understanding will ultimately allow us to implement knowledge-based improvements towards enhanced photocatalytic efficiencies, selectivities and stabilities.
In this work, we examine the reaction mechanism of photocatalytic alcohol reforming on a model system (co-catalyst loaded rutile $TiO_2(110)$). By judicious choice of surface preparation and catalyst loading, we are able to unravel the photochemical mechanism on an atomic scale. By changing the reaction conditions e.g. temperature, photochemical reaction steps of the isotopically labeled reactant can clearly be disentangled from chemical thermal reaction steps in the mechanisms. A detailed kinetic analysis reveals, that the photocatalytic reaction rate depends linearly on the photon flux, indicating that only one charge transfer of this two-step process is facilitated photochemically.

4:30 PM ET08.07.06
Ammonia Synthesis on the Fe(111) Surface—Reaction Mechanism and Kinetics Qi An[1], Jin Qian[2], Alessandro Fortunelli[3,2], Robert Nielsen[4] and William Goddard[4]; [1]University of Nevada, Reno, Reno, Nevada, United States; [2]Materials Science, Caltech, Pasadena, California, United States; [3]Consiglio Nazionale delle Ricerche, Pisa, Italy; [4]Chemistry, Caltech, Pasadena, California, United States.

The Haber-Bosch (HB) process converting nitrogen gas (N_2) and hydrogen gas (H_2) into the ammonia (NH_3) consumes 1–2% of the world's energy supply and generates more than 300 million tons of carbon dioxide annually. It is essential to optimize the efficiency of HB process extensively to save energy consuming and to reduce CO_2 production. However, the reaction mechanisms of HB process at industrial conditions are not fully understood. Here, we employed density functional theory to predict reaction mechanisms and kinetics for NH_3 synthesis on Fe (111) surface which is more efficient for NH_3 synthesis than other surfaces such as (100) and (110). First of all, the free energies of all steps are predicted under experimental condition of 673 K and 20 atm and industry condition of 730 K and 200 atm. Then we built the free energy diagrams into a kinetic Monte Carlo model to predict the steady state catalytic rates and compare with single-crystal experiments. We predicted a turnover frequency (TOF) of 17.7 s^{-1} per 2 × 2 site (5.3 × 10^{-9} mol/cm^2/sec) under condition of 673 K and 20 atm. This agrees very well with single crystal experiment of TOF = 10 s^{-1} per site.

4:45 PM ET08.07.07
Spatial Tailoring of Dopant Position in Solids for Enhanced Visible Light Photocatalytic Performance Pragathi Darapaneni[1], Natalia da Silva Moura[1], Darrell Harry[2] and James A. Dorman[1]; [1]Louisiana State University, Baton Rouge, Louisiana, United States; [2]Chemical Engineering, Southern University, Baton Rouge, Louisiana, United States.

Transition metal (TM) doped semiconductor materials are extensively employed for light harvesting and photocatalytic applications to increase the charge mobility for better performance. The position and site occupancy of the dopant dictate the physical properties of these materials such as light absorption, separation of charge carriers, and the surface reaction kinetics. Commonly used bulk characterization techniques are often indifferent to surface vs. bulk dopant occupancy. Therefore, this work addresses the phenomenon of spatially controlled dopant incorporation for controlled optical and photocatalytic properties.
In this work, highly doped $TiO_2:Ni^{2+}$ (15 mol%) nanoparticles are synthesized via sol-gel chemistry. The drying and annealing of the aged sol are shown to affect the segregation of NiO onto the surface of TiO2. Specifically, it is possible to control the dopant position by varying the moisture exposure time, indicating that the ambient water layer on the surface of TiO_2 plays an important role on surface energetics. The effect of moisture and annealing rate on the dopant position was systematically studied using steady-state and time-resolved methods (XRD, UV-Vis, Raman, TGA/DSC, and FTIR) to extract crystallization temperatures, optical absorption, bond formation, and surface hydroxyl concentration. XRD results show that the vacuum dried TiO$_2$:Ni powders formed a doped anatase phase while the air dried powders formed segregated anatase and NiO phases upon annealing. Furthermore, rapid annealing of the air-dried TiO$_2$:Ni powders formed a metastable anatase doped phase while slow annealing resulted in the segregation of NiO phase, which

can also be observed in TGA/DSC. The annealing processes produce a shift from discrete peaks to a broad absorption based on the dopant position. The evolving local environment is probed via x-ray absorption spectroscopy (XAS) and High-Resolution TEM to elucidate the difference in the dopant local environment with photocatalytic performance using photoluminescence (PL) spectrometer. Moreover, the charge carrier recombination kinetics in these NPs can be investigated using time-resolved PL measurements to understand the modified reaction pathways. This ability to incorporate higher dopant concentrations while engineering the dopant position in nanostructures will assist in the development of improved photocatalytic devices. Finally, a similar trend of dopant segregation was observed with other first row TM doped TiO_2 powders upon slow annealing, suggesting that the segregation of TM dopants in TiO_2 is a function of the dopant size.

SESSION ET08.08: Poster Session II: Non-Carbon Catalysis
Session Chairs: Gugang Chen, Yu Han, Yugang Sun and Lin Wang
Wednesday Afternoon, November 28, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET08.08.01
Selective Formation of Li$_2$O in a Lithium-Air Battery <u>Jaclyn Lunger</u>, Livia Giordano and Yang Shao-Horn; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Although current electric vehicles rely on lithium-ion technology, lithium-ion batteries cannot provide a sufficiently far driving range at low cost [1]. Lithium-air batteries offer a promising alternative to conventional lithium-ion batteries due to their high theoretical energy density, close to that of gasoline. Although lithium peroxide is the discharge product typically observed in lithium-air batteries, lithium oxide is the preferred product with a specific capacity 1.3 times greater than that of lithium peroxide [2]. In addition, many electrolytes have been found to react significantly with lithium peroxide and with the superoxide ion, whereas lithium oxide may be less reactive with the electrolyte [3]. Because the free energies of reaction for lithium oxide and lithium peroxide are similar (-561 kJ/mol and -571 kJ/mol respectively), it should be possible to design a catalyst that selectively forms lithium oxide at room temperature. Additionally, it is important that such a catalyst also reduces ORR/OER potential losses, which currently inhibit lithium-air battery efficiency.

To design a catalyst selective for lithium oxide formation, it is necessary to understand the reaction pathways for the growth of lithium oxide and lithium peroxide. While the reaction mechanism describing electrochemical growth of lithium peroxide has been well studied [4], much less is known about the initial nucleation of lithium peroxide or lithium oxide on the surface of a catalyst. In this study, the initial nucleation pathways for both lithium peroxide and lithium oxide are identified using the ruthenium dioxide (110) surface as a model catalyst. The lowest energy interfaces between lithium peroxide and lithium oxide and the ruthenium dioxide (110) surface are identified by employing a lattice matching algorithm. Density functional theory is then used to identify the charge and discharge pathways which offer the lowest overpotentials. Initial growth of lithium oxide on ruthenium dioxide (110) is found to have a discharge overpotential of 0.58 V, rate limited by adsorption of lithium ions. The removal of the final layer of lithium oxide on ruthenium dioxide (110) is found to have a charge overpotential of 0.44 V, rate limited by the desorption of oxygen. The effects on the charge/discharge overpotentials due to straining and doping the ruthenium dioxide (110) catalyst are studied to identify design principles for a catalyst that is both selective for lithium oxide formation and offers low ORR/OER overpotentials.

[1] Zu C., Li H. Energy Environ. Sci., 2011, 4, 2614-2624
[2] Lu, Y-C., Gasteiger, H. A., Parent, M. C., Chiloyan, V. & Shao-Horn, Y. Electrochem. Solid State, 2010, 13, A69-A72
[3] Freunberger, S. A. et al. J. Am. Chem. Soc., 2011, 133, 8040-8047
[4] Hummelshoj, J. S., Luntz, A. C., Norskov, J. K. J. Chem. Phys. 2013, 138, 034703

ET08.08.02
Computational High-Throughput Screening and Characterization of Catalytic Mass Activities of Tailored Pt Electrocatalysts for the Oxygen Reduction Reaction <u>Marlon Rueck</u> and Alessio Gagliardi; Department of Electrical and Computer Engineering, Technische Universität München, Munich, Germany.

Tailored Pt electrocatalysts harbor great potential to enhance the catalytic mass activity for the oxygen reduction reaction (ORR) in fuel cells [1]. Due to elaborate experimental synthesis and innumerable variations of nanostructures, computational high-throughput screening may highly promote the search for promising electrocatalysts. In our present work, we computationally screen through a plethora of distinct Pt nanostructures where an optimization algorithm tweaks the fine adjustment on the atomic-scale. Precise characterization of tailored electrocatalysts within feasible timescales is the critical step in high-throughput screenings. To this end, we employ our recently developed model [2] which rapidly predicts the catalytic mass activities of the screened nanostructures in absolute units of A/mg_Pt. Our study discloses nanostructures with high mass activities up to 3.86 A/mg_Pt. To further support experimental synthesis, we analyze the size dependence of the nanostructures on the catalytic mass activity. Summing up, our work comprises the crucial steps from screening and characterization to size dependence of tailored Pt electrocatalysts aiming at experimental and theoretical collaboration in nanoparticle synthesis.

[1] F. Calle-Vallejo, M. D. Pohl, D. Reinisch, D. Loffreda, P. Sautet and A. S. Bandarenka, Chem. Sci., 8(3), 2283–2289, 2017.
[2] M. Rück, A. Bandarenka, F. Calle-Vallejo, A. Gagliardi, 2018. arXiv:1805.11695 (submitted)

ET08.08.03
Advanced Structural Characterisation of La-Doped Ceria Nanocubes for Enhanced Redox Ability Colm O'Regan[1], Alberto Casu[1], Andrea Falqui[1], Danilo Loche[2], Lucy Morgan[2], Gavin Mountjoy[2] and <u>Anna Corrias</u>[2]; [1]King Abdullah University of Science and Technology, Thuwal-Jeddah, Saudi Arabia; [2]University of Kent, Canterbury, United Kingdom.

Ceria nanomaterials possess an exceptional reactivity due to the ability of the cerium ion to switch easily between 3+ and 4+ oxidation states, via the formation of oxygen vacancies within the ceria fluorite structure. This effect is enhanced at the nanoscale, and can be tailored by changing both the size and the shape of nanoparticles. In order to further enhance the ceria redox ability, doping of ceria with another element, such as lanthanum, has proved effective *via* an increased mobility of the oxygen vacancies.

With this aim, powder X-ray Diffraction (XRD), and transmission electron microscopy (TEM) techniques have been used to study the solid miscibility of

La in samples of ceria nanocubes with nominal lanthanum doping up to 10 mol%, and to study the effect of doping on the morphology of the lanthanum-doped nanocubes.

Low-magnification TEM imaging shows lanthanum-doped ceria nanoparticles have cubic morphologies, and a more regular cubic shape with sharper facets than pure CeO_2 nanoparticles. This suggests the beneficial role of La on maintaining a well-defined cubic shape during nanoparticle growth, via stabilisation of the oxygen vacancies, and formation of highly reactive <100> terminated facets.

Additionally, XRD and aberration-corrected High Resolution TEM (HRTEM) imaging confirmed the cubic (Fm3m) fluorite single crystalline structure of the lanthanum-doped ceria nanocubes. In particular, the results of 2D-Fast Fourier Transform (2D-FFT) analysis conducted on HRTEM data were always consistent with the pure CeO_2 structure, confirming that the introduction of La did not give rise to the local formation of secondary phases. A shift in the peaks of the XRD patterns was observed with increasing La content up to approximately 7 mol%, suggesting the latter value is approximately the limit of the La solid solubility. Indeed, this was further confirmed by Energy Dispersive X-Ray Spectroscopy (EDS) spatially resolved chemical analysis, performed with subnanometer resolution by Scanning TEM (STEM). This revealed that the largest observed lanthanum concentration is equal to 7 mol%, in the sample with 10 mol% nominal lanthanum doping. Chemical mapping carried out using STEM-EDS also showed the La was homogeneously distributed throughout the CeO_2 nanocubes for all investigated samples, thus proving the formation of an evenly La-doped structure.

Further characterisation is in progress to confirm that these lanthanum-doped nanocubes do enhance redox ability.

ET08.08.04
Atomically Dispersed Eletrocatalysts for High-Efficiency Ambient N_2 Fixation Lili Han[1], Xijun Liu[2], Jun Luo[2] and Huolin Xin[1]; [1]Brookhaven National Laboratory, Upton, New York, United States; [2]Tianjin University of Technology, Tianjin, China.

NH_3 synthesis by the electrocatalytic N_2 reduction reaction (NRR) under ambient conditions is regarded as an appealing alternative to the industrial method that requires high temperature and pressure. Finding a material that can efficiently catalyze electrochemical N_2 fixation at ambient condition is a subject of considerable current interest. Atomically dispersed catalysts with mononuclear metal complexes or single metal atoms anchored on supports would be a promising candidate, because of their maximum atom efficiency, unique catalytic performances, and the similarity of the metal coordination environment to the ligand fields in molecular catalysts. A series of cost-effective and optimized atomically-dispersed eletrocatalysts for NRR will be reported. Our results show that the catalysts are featured with high density of single metal atoms supported on hierarchically porous carbon frameworks. They exhibited remarkable selectivity of NH_3 formation and high NH_3 yield rate at low applied potentials at room temperature. Moreover, the catalysts show negligible activity decay in an NRR electrolysis as long as 50,000 s. On the basis of our results and the previously reported work, a possible mechanism for NRR on the catalyst will be proposed to provide a fundamental insight into the high-efficiency NRR.

ET08.08.05
Efficient Photocatalytic and Photoelectrocatalytic Generation of Hydrogen Peroxide by Organic Semiconductor Catalysts Maciej Gryszel and Eric D. Glowacki; LInköping University, Norrköping, Sweden.

One of the biggest challenges of sustainable development is efficient solar energy harvesting and storage. Huge progress in photovoltaics enabled economically feasible solar-driven electricity generation, however an issue of the energy storage remains unresolved. One emerging possibility is photocatalytic oxygen reduction to the high-energy product hydrogen peroxide. Hydrogen peroxide is easier to store than hydrogen. Herein we present our recent work on photocatalysis and photoelectrocatalysis with organic semiconductors which efficiently produce hydrogen peroxide. When the organic semiconductor is in contact with oxygenated aqueous solution, the light driven 2-electron/2-proton redox cycle leads to photoreduction of oxygen to hydrogen peroxide. We show examples of n type, p type, and ambipolar organic semiconductors performing photochemical oxygen reduction, both as stand-alone photocatalysts and as components in photoelectrochemical cells. Many of these catalytic systems are stable and effective in a wide pH range from 1-12. This demonstration of efficient organic semiconductors as aqueous photocatalysts possibly opens new avenues for their catalytic applications.

ET08.08.06
Biomass Derived Nitrogen-Doped Powdered Activated Carbon for Efficient Electrocatalytic Production of Hydrogen Peroxide Yudong Xue[1,2,3], Shili Zheng[1] and Yi Zhang[1]; [1]Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China; [2]Department of Chemical & Environmental Engineering, Yale University, New Haven, Connecticut, United States; [3]University of Chinese Academy of Sciences, Beijing, China.

Recently, the market for hydrogen peroxide is expanding in various industrials, with the increasing importance of green chemistry. At present, hydrogen peroxide is synthesized by the so-called anthraquinone method at a large scale. The in-situ synthesis of H_2O_2 based on advanced technologies is attracting much interest as a simple H_2O_2 production method. Among them, electrochemical methods are environmental-friendly and effective for the direct generation of hydrogen peroxide with high production rate and simple process.
Hydrogen peroxide can be electrochemical generated by the two-electron oxygen reduction reaction (ORR) on the surface of electrocatalysts. Considerable attempts have been made to prepare appropriate and cost-effective cathode materials to enhance the ORR activity and current efficiency for H2O2 electro-generation. For this purpose, there are various materials reported including carbon-based materials ($g-C_3N_4$, graphite, carbon nanotubes, graphene, graphite felt and carbon cloth), transition metal oxides (Nb_2O_5, CeO_2, Fe_2O_3 and Co_3O_4) and precious metal nanomaterials. Development of low-cost carbon-based metal-free catalyst with high ORR catalytic activity and low cost is emerged as an effective strategy for the replacement of precious metal.
As carbon-rich precursor, biomass has served as the raw material for the fabrication of carbon-based materials for a long time. With the choice of suitable activators, various works have reported that porous carbon derived from biomass can obtain well-defined micropore size distribution and an ultrahigh specific surface area. Activated carbon materials are applied into the development of catalyst in energy storage/conversion devices. Furthermore, considering the advantages of nitrogen doping for the enhancing of electrocatalytic activity, nitrogen-rich biomass and their derivatives have been recently chosen as promising precursors for nitrogen-doping carbon catalysts.
As a typical low-cost and easily obtained nitrogen-rich biomass resource, Ramie is widely distributed in the east and south of China as textile, feeding and paper raw materials. We developed nitrogen-doped powered activated carbon under appropriate temperature with high surface area from ramie biomass as a highly efficient electrocatalyst for hydrogen peroxide production. Electrochemical characterizations revealed that the as-prepared catalyst showed superior ORR selectivity through a two-electron pathway and extraordinary long-term stability. The nitrogen atoms on the catalyst surface was derived from the biomass and deconvoluted by XPS techniques, which is the important factor for the enhancement of electrocatalytic performance. The present work paves a way for the development of biomass-derived carbon material for electrochemical applications.

ET08.08.07
Development of Photocatalysts Based on the Fe-Ti-O System—An Efficient Combination for Artificial Photosynthesis Renato V. Goncalves; Physics, University of Sao Paulo, Sao Carlos, Brazil.

Conversion of solar energy to hydrogen fuel by artificial photosynthesis is considered one of the most important technologies breakthroughs to solve energy and environmental problems. Artificial photosynthesis process was inspired by photosynthesis in nature and has been studied since the pioneer work reported by Fujishima and Honda in 1972. The main challenge of artificial photosynthesis reactions is the development of efficient and robust semiconductor based-photocatalysts with suitable band structures to absorb visible light and generate electrons and holes into their conduction and valence bands, respectively, with potential for overall water splitting. Very recently, Fe_2TiO_5 (FTO) structure has been the most widely studied Fe–Ti–O combination material with pseudobrookite structure to overcome the challenges of the reaction. Herein, we prepared several approaches for the development of Fe_2TiO_5 photocatalysts for split water in H_2 and O_2 using visible light. The FTO has a bandgap of around 2.0 eV, with adequate electronic and structural properties for the reaction of artificial photosynthesis to produce H_2 and O_2 efficiently.

ET08.08.08

Ce-Substituted LaFeO₃ Perovskite-Type Oxides with Enhanced Catalytic Performance and Sulfur Resistance for NH₃-SCR Dae-Yeon Won, Woojin Lee, <u>Hyo-bin Wi</u> and Seung-Yeop Kwak; Seoul National Univ, Seoul, Korea (the Republic of).

We synthesized Ce-substituted $LaFeO_3$ perovskite-type oxides (LCFO) via Pluronic F127-assisted hydrothermal process. Obtained LCFOs exhibited several micrometer-sized spherical morphology. Crystal structure of LCFO was pure $LaFeO_3$ perovskite structure with small amount of cerium because lanthanum ions were perfectly substituted by cerium ions. Increasing the ratio of Ce to La ions, however, it was found that cerium oxides were formed by unsubstituted Ce ions. The catalytic properties of LCFOs were evaluated by the efficiency of selective catalytic reduction of nitric oxide with ammonia (NH_3-SCR). Pure $LaFeO_3$ oxide (LFO) showed poor catalytic performance for NH_3-SCR, which is consistent with previous studies. On the other hand, NO conversion efficiencies were significantly enhanced in LCFO samples, especially in pure phased LCFO. Furthermore, the LCFO catalyst with single crystal structure exhibited high resistance against SO_2 gas. This results indicated the substituted Ce ions generated new type of active sites with enhanced catalytic activity and SO_2 tolerance.

ET08.08.09

Mediated Photoelectrochemical Oxidation of Water on WO₃ by Silver (II) <u>Taehwa Jeon</u>[1], Damián Monllor–Satoca[1, 3], Gun-hee Moon[1], Wooyul Kim[5], Hyoung-il Kim[4], Hyunwoong Park[2] and Wonyong Choi[1]; [1]Division of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of); [2]School of Energy Engineering, Kyungpook National University, Daegu, Korea (the Republic of); [3]School of Engineering, Universitat Ramon Llull, Barcelona, Spain; [4]Department of Civil and Environmental Engineering, Yonsei University, Seoul, Korea (the Republic of); [5]Department of Chemical and Biological Engineering, Sookmyung Women's University, Seoul, Korea (the Republic of).

Ag(I) is a common electron scavenger used in photocatalysis for promoting oxidative pathways through photogenerated holes, preventing deleterious electron-hole recombination. Albeit its straightforward reduction to metallic state (i.e., Ag^0), it can also capture holes to generate the highly reactive Ag(II) species, provided the proper reactive conditions are given. In this contribution, we demonstrate, for the first time, mediated photoelectrochemical oxidation of water and concurrent oxygen evolution by the Ag(I)/Ag(II) redox cycle with high efficiencies. In the presence of Ag(I), photoelectrochemical (PEC) performance of WO_3 electrodes was enhanced (biased at 1.23 V vs. RHE) in a mild acidic nitrate medium (pH 5) in terms of steady-state photocurrent (>4-fold), and O_2 evolution (>4-fold) and its Faradaic efficiency (40% without Ag(I) vs. 75% with Ag(I)). During the PEC reaction, the electrolyte solution acquires a brown color, caused by the formation of $Ag^{II}NO_3^+$ complex. Upon turning both potential bias and light off, photocurrent drops to zero whereas O_2 evolution continues over ~10 h (homogeneous water oxidation) leading to the overall Faraday efficiency of 100%, and simultaneously the electrolyte is gradually bleached. This confirms the Ag(II) complex-mediated water oxidation which occurs during the PEC and the unbiased dark periods. This phenomenon is found neither in the Ag(I)-free PEC reactions nor in the photocatalytic (i.e., bias-free) reactions with Ag(I). The various spectroscopic analyses (UV-Vis, XRD, XPS, SEM/EDS, HR-TEM/EELS, etc.) suggest that Ag^0/Ag_2O core-shell structure and $AgNO_3^+$ complexes play the heterogeneous and homogeneous water oxidation reactions, respectively.

ET08.08.10

Loading Effect of Various Metal Oxide Colloids as an Electron Mediator on Visible-Light-Responsive Photocatalyst Particles in Photocatalyst Panels for Z-Scheme Water Splitting <u>Hiromasa Tokudome</u>[1, 2], Sayuri Okunaka[1, 2], Shingo Oozu[1, 2], Qian Wang[3], Takashi Hisatomi[4] and Kazunari Domen[3, 4]; [1]TOTO Ltd, Chigasaki-city, Japan; [2]Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPChem), Chiyoda-ku, Japan; [3]Department of Chemical System Engineering, School of Engineering, The University of Tokyo, Bunkyo-ku, Japan; [4]Center for Energy & Environmental Science, Shinshu University, Nagano, Japan.

Photocatalytic water splitting utilizing abundant sunlight including visible light is an active area of research focused on providing a renewable hydrogen. In the past two decades, a lot of visible light responsive photocatalysts have been developed to oxidize and/or reduce water, but only a few were known to overall split water into H_2 and O_2 in the stoichiometric amount. On the other hand, Z-scheme system is known to realize overall water splitting using two kinds of visible light responsive photocatalyst particles, which were active for either H_2 or O_2 evolution, with/without appropriate mediators such as redox ions or conductive materials. We recently developed a Z-scheme-type photocatalyst panel consisting of mixed films of two visible-light-active photocatalysts (La, Rh-doped $SrTiO_3$ and $BiVO_4$ for H_2 and O_2 evolution) and a colloidal electron mediator (gold or indium-tin-oxide) on a glass substrate. It showed relatively high activity with a solar-to-hydrogen energy conversion efficiency of 0.1%[1,2]. In this study, we prepared a Z-scheme-type photocatalyst panel composed of $BiVO_4$ and Rh-doped $SrTiO_3$ loaded with various metal oxide colloids as a low-cost and scalable electron mediator and examined the water splitting activity.

Z-scheme-type photocatalyst panels were prepared by a screen-printing on borosilicate glass substrates using a viscous paste including Rh-doped $SrTiO_3$ loaded with various metal oxide colloids by impregnation or adsorption method and $BiVO_4$ particles. The panels produced hydrogen and oxygen from pure water in the stoichiometric ratio under visible light irradiation. The water splitting activity varied depending on the kind of the loaded metal oxide colloids. This result showed that the colloids acted as an electron mediator between the two photocatalysts.

1) Q. Wang, T. Hisatomi, Q. Jia, H. Tokudome, M. Zhong, C. Wang, Z. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y. Li, I-D. Sharp, A. Kudo, T. Yamada, K. Domen, Nat. Mater., 2016, 15, 611–615.
2) H. Tokudome, S. Okunaka, H. Kameshige, T. Nakamura, Q. Wang, T. Hisatomi, Q. Jia, K. Domen, MRS fall meeting and exhibit, 2017.

ET08.08.11

Improvement of Z-Scheme Water Splitting Activity on Nano ITO-Mediated Printable Photocatalyst Panels by Loading Co-Catalyst <u>Sayuri Okunaka</u>[1, 2], Hiromasa Tokudome[1, 2], Qian Wang[2, 3], Takashi Hisatomi[2, 4] and Kazunari Domen[2, 3, 4]; [1]TOTO Ltd, Chigasaki-city, Japan; [2]Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPChem), Chiyoda-ku, Japan; [3]The University of Tokyo, Bunkyo-ku, Japan; [4]Shinshu University, Nagano, Japan.

Photocatalytic water splitting has been widely investigated as a potential method to produce hydrogen from renewable solar energy. Although two types of semiconductor-based systems (heterogeneous system and photoelectrochemical system) have extensively been studied for photo-induced water splitting so

far, it is necessary to develop a scalable, versatile and cost-effective system for the practical application. Photocatalyst panels, wherein semiconductor particles are fixed on substrates such as glass, have a potential to be employed as a cost-effective system on large scale. To utilize wide range of visible light, it is necessary to employ narrow bandgap materials and/or introducing Z-scheme mechanism. Recently, the authors' group reported that the composite-type photocatalyst panels, which composed of La, Rh-codoped $SrTiO_3$ as the hydrogen evolution photocatalyst (HEP), Mo-doped $BiVO_4$ as the oxygen evolution photocatalyst (OEP) and gold (Au)/ indium-tin-oxide (ITO) nanocolloids as the electron mediator, for Z-scheme water splitting.[1] These panels were prepared by using simple screen-printing method. The obtained printable panels evolved hydrogen and oxygen from pure water in the stoichiometric ratio under visible light irradiation and showed relatively high activity with a solar-to hydrogen energy conversion efficiency (STH) of ca. 0.1%.[1,2]

In this study, we investigated the effect of co-catalyst loading on the photocatalytic water splitting activity of the printable ITO nanocolloids-mediated photocatalyst panels. The water splitting activity of these panels was changed by changing the metal species and loading amount of co-catalyst. By loading appropriate co-catalyst, the water splitting activity was greatly enhanced and achieving 0.4% STH, which is four times greater than photocatalyst panels without co-catalyst loading.

ET08.08.12

Real Time Imaging of Nucleation, Growth and Corrosion Behaviors of Electrocatalysts Hao Shan, Yanling Ma, Fenglei Shi, Tao Deng and Jianbo Wu; Shanghai Jiao Tong University, Shanghai, China.

The core-shell catalysts with atomic layered surface Pt through liquid phase atomic layer deposition has been proven to be one of the most promising oxygen reduction (ORR) electrocatalysts with high activity and low consume of Pt.[1-5] It is important to directly observe how the atomic layers grow via in situ technique. On the other hand, corrosion is a major and unavoidable challenge for the degradation of properties of multimetallic core-shell electrocatalysts during electrocatalysis, which restricts the practical application of this type electrocatalysts severely.[6-7] Therefore, it has been an urgent issue to understand the evolution and mechanism of corrosion of Pt-based core-shell catalysts during the reaction with an aim to the effective utilization of the catalysts. [8]

In this presentation, we will first report a 3D growth mechanism for the formation of core−shell nanostructures involving a hybrid process with initial island growth and surface diffusion. The desired surface structure can be achieved by adjusting the competition between island deposition and surface diffusion.[9] Then, we will show the corrosion behavior of Pd@Pt core-shell electrocatalysts in the etching solution, which depends on the effects of geometry and surface defect.[10-11] Finally, we can demonstrate the capability of electrochemistry inside of TEM, showing both the oxidative etching and the re-deposition behaviors during the cyclic voltammetry in TEM.

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ET08.08.13

A Double-Anionic Oxides Based Organic-Inorganic Hybrid Compound for Simultaneously Catalytically Oxidative and Hydrolytic Decontamination of Chemical Warfare Agent Simulants Jufang Hu[1,2]; [1]Beijing Institute of Nanoenergy and Nanosystems, Academy of Sciences, Beijing, China; [2]College of Optoelectronic Engineering, Shenzhen University, Shenzhen, China.

Rapid transformation of chemical warfare agents (CWAs) to environmentally benign products is a significant issue, and considerable efforts have been devoted to the catalytic removal of CWAs. Although many homogenous and heterogeneous catalysts for CWA removal have been developed, a broad-spectrum and simultaneous hydrolysis catalyst (for nerve agent removal) and oxidation catalyst (for mustard removal) is fairly needed. In this work, an organic-inorganic hybrid compound, $H_{13}[(CH_3)_4N]_{12}[PNb_{12}O_{40}(V^VO)_2(V^{IV}_4O_{12})_2]22H_2O$ (**1**), based on two different anionic oxide fragments (also known as polyoxometalates, primarily constituted by Mo, W, V, Nb centers and oxo ligands), was hydrothermally synthesized, structurally thoroughly characterized, and catalytically tested with the broad-spectrum reactivity in the decontamination of chemical warfare agents. Compound **1** crystallizes in the tetragonal I-4 space group and contains bicapped polyoxoniobate $(PNb_{12}O_{40}(VO)_2)$ and tetranuclear polyoxovanadate, which are independent on each other, a complexe scarcely seen in polyoxometalate chemistry. Interestly, compound **1** effectively catalyzes both hydrolysis of the nerve agent simulant, diethyl cyanophosphonate (DECP), and selective oxidation of the sulfur mustard simulant, 2-chloroethyl ethyl sulfide (CEES) under mild conditions. In particular, in the oxidative decontamination system 100% CEES was transformed selectively to nontoxic 2-chloroethyl ethyl sulfoxide and vinyl ethyl sulfoxide using nearly stoichiometric 3% aqueous H_2O_2 with a turnover frequency (TOF) of 16000 h^{-1}. The catalytic performance is maintained even after ten runs and CEES is completely decontaminated in 3 mins without formation of the highly toxic sulfone by-product. The combination of polyoxoniobates and polyoxovanadates give this compound those noteworthy catalytic properties, and a three-step oxidative mechanism is proposed.

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ET08.08.14

Continuous Hydrothermal Synthesis of Catalytic Metal Oxide Nanoparticles in Supercritical Water Elizabeth G. Rasmussen, Brian R. Pinkard, Justin Davis, John C. Kramlich, Per G. Reinhall and Igor V. Novosselov; Mechanical Engineering Department, University of Washington, Seattle, Washington, United States.

Metal oxide nanoparticles have been studied at length for their catalytic properties in many industries including chemical manufacturing, energy-related

applications and environmental remediation. Given these advances in their applications, the tunable synthesis is of great interest, especially regarding control of crystal structure. In this study iron oxide (Fe_2O_3) and zirconium oxide (ZrO_2) nanoparticles were synthesized using a continuous-flow supercritical water reactor. The products were characterized for both size and crystalline structure by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD). Additionally, Raman spectra samples taken showed a decreased presence of the toxic organic solvent Dimethylformamide (DMF) showing advancement in completely eliminating such reagents in final products. Thus, the process presented can be compatible for green and sustainable chemistry in a way that reduces the environment load. The optimization of this technique is discussed and its advancement forward of the current bounds of continuous hydrothermal synthesis for catalysts applications is reviewed.

ET08.08.15
Intermetallic Pt-Mn/C Nanoparticles as ORR Electrocatalysts <u>Mahdi Ahmadi</u> and Héctor D. Abruña; Cornell university, Ithaca, New York, United States.

The sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode remains as one of the main challenges for commercial viability of alkaline exchange membrane fuel cells (AEMFCs). It is therefore, of great interest to explore the development of electrocatalysts with superior activity and stability relative to the coinventional carbon supported Pt nanoparticles (NPs).
In this work we have studied the effects and evolution of structure and surface composition of Pt-Mn NPs on their electrocatalytic activity for the ORR in alkaline media. Pt-Mn NPs were synthesized using solvothermal methods and were supported on C via impregnation. An ordered intermetallic phase was obtained by heat treatment. We have investigated the crystalline structure of these NPs using X-ray diffraction (XRD) and their size, morphology and composition using TEM/STEM, EELS and EDX. Cyclic voltammetry (CV) and rotating disk electrode (RDE) voltammetry were used to assess their electrocatalytic activity and stability.
The Pt-Mn NPs were electrochemically dealloyed in acidic media, through potential cycling, leading to the formation of a ~1nm thick Pt shell on an ordered Pt_3Mn core. Enhanced mass and specific activity resulted by such electrochemical dealloying. The stability of the electrocatalyst was tested after 4,000 potential cycles in alkaline media following the DOE protocol (0.6-1.0 V vs reversible hydrogen electrode). In alkaline media, Mn surface segregation ensued, leading to a lower electrocatalytic activity when compared to the freshly dealloyed catalyst.

SESSION ET08.09: Carbon Activation Catalysis
Session Chairs: Gugang Chen and Jose Rodriguez
Thursday Morning, November 29, 2018
Hynes, Level 3, Room 306

8:30 AM *ET08.09.01
Descriptors for Transition-Metal Oxides and Implications in Selective Catalysis <u>De-en Jiang</u>; Department of Chemistry, University of California, Riverside, Riverside, California, United States.

Descriptors from scaling relations are at the forefront of theoretical studies in the search for effective catalyst design principles and in the prediction of catalytic activity from first principles. We propose an intuitive and widely applicable structural descriptor for transition metal oxides from first principles. We demonstrate that our descriptor can provide the bridge between the structural, the electronic, and the energetic properties for TMO surfaces. We then use it to accurately predict C-H activation energies with low deviations from DFT calculations. By building upon the compositional diversity of the perovskites, we further establish some descriptors to correlate with the key reaction steps of methane activation on the oxide surfaces. From the analysis of first and second C-H activation energies and their correlation with the hydrogen adsorption energy on a variety of ABO_3 perovskites, general trends emerge that an optimal range of hydrogen adsorption energy strikes the right balance between easy first C-H activation and difficult second C-H activation energies to avoid further oxidation.

9:00 AM ET08.09.02
First-Principles Study of *n*-butane Monomolecular Cracking on Zeolites and 2D Bilayer Aluminosilicate Models—Reaction Mechanism and Effects of Spatial Confinement <u>Mengen Wang</u>[1,2], Jianqiang Zhong[1], Anibal Boscoboinik[1] and Deyu Lu[1]; [1]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; [2]Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York, United States.

Zeolites are nanoporous industrial catalysts (e.g. consisting of $[AlO_4^-]$ and $[SiO_4]$ tetrahedra) with catalytically active sites located inside the channels and nano-cages, rendering them inaccessible for surface science measurements. Two-dimensional (2D) ultrathin (~0.5 nm) bilayer aluminosilicate films consisting of hexagonal prisms with acidic hydroxyl groups exposed on the surface have been synthesized on Ru(0001) surface as a zeolite model system to study gas molecule adsorption[1] and chabazite (CHA)-based catalysts[2,3]. DFT studies were performed to investigate the dehydrogenation and monomolecular cracking of *n*-butane molecules over the acidic hydroxyl groups of aluminosilicate films. Intrinsic energy barriers of dehydrogenation, terminal and central C-C bond cracking on aluminosilicate films were found to be ~0.6 eV higher than those of the bulk CHA. We further investigated the effects of the zeolite channel and cage sizes on the *n*-butane adsorption and monomolecular cracking for six different 3D nanoporous zeolite frameworks (TON, MEI, VFI, FER, CHA, and MEL). We found that as the confinement of straight channels or nano-cages decreases, *n*-butane adsorption becomes weaker and intrinsic energy barrier for terminal C-C cracking increases. The 2D bilayer film surface, which may be considered as zeolite cages at the infinite cage size limit, has the smallest adsorption energy and highest intrinsic energy barrier. Comparison of the reaction pathway of *n*-butane terminal C-C cracking in 3D nano-cages and on bilayer aluminosilicate film surface revealed that the decrease of the intrinsic energy barriers in bulk zeolites is caused by the stabilization of the transition states in the 3D nano-cages.

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9:15 AM ET08.09.03
Exploring Non-Oxidative Dehydrogenation of Alcohols Using Reaction of Ethanol Over Transition Metals and Bimetallic Catalysts Fatima Jalid[1, 2],
Tuhin Suvra Khan[1] and Mohammad A. Haider[1]; [1]Department of Chemical Engineering, Indian Institute of Technology Delhi, Delhi, India; [2]Department of Chemical Engineering, National Institute of Technology Srinagar, Srinagar, India.

The selective dehydrogenation of alcohols to carbonyl compounds is an important class of reaction as aldehydes and ketones produced are essential intermediates in the chemical process industry. The process can be made environmentally sustainable by integrating it with the renewable biomass-derived feedstock and employing a non-oxidative process, which prevents catalyst inhibition due to water formation and supresses over-oxidation of products. To gain insights into the non-oxidative dehydrogenation (NODH) of biomass derived alcohols over transition metal catalysts, a microkinetic model (MKM) using ethanol as a model molecule has been developed. Previously, a similar study has been conducted to understand the hydro-deoxygenation trends[1]. The NODH of ethanol was first demonstrated by Church and Joshi in 1951, wherein Cu catalyst was employed with Co and Cr as promoters[2]. Since then, catalysts mostly based on Cu have been utilized for NODH of alcohols. The NODH of ethanol may proceed via the initial C-H, O-H, C-O or C-C bond scission leading to the production of acetaldehyde, hydrogen, ethane, carbon monoxide, water and methane. For the production of aldehydes and ketones, the process should be made selective for acetaldehyde and hydrogen production. At the reaction conditions of 473K and 10% reactant conversion, the activity trend for acetaldehyde production from ethanol followed the order; Pt > Cu > Pd > Co > Ni > Ag > Au > Rh > Ru > Re. At these conditions, Pt showed the highest activity (TOF ~ $10^4 s^{-1}$), followed by Cu (TOF ~ $10^3 s^{-1}$). As Cu is the cheaper metal, therefore, it is widely used for this process. Followed by acetaldehyde, ethane was the other major product formed. However, all the metals except Au and Ag were selective towards aldehyde production. From the coverage analysis done in the MKM, it was determined that the surface of Cu was covered with the intermediate, CH_3CH_2O whereas most of the metal catalysts viz. Pt, Pd, Co, Ni, Rh, Ru, Re were covered with the intermediate CH_3CO, suggesting difficult C-H bond activation of CH_3CH_2O on Cu. Inspired from this fact, a bimetallic catalyst was proposed wherein Cu with was combined with a metal having low C-H activation barrier (such as Ni, Pd, Pt, Rh). These bimetallic alloys were found to show higher reactivity (TOF > $10^3 s^{-1}$) as compared to Cu for aldehyde formation. Earlier experimental studies on ethanol NODH over the bimetallic NiCu measured lower activation barrier of 45 kJ/mol, than that of Cu catalyst (Ea = 70 kJ/mol) and increased catalyst stability owing to lesser Cu sintering in the presence of Ni[3].

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9:30 AM ET08.09.04
Nanoarray-Based Monolithic Catalysts for Propane Oxidation—Enhanced Activity by Copper Manganese Oxide and Co Dopant Effect Sheng-Yu
Chen, Wenxiang Tang, Junkai He, Puxian Gao and Steven L. Suib; Univ of Connecticut, Storrs, Connecticut, United States.

With growing demands of fossil fuel, advanced technologies of exhaust treatment are getting more concern in order to control the deteriorating air pollution from vehicles and factories. A series of nanoarray-based manganese oxide catalysts were developed by one-pot hydrothermal synthesis to fabricate nanorod arrays on the cordierite honeycomb substrates. Compared to monolithic catalysts with a traditional alumina support, nanoarray-based monolithic catalysts possess advantages, e.g. efficient open surfaces, reduced usage of porous supports, low pressure-drop, less agglomeration of nanoparticles. Copper manganese oxide ($CuMn_2O_4$) nanosheets were introduced to enhance the oxidative activity for hydrocarbons. The $CuMn_2O_4$nanosheets coated nanoarray-based catalyst, NA-$CuMn_2O_4$, shows efficient 90% propane (C_3H_8) conversion at around 400 °C, which is 50 °C and 75 °C lower than $CuMn_2O_4$ wash-coated catalyst (WC-$CuMn_2O_4$) and Pd loaded catalyst (WC-Pd), respectively. The benefit of nanoarray morphology was demonstrated by correlating the variation of surface area to the reactivity. The incorporation of cobalt ions was found to increase the specific surface area and thus enhance C_3H_8 conversion of $CuMn_2O_4$. The $CuMn_2O_4/MnO_2$ nanoarray-based monoliths are promising types of emission control devices.

9:45 AM ET08.09.05
Selective CO Production by Photoelectrochemical Methane Oxidation on TiO_2 Da He, Wei Li and Dunwei Wang; Boston College, Chestnut Hill, Massachusetts, United States.

The inertness of the C−H bond in CH_4 poses significant challenges to selective CH_4 oxidation, which often proceeds all the way to CO_2 once activated. Selective oxidation of CH_4 to high-value industrial chemicals such as CO or CH_3OH remains a challenge. Photocatalytic reactions hold great promise for practical applications but have been poorly studied. Existing demonstrations of photocatalytic CH_4 oxidation exhibit limited control over the product selectivity, with CO_2 as the most common product. The yield of CO or other hydrocarbons is too low to be of any practical value. In this work, we show that highly selective production of CO by CH_4 oxidation can be achieved by a photoelectrochemical (PEC) approach. Moreover, our results revealed that the selectivity toward CO also depends on the substrate types and applied potentials. Based on the experimental results, we proposed a reaction mechanism that involves synergistic effects by adjacent Ti sites on TiO_2. Spectroscopic characterization and computational studies provide critical evidence to support the mechanism. Furthermore, the synergistic effect was found to parallel heterogeneous CO_2 reduction mechanisms. Our results not only present a new route to selective CH_4 oxidation, but also highlight the importance of mechanistic understandings in advancing heterogeneous catalysis.

10:00 AM BREAK

10:30 AM *ET08.09.06
Novel Inverse Oxide/Metal Catalysts for C1 Chemistry Jose A. Rodriguez[1, 2]; [1]Brookhaven National Laboratory, Upton, New York, United States; [2]Chemistry, SUNY Stony Brook, Stony Brook, New York, United States.

Inverse oxide/metal catalysts have shown to be excellent systems for studying the role of the oxide and oxide-metal interface in catalytic reactions. These systems can have special structural and catalytic properties due to strong oxide-metal interactions difficult to attain when depositing a metal on a regular oxide support. Oxide phases which are not seen or are metastable in a bulk oxide can become stable in an oxide/metal system opening the possibility for new chemical properties. Using these systems it has been possible to explore fundamental properties of the metal-oxide interface (composition, structure, electronic state) which determine catalytic performance in the oxidation of CO, the conversion of methane, the water-gas shift, and the hydrogenation of CO_2 to methanol. Systematic studies have been performed for the deposition of nanoparticles of CeO_2, TiO_2, FeO_x and MgO on surfaces of late transition metals . The nature of the metal substrate has a large effect on the physical and chemical properties of the supported oxide. Recently, there has been a significant advance in the preparation of oxide/metal catalysts for technical or industrial applications. One goal is to identify methods able to control in a precise way the size of the deposited oxide particles and their structure on the metal substrate.

11:00 AM ET08.09.07

Pt/Sn-Based Nanoparticles in Ionic Liquids as Nanocatalysts for the Selective Hydrogenation of Cinnamic Aldehyde Christine Dietrich and Silke Behrens; Karlsruhe Institute of Technology, Karlsruhe, Germany.

Bimetallic nanoparticles have attracted a lot of attention because they show multiple functionalities and prominent catalytic activity, selectivity as well as thermal and/or chemical stability over their monometallic counterparts. Due to synergistic effects, modified electronic and/or geometric surface structures, high catalytic activities and selectivities have been achieved for chemical reactions even if one of the constituents is less or even inactive. Although the controllable synthesis of nanoparticles has developed rapidly over the recent years, more accurate control over nucleation and growth stages is needed for bimetallic nanocrystals. Since bimetallic nanocrystals are composed of different metal atoms, the composition and atomic distribution not only influences the final nanoparticle architecture but also the catalytic properties. The catalytic performance is highly sensitive to the nature of atomic ordering (i.e., random alloy, intermetallic compound) even if the overall composition and stoichiometry are the same. Here, we address the synthesis of bimetallic Pt/Sn-based nanoparticles with tunable composition and structure by exploiting the beneficial properties of ionic liquids (ILs). Small nanoparticles are obtained in a one-pot synthesis by reducing the metal salt precursors with triethylborohydride in the IL. The weakly coordinating IL anions and cations directly control particle nucleation and growth processes enabling nanoparticle synthesis without addition of stabilizing additives or strongly coordinating capping molecules. The nanoparticles form sols of very high colloidal stability in the IL, which is particularly interesting in view of their use as quasi-homogeneous catalysts. The composition and structure of the nanoparticles is tailored by the nature of the metals salt precursors, their initial molar ratio and the nature of the IL. Investigations by X-ray diffraction, X-ray photoelectron spectroscopy and transmission electron microscopy reveal the formation of random-type alloy or intermetallic nanoparticles. The catalytic performance of the bimetallic nanoparticles is evaluated in hydrogenation reactions. The selective hydrogenation of cinnamaldehyde, for example, is used to probe the catalytic performance of the Pt/Sn nanoparticles, demonstrating the effect of tin alloying on the catalytic activity and selectivity to the α,β-unsaturated cinnamic alcohol. In general, the selective hydrogenation of α,β-unsaturated aldehydes is a critical step in the synthesis of various fine chemicals. As compared to their monometallic counterparts, both a higher catalytic activity and selectivity to the α,β-unsaturated cinnamic alcohol is achieved for the Pt/Sn-based nanoparticles.

11:15 AM ET08.09.08
Supported Transition Metal Catalysts for Methane to Methanol Oxidation Darinka Primc[1, 2], Julie Fornaciari[1, 2], Adam Z. Weber[2] and Alexis T. Bell[1, 2]; [1]Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, California, United States; [2]Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Methane is a relatively inexpensive, abundant resource, and its partial transformation to chemicals and chemical fuels presents attractive pathways for its utilization. Conventional synthesis of methanol involve a multistep process, which requires high energy input and high cost [1]. Alternatively, methane oxidation using a catalyst in an electrochemical cell is a promising single-step approach to achieve a direct conversion of methane to methanol at lower temperatures and low cost [2].

Catalysts need to be developed for this energetically challenging process. There specific electrocatalysts play a dual role: the activation of the relatively inert C-H bond enabling oxidative hydroxylation of methane, and simultaneously inhibit further methanol oxidation. To date, a variety of the catalysts, including supported metals (Pd, Ru, Au, Ag) and metal oxides (V_2O_5, Fe_2O_3, CoO, Mn_2O_3, MoO_3, CrO), have been tested in electrochemical cell and shown promise for the direct oxidation of methane [2]. However, further systematic studies are essential for understanding the mechanism for methane oxidation, enabling the rational design of the catalysts. In this regards single atom catalysts (SAC) are particulars interesting [3]. In addition of showing potential for high methane conversion and methanol selectivity, these catalysts are able to overcome the complicated multiple components and are regarded as ideal model catalysts to identify active sites and facilitate understanding of the reaction process at a molecular level. In spite of great interest; however, it still remains challenging to achieve atomically dispersed metals in high loadings for efficient catalysis. Moreover, for electrochemical methane-to-methanol conversion it is concurrently of importance to develop supported SAC which provide active sites along with hierarchical porosity enabling optimal mass/electron transport.

In this study, first-row transition metal oxides as well as single atom catalysts, supported on carbon supports, have been investigated. The catalysts are synthesized with a ligand-based approach and subsequently characterized for electrochemical methane-to-methanol oxidation. In-depth structural and chemical analyses of catalysts using a combination of various spectroscopy techniques is used to establish structure-property relationship. These insights will provide valuable basis for a scientific-guided approach toward new metal oxide and supported single-atom catalysts for this challenging process.
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11:30 AM ET08.09.09
Bifunctional Catalysts Based on Colloidal Nanoparticles in the Single-Step Synthesis of Dimethyl Ether Manuel Gentzen, Joerg Sauer and Silke Behrens; Karlsruhe Institute of Technology, Karlsruhe, Germany.

The development of new routes to base chemicals and fuels from renewable resources has drawn much attention worldwide. Synthesis gas (CO + H_2) derived from renewable sources (e.g., biomass) and its conversion to dimethyl ether (DME) provides one attractive option with respect to a wide range of applications (e.g, as liquefied petroleum gas, intermediate product for base chemicals or as clean diesel substitute). In the conventional two-step DME process, synthesis gas is converted to methanol over Cu-based catalysts in the first stage, which is subsequently dehydrated to DME over an acidic catalyst in the second stage. Alternatively, DME can be manufactured from synthesis gas in a single-step in the syngas-to-dimethylether (STD) process with methanol as an intermediate [1]. The STD process has many technical and economic advantages and allows for higher CO conversions. The design of efficient bifunctional STD catalysts with balanced methanol and dehydration functionalities and long term stability, however, remains a crucial issue. In this context, model systems derived from well-defined nanoparticles contribute to a more fundamental understanding of structure-performance relationships, enabling the future more rational design of highly efficient catalysts. Herein, we present the synthesis of small, uniform nanoparticles via reductive stabilization. The colloidal nanoparticles are deposited on the dehydration catalyst (i.e., different types of solid acids), and in this way, serve as the key building blocks for the methanol active component in bifunctional STD catalysts [2,3,4]. This strategy provides us with a flexible nanoparticle toolbox which reduces the influence of the catalyst preparation history and ensures a high comparability. The catalytic properties of the nanoparticle-derived, bifunctional catalysts are investigated in a single continuous-flow reactor, using a simulated biomass-derived, CO-rich synthesis gas and different reaction parameters. The bifunctional catalysts revealed high CO conversions and DME selectivities. The effect of the materials characteristics of the two catalytically active components on the overall catalytic performance is elucidated. Long-term studies of selected bifunctional catalysts displayed outstanding stability under the reaction conditions.

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11:45 AM ET08.09.10
The Addition of La Via Double Flame Spray Pyrolysis and Its Effect on Catalyst Activity and Selectivity Towards the Dry Reforming of Methane Jonathan Horlyck, Emma Lovell, Jason Scott and Rose Amal; University of New South Wales, Sydney, New South Wales, Australia.

The active and stable catalysis of methane dry reforming relies upon the ability of the material to inhibit carbon formation. Central to this is the ability of a catalyst support to remove oxygen from the acidic carbon dioxide gas, storing or transporting this oxygen, before releasing it to oxidise an adsorbed CH_x intermediate species (Djinović et al., 2012). For the first time, an aerosol method was used to mix lanthanum with cobalt/alumina materials to improve support basicity. Double flame spray pyrolysis was used to synthesise heterogeneous mixtures of cobalt oxide, alumina and lanthanum oxide. Lanthanum loadings of up to 15 wt% were investigated at two separate nozzle distances (11 and 18cm). The lanthanum content in the materials and the nozzle distance separating the flames were both found to have a key influence over material composition and properties.

The structure of the supported cobalt catalysts was characterised by high-resolution transmission electron microscopy, X-ray diffraction, XANES, carbon dioxide temperature programmed desorption, X-ray photoelectron spectroscopy and hydrogen temperature programmed reduction. Catalytic activity and stability for methane dry reforming was determined via testing in a fixed bed reactor over a temperature range of 500-800 ºC, while catalyst activity was determined at a fixed temperature of 700 ºC for 48 hours.

The addition of La to the system gave rise to the substitution of La^{3+} into the Al_2O_3 lattice, as shown by high-resolution transmission electron microscopy and XANES. Hydrogen temperature programmed reduction showed that doping with La and increasing the nozzle distance limited $CoAl_2O_4$ spinel formation and facilitated the production of readily reduced Co species. The addition of La also resulted in an increase in material basicity, independent of nozzle distance, lending the catalysts a strong resistance to carbon formation.

Methane conversion and catalyst stability at 700 ºC were enhanced via the addition of La. Maximum methane conversions of 89-93% were observed for the two samples with the greatest (15 wt%). This remarkable conversion is very promising when compared to the other Co-based dry reforming catalysts. Additionally, the catalysts with 15 wt% La loading showed no sign of catalyst deactivation or carbon formation, indicating high selectivity towards the desired reaction.

SESSION ET08.10: Selective Catalysis-Industrial Perspective
Session Chairs: Gugang Chen and Yugang Sun
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room 306

1:30 PM *ET08.10.01
Surfactant-Mediated Patterned Growth of Atomically Thin Transition Metal Dichalcogenides Avetik Harutyunyan; Honda Research Institute USA Inc, Columbus, Ohio, United States.

Atomically thin transition metal dichalcogenides (TMD) with diversity of their compositions, crystallographic structures, "sandwich" heterostructures and tunability open unique opportunity to create new catalysts for various applications. Yet, capitalizing this potential demand controllable growth of patterned monolayers over larger areas on arbitrary surfaces without interfering with their intrinsic properties. Therefore, developing facile growth pathway that provides lithography-free direct patterned monolayers on various substrates is of central importance. To this end, understanding the fundamental science of how additives nucleate and enhance the growth of TMD monolayers becomes essential since they can facilitate monolayered growth, their properties and selection of the substrates. We find that alkali metal halide salt additive behaves as a surfactant in the growth of TMD monolayers by chemical passivation of the edges that reduces the strain and thereby kinetically transfer 3D island growth mode into layered growth mode. This insight allows the growth of TMD monolayers with desirable patterns on predefined location of the various substrates using pre-deposited salt layer as a water-removable template. The discovery of surfactant-mediated growth pathway not only enables substrate diversity but also provides opportunity to exploit lithography-free patterned TMD monolayers.

2:00 PM ET08.10.02
Material Discovery and Design Principles for Stable, High Activity Perovskite Cathodes for Solid Oxide Fuel Cells Ryan Jacobs, Tam Mayeshiba, John Booske and Dane Morgan; University of Wisconsin--Madison, Madison, Wisconsin, United States.

The discovery of new materials with high oxygen reduction reaction (ORR) catalytic activity and high thermodynamic stability under typical cathode operating conditions are crucial for the development of improved solid oxide fuel cell (SOFC) and related technologies. We have used high-throughput density functional theory (DFT) methods enabled by the MAterials Simulation Toolkit (MAST),[1] combined with multicomponent phase stability analysis using the Python Materials Genomics (Pymatgen)[2] toolkit, to screen a wide composition space of 2145 perovskite materials (chemical formula $A_{1-x}A'_xB_{1-x}B'_xO_3$) for candidates that have high surface exchange coefficient k^* and are thermodynamically stable under typical SOFC operating conditions.

Recent computational work has demonstrated there exists a linear relationship between the calculated bulk O p-band center and experimental surface exchange coefficient (k^*) values for numerous perovskites.[3] Therefore, the O p-band center is a useful descriptor for k^*, which is strongly correlated with overall ORR activity for perovskite materials.[3] We have employed a three-stage screening procedure to down-select promising candidate materials. Candidate materials were eliminated if they had (i) Predicted k^* less than the commercial SOFC cathode material (La, Sr)(Co, Fe)O_3, (ii) Calculated thermodynamic phase instability > 47 meV/atom (calculated value of (La, Sr)(Co, Fe)O_3) above the convex hull under SOFC operating conditions, and (iii) Electronic structure that had a nonzero electronic bandgap and thus likely to have poor electronic transport. This computational search has yielded 52 promising materials with good predicted stability in typical SOFC operating conditions and predicted k^* values similar or better than leading ORR perovskite catalysts.[4] We have also analyzed trends in predicted k^* and stability to suggest material design principles based on compositional doping to maximize both the stability and catalytic activity.

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2:15 PM ET08.10.03
Reactive Metal-Support Interaction in 2D MXene Zhe Li and Yue Wu; Iowa State University, Ames, Iowa, United States.

The reactive metal-support interaction (RMSI) offers electronic, geometric and compositional effects that can be used to tune catalytic active sites. Generally, supports other than oxides are disregarded as candidates for RMSI. In this presentation, we will discuss an example of non-oxide based RMSI between Pt and Nb_2CT_x MXene, a recently developed, two-dimensional (2D) metal carbide. The surface functional groups of the 2D carbide can be reduced, and a Pt-Nb surface alloy is formed at a moderate temperature (350 °C). Such an alloy exhibits weaker CO adsorption than monometallic Pt. Water-gas shift (WGS) reaction kinetics reveal that the RMSI stabilizes the nanoparticles and creates alloy-MXene interfaces with higher H_2O activation ability compared to a non-reducible support or a bulk niobium carbide. This RMSI between Pt and the niobium MXene support can be extended to other members of the MXene family and opens new avenues for the facile design and manipulation of functional bimetallic catalysts.

2:30 PM ET08.10.04
Electride Concept in Intermetallic LaTMSi (TM=Sc,Fe,Co,Ru) for Catalytic Ammonia Synthesis Jiazhen Wu, Yutong Gong, Junjie Wang, Masaaki Kitano and Hideo Hosono; Tokyo Institute of Technology, Yokohama, Japan.

An electride is a compound in which electrons serve as anions. Due to the weakly bound nature of the anionic electrons, electrides exhibit a variety of interesting properties, such as low work function, which enables an easy electron donation to materials with high work functions. Therefore, recently, these materials have been successfully employed as promotors to catalysts for ammonia synthesis [1]. Importantly, the reaction bottleneck was shifted from the sluggish N_2 dissociation to NH_x formation, providing an alternative route to synthesize ammonia beyond the industrial Haber-Bosch process. However only few electrides have been discovered so far and most of them are chemically unstable in the presence of air and water, so the exploration of new electrides and the concept of electride are urgent issues for both chemical interests and catalytic applications in the materials society.

In the present presentation, we show that LaTMSi, (TM=Sc, Mn, Fe, Co, Ru) are new electride candidates and show robust chemical stability in ambient conditions. [2,3] LaScSi contains multiple types of symmetry-distinct interstitial voids accommodating tiered electron anions. [2] When loaded with Ru, it shows outstanding activity for ammonia synthesis under mild conditions (0.1 MPa, 400ºC), with its turnover frequency (TOF~0.1 s^{-1}) one order of magnitude higher than those of oxide-based Ru catalysts. When Sc is replaced by Mn, Fe, Co or Ru, the transition metal atoms become activation centers and the compounds show a self-promotion behavior with high catalytic activity without loading additional metals. As with other electrides, these compounds show reversible hydrogen storage ability, and electron anions (H vacancies) exchange with H anions rapidly, providing many activated H for the catalytic reactions. Importantly, the transition metal atoms, implanted into the lattice, are activated and work effectively to cleave the N_2 triple bonds and modify the rate-determining step from the N_2 dissociation to NH_x formation. The good catalytic performance will be interpreted on a basis of the electride concept and a "hot-atom" mechanism by combining the experimental observations and theoretical simulations.

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2:45 PM ET08.10.05
Developing Fe-Based Electrocatalysts for Ambient Ammonia Synthesis Lin Hu, Jun Wang and Xiaofeng Feng; University of Central Florida, Orlando, Florida, United States.

Considering the limited supply of fossil fuels, there is an urgent need to use renewable energy to drive NH_3 production, as the current Haber-Bosch process for NH_3 synthesis is energy-intensive and consumes 3−5% of the world's natural gas production. Electrochemical NH_3 synthesis may provide a promising strategy, which can enable sustainable, distributed production of NH_3 when powered by solar- or wind-generated electricity. However, the development of such a process has been impeded by the lack of efficient catalysts for the N_2 reduction reaction (N_2RR) under ambient conditions. Many catalysts show a Faradaic efficiency <1% for N_2RR under ambient conditions. Here, we report the development of Fe-based electrocatalysts for N_2RR with a Faradaic efficiency of up to 8.29%. An Fe/Fe_3O_4 sample was prepared by in situ reduction of a pre-oxidized Fe foil in 0.1 M phosphate buffer solution (PBS). The resulting Fe/Fe_3O_4 catalyst shows greatly enhanced activity and selectivity for N_2RR under ambient conditions than the original Fe foil, achieving a Faradaic efficiency of 8.29% for NH_3 production at −0.3 V vs RHE in the 0.1 M PBS electrolyte, which is around 120 times higher than that of the Fe foil. The high selectivity is enabled by an enhancement of the intrinsic N_2RR activity as well as an effective suppression of the undesired hydrogen evolution reaction. Comparations with Fe/Fe oxide samples prepared at different pre-oxidation temperatures indicate that the N_2RR activity may depend on the ratio between Fe and Fe oxide. In addition, the N_2RR selectivity of the Fe/Fe_3O_4 catalyst is superior to that of the Fe, Fe_3O_4, and Fe_2O_3 nanoparticles, which provides new insights into the understanding and development of efficient, cost-effective electrocatalysts for ambient NH_3 synthesis.

3:00 PM BREAK

3:30 PM *ET08.10.06
Catalysis for Petrochemical Production Deng-Yang Jan and Jeffery Bricker; UOP - Honeywell, Des Plaines, Illinois, United States.

Producing petrochemicals and fuels with minimal capital investment and operating cost requires maximizing the formation of target molecules, while minimizing the formation of unrecoverable side product under the economic operating conditions with uninterrupted operation.

One approach to understand what is required to attain the theoretically attainable performance is to lay out the elementary steps of the systems and identify thermodynamic limitations and sources of deficiencies. In this presentation we show how the material and process approaches are adopted to help circumvent the thermodynamic limitations and improve efficiencies of the elementary steps and overall process in petrochemical production.

4:00 PM ET08.10.07

Highly Active and Stable Carbon Nanosheets Supported Iron Oxide Nanocatalysts for Fischer-Tropsch to Olefins Synthesis Yunyun Zhou[1, 2], Sittichai Natesakhawat[1, 3], Thuy Duong Nguyen Phan[1, 2], Douglas Kauffman[1], Christopher Marin[1], Huolin Xin[4], Eli Stavitski[5], Klaus Attenkofer[5], Yijie Tang[6], Yisong Guo[6], Iradwikanari Waluyo[5], Amitava Roy[7], Jonathan Lekse[1], John Baltrus[1], Christopher Matranga[1] and Congjun Wang[1, 2]; [1]National Energy Technology Laboratory, Pittsburgh, Pennsylvania, United States; [2]AECOM, Pittsburgh, Pennsylvania, United States; [3]Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, United States; [4]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; [5]National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York, United States; [6]Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; [7]Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, Louisiana, United States.

Fischer-Tropsch to olefins (FTO) synthesis has drawn significant attention due to the high demand of light olefins as building blocks for the chemical industry, the desire to reduce the dependence on petroleum cracking for these chemicals, and the need for improving environmental sustainability. Iron-based catalysts have emerged as promising FTO catalysts because of their low cost and excellent catalytic performances. We have designed a promising nanocatalyst of porous interconnected carbon nanosheets supported iron oxide nanoparticles for FTO synthesis. The catalysts demonstrate an extremely high iron time yield (FTY) of 1882 $\mu mol_{CO}/g_{Fe}s$ with 41% selectivity for light olefins and excellent stability (> 100 h time on stream). Our FTY value is found to be one of the highest FTYs and in particular, is 50 to ~1300 times higher compared with those catalysts exhibiting similar light olefins selectivity reported in literature. Mössbauer characterization demonstrates the presence of catalytically active iron carbide species after FTO reaction. *ex situ* XAFS measurements reveal that the carbon nanosheets support stabilizes metallic iron during the initial catalyst reduction step, which leads to more carbon uptake under FTO reaction conditions to more efficiently form highly active iron carbide phase. In contrast, a control sample with carbon nanotubes as the catalyst support exhibits oxidized iron in the catalyst after removal from H_2 reduction pretreatment, suggesting substantially reduced stabilizing effect of carbon nanotubes towards supported metallic iron nanoparticles. This results in inefficient formation of iron carbide species under FTO conditions. Additional EXAFS results further confirm the buildup of iron carbide phase as a function of time on stream in the carbon sheets supported catalysts, whereas a much smaller portion and negligible growth of iron carbide phase was observed in the carbon nanotube supported catalysts under the same reaction conditions.

4:15 PM ET08.10.08

Hydrocracking Catalyst Optimization for Upgrading Heavy, Polyaromatic Oil Fractions Mark Kaminsky[1], Sarah Kobasilja[1], Tatiana Pilyugina[1], Kareemuddin Shaik[2], Lianhui Ding[2] and Essam Al-Sayed[3]; [1]Aramco Services Co., Cambridge, Massachusetts, United States; [2]Research and Development Center, Saudi Aramco, Dhahran, Saudi Arabia; [3]Technical Services Dept., Aramco Services Co, Houston, Texas, United States.

Introduction
Changes in global supply and demand for fuels versus chemicals has increased the incentive to better control how much of each is produced from a barrel of crude oil. In addition, as the value of crude oil increases, there is incentive to improve the efficiency of upgrading a barrel of crude, in particular the bottom of the barrel resid. Such highly aromatic resid fractions, which used to end up in petroleum coke or asphalt, are being upgraded to more valued products with new catalytic and process advances. This is partly driven by further restrictions on the burning of petroleum coke, which makes delayed coking less desirable. Hydrogen addition, via hydrocracking, avoids the production of such petroleum coke from the resid fractions, transforming them into more useful fuel and chemical products.
Discussion
This talk will describe two aspects of hydrocracking catalyst development to upgrade heavier crude oil fractions. In the first part, we will present results on the development of a multifunctional hydrocracking catalyst, comprising both homogeneous organometallic and heterogeneous zeolite components. The homogeneous components are oil soluble organometallic compounds of Mo or Fe that are designed to transform *in situ* into unsupported nanoparticle metal sulfides that hydrocrack the large asphaltenic molecules, which tend to foul heterogeneous zeolitic pores. The mesoporous zeolites will then more effectively hydrocrack the smaller products of the asphaltenes and maltenes cracking, in order to make chemicals/fuels with less pore plugging. However, with time on stream, the nanoparticles might sinter and become less active. We will present results on the sintering rates of the Mo and Fe nanoparticles at various conditions in the presence of zeolites. Since the nanoparticles and zeolite crystals are both in the same hydrocracking reactor, it is important to understand their interaction under reaction conditions via characterization of the used catalytic materials. Such catalyst characterization will shed light on the interaction and deactivation mechanisms of these catalyst species.
In the second part of hydrocracking catalyst development we will present data on the synthesis of nano-sized Beta zeolite crystals and the effect of zeolite crystal size and shape on hydrocracking activity. Details of the synthesis method for preparation of the nano-sized Beta will be presented in addition to activity studies using a highly aromatic LCO (Light Cycle Oil) feedstock for the hydrocracking reaction.

4:30 PM ET08.10.09

Electroreduction of Oxygen at Nanostructured Methanol Tolerant Cathodes for Mixed-Reactant Direct Methanol Fuel Cells Juan C. Abrego[1], Youling Wang[1], Alonso Moreno-Zuria[2], Francisco Cuevas-Muniz[2], Luis G. Arriaga[2], Shuhui Sun[1] and Mohamed Mohamedi[1]; [1]Energie, Materiaux et Telecommunications (EMT), Institut National de la Recherche Scientifique (INRS), Varennes, Quebec, Canada; [2]Centro de Investigacion y Desarrollo Tecnologico en Electroquimica, Queretaro, Mexico.

Energy sources for all kind of electronic devices are under constant pressure to achieve higher efficiency levels by increasing the energy density and decreasing both volume and weigh while reducing the cost of portable power sources at the same time [1]. Mixed-reactant microfluidic direct methanol fuel cells (MR-µDMFCs) represent a promising power supply alternative for electronic portable devices in the future, due to their simplicity of design, fabrication and operation. Theoretically, they can achieve higher energy density in comparison with other DMFCs. The main challenge arises from the need for selective electrocatalysts [2]. The synthesis of cathode materials with high mass specific activity towards the oxygen reduction reaction (ORR) and no activity towards the methanol oxidation reaction (MOR) is crucial for the development and commercialization of MR-µDMFC.

In the present work, we report a two-step synthesis by pulsed laser deposition (PLD) of two Pt-based catalysts having a layer onto layer structure. For the two catalysts, first an ultra-low loading Pt layer is deposited directly on carbon nanotubes and further coated with a porous Ag layer or a porous Mn_2O_3 layer, obtaining Ag/Pt/CNTs and Mn_2O_3/Pt/CNTs, respectively. According to the physicochemical characterization, these layers don't present electronic interaction with each other. The resulting binary materials exhibit electrocatalytic activity similar to Pt towards the ORR in alkaline media. The RRDE studies reveal that the ORR on both Pt/CNTs and Mn_2O_3/Pt/CNTs, is carried out through a 3.9 electron transfer mechanism, while on Ag/Pt/CNTs, the transfer is about 3.7 electron. Interestingly, the bilayer cathodes show no activity for the MOR. Furthermore, those materials demonstrate to be tolerant to methanol concentration as high as 5 M. The results suggest that the superficial Ag and Mn_2O_3 components discriminate between the molecular volume of O_2 and MeOH. Lastly, in order to compare the performance of the methanol-tolerant cathodes in a fuel cell, the materials are tested in a passive, air-breathing MR-µDMFC in conditions close to real application.

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4:45 PM ET08.10.10

Epitaxial and Atomically Thin Graphene–Metal Hybrid Catalyst Films—The Dual Role of Graphene as the Support and the Chemically-Transparent Protective Cap Ali Abdelhafiz and Faisal Alamgir; Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Commercialization of polymer electrolyte membrane (PEM) fuel cell materials has been of a great interest over the past decade. At the cathode side, the oxygen reduction reaction (ORR) is the key reaction where sluggish kinetics is present, for which Pt remains the catalyst of choice. In order to leapfrog the current limits to Pt use, three main objectives have to be achieved. First, is a reduction of Pt loading; second, is an enhancement of the mass activity per Pt atom; and third is an increase the catalyst durability. Herein, we demonstrate the dual role of single graphene layer, both as a growth template and as a protective cap for 2D Pt monolayers catalysts, where all three objectives can be achieved.

Using iterative under potential deposition (UPD), atomic layers of Pt catalyst are grown on top of a single layer graphene. X-ray absorption spectroscopic (XAS) and scanning transmission electron microscopy (STEM) analyses show that Pt growth is dictated by the graphene-templated epitaxy. Pt/graphene intimacy induces a localized compressive strain on Pt monolayers ranges 3-10%, owing to structural defects, with an overall compressive strain of 3.5% according to extended x-ray absorption fine structure (EXAFS) analysis. In addition, cyclic voltammetry (CV) analysis shows fully-wetted Pt monolayers coverage of graphene under-layer with only a ~1 nm ultra-thin layer of Pt, while ripening was suppressed as shown through STEM images. Atomic Force Microscopy (AFM) analysis demonstrates that Pt monolayers prefer to follow Frank-van der Merwe growth (i.e. layer-by-layer growth mode) rather than Volmer-Weber growth (i.e. island growth mode), where root mean square (rms) of surface roughness remains quite similar while increasing Pt loading is increased.

Pt/graphene hybrid catalysts show superior catalytic activity for ORR relative to the graphene-free counterparts or state of the art Pt commercial catalyst. A combination of the graphene-imposed compressive strain and electron transfer, push the Pt d-band center up, lowering the overpotential needed for ORR to occur. Furthermore, the graphene/Pt cap hybrid shows the graphene protecting Pt MLs from both dissolution and from ripening, with almost no Pt loss after 5000 fuel cell operating cycles. Our demonstration of a graphene-Pt hybrid opens the door for graphene/metal or metal/graphene architectures with potential applications in, and not limited to, energy, thermo-electric and electronics field.