

SYMPOSIUM ET13

Materials for Multifunctional Windows
November 26 - November 28, 2018

Symposium Organizers

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Symposium Support

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* Invited Paper

SESSION ET13.01: Luminescent Solar Concentrating Windows I
Session Chairs: Christopher Barile and Rachel Evans
Monday Morning, November 26, 2018
Hynes, Level 3, Room 303

8:00 AM IN MEMORY OF PAUL O'BRIEN

8:30 AM *ET13.01.01

Luminescent Sunlight Collectors Based on Engineered Quantum Dots [Victor I. Klimov](#); Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Luminescent solar concentrators (LSCs) are envisioned to reduce the cost of solar electricity by decreasing the usage of more expensive photovoltaic (PV) materials and diminishing the complexity of multi-cell PV modules. The LSC concept can also enable unconventional solar-energy conversion devices such as PV or "solar" windows that can be especially useful in highly populated urban areas. Due to their high emission efficiencies and readily tunable emission and absorption spectra, colloidal quantum dots (QDs) have emerged as promising LSC fluorophores. The focus of this presentation is on both fundamental studies of luminescent concentration exploiting nearly ideal LSC characteristics of engineered QDs [1, 2] as well as practical, high-performance devices demonstrating commercial viability of a QD-LSC approach [3]. Specific topics of discussion will include practical concentration limits tested using nearly perfect QD emitters with >95% quantum efficiencies [1], various approaches to Stokes-shift engineering [4, 5], single- and double-layer LSC architectures, as well as cost/efficiency considerations for QD-LSCs [3, 6]. The overall conclusion of the reviewed studies is that engineered QDs represent a promising materials platform for realizing inexpensive, high-efficiency sunlight collectors applicable as both semi-transparent building-integrated solar windows and stand-alone, large-area LSC-PV modules.

1. Song, H.J., B.G. Jeong, J. Lim, D.C. Lee, W.K. Bae, and V.I. Klimov, Performance Limits of Luminescent Solar Concentrators Tested with Seed/Quantum-Well Quantum Dots in a Selective-Reflector-Based Optical Cavity. *Nano Letters* **18**, 395-404 (2018)
2. Klimov, V.I., T.A. Baker, J. Lim, K.A. Velizhanin, and H. McDaniel, Quality Factor of Luminescent Solar Concentrators and Practical Concentration Limits Attainable with Semiconductor Quantum Dots. *ACS Photonics* **3**, 1138-1148 (2016)
3. Li, H., K. Wu, H.-J. Song, and V.I. Klimov, Doctor-blade deposition of quantum dots onto standard window glass for low-loss large-area luminescent solar concentrators. *Nature Energy* **1**, 16157 (2016)
4. Meinardi, F., A. Colombo, K.A. Velizhanin, R. Simonutti, M. Lorenzon, L. Beverina, R. Viswanatha, V.I. Klimov, and S. Brovelli, Large-area luminescent solar concentrators based on 'Stokes-shift-engineered' nanocrystals in a mass-polymerized PMMA matrix. *Nature Photonics* **8**, 392-399 (2014)
5. Meinardi, F., H. McDaniel, F. Carulli, A. Colombo, K.A. Velizhanin, N.S. Makarov, R. Simonutti, V.I. Klimov, and S. Brovelli, Highly efficient large-area colourless luminescent solar concentrators using heavy-metal-free colloidal quantum dots. *Nature Nanotechnology* **10**, 878-885 (2015)
6. Wu, K.F., H.B. Li, and V.I. Klimov, Tandem luminescent solar concentrators based on engineered quantum dots. *Nature Photonics* **12**, 105 (2018)

9:00 AM *ET13.01.02

Photonic Structures for Solar Concentrators and Module Thermal Management [Vivian Ferry](#); University of Minnesota, Minneapolis, Minnesota, United States.

The first part of the talk will discuss our recent research in applying photonics to luminescent solar concentrators. Luminescent solar concentrators downshift and concentrate incident sunlight onto edge-mounted solar cells, and the tunability and high quantum yield of semiconductor nanocrystals make them natural candidates as the luminescent material. Our work focuses on the integration of photonic mirrors with LSCs, which reduce losses to the escape cone and redirect the angle of light propagation through the concentrator. We will discuss how the design of the mirrors changes for different luminophores and LSC geometries, and on experimental LSCs that use both Cd-based and Si nanocrystals as the luminescent material.

The second part of the talk will discuss spectrally-selective structures used for light management in photovoltaic modules. These structures are designed to enhance transmission of sunlight above the bandgap of Si to improve photocurrent, and enhance reflection of light below the bandgap to reduce module operating temperature. We will show how the structures change at different interfaces within the module, the importance of designing mirrors that operate under diffuse illumination, and the effect of geographical location on mirror performance. Finally, we show how the mirror performance evolves as a function of number of layers, and that significant energy yield improvements can be realized with less than 10 layers.

9:30 AM BREAK

10:00 AM *ET13.01.03

Luminescent Solar Concentrators—Investigation of New Active Materials for Improved Efficiency and Scalability Katerina Nikolaidou¹, Benaz Mendewala¹, Christine Hoffman³, Boaz Ilan³, Jennifer Lu² and Sayantani Ghosh¹; ¹Physics, University of California, Merced, Merced, California, United States; ²Materials Science and Engineering, University of California Merced, Merced, California, United States; ³Applied Math, University of California, Merced, Merced, California, United States.

The recent re-emergence of luminescent solar concentrators (LSCs) as viable devices for solar energy harvesting can be attributed to the impressive progress in materials development and engineering. The resultant products have demonstrated effective broadband absorption, high external quantum yield (QY) and spectral properties that allow for almost negligible self-absorption (SA) losses. Our research has focused on investigating the ramifications of different active materials and device architectures on LSC performance, including efficiency and photostability. I will begin with a discussion of our work regarding the use of near infra-red lead sulphide (PbS) quantum dots (QDs) as in planar LSCs. The results of this study indicated that PbS LSCs generate nearly twice the photocurrent in silicon cells compared to a traditional dye and cadmium selenide QDs, achieving an integrated optical efficiency η_{opt} of 12.6%. This was primarily due to the broadband absorption of PbS, and a smaller overlap between the absorption and emission spectra, which reduces SA. However, despite the superior performance, PbS also exhibits a gradual and permanent photo-oxidation, which decreases the photocurrent at the rate of 0.1% per minute. Tuning the device architecture led to some improvements in PbS-based LSCs, as we demonstrated next, fabricating solid and hollow cylinders from a composite of QDs in polymethylmethacrylate. The experimental results were in good agreement with theoretical calculations, with hollow LSCs having a higher absorption of incident radiation and lower SA compared to solid cylindrical and planar geometries with similar geometric factors. In addition to optical efficiency almost thrice that of planar LSCs, these also exhibited improved photo-stability under both laboratory and external ambient conditions. Most recently, we have begun exploring the suitability of organic-inorganic hybrid perovskite (PVSK) thin films as the active medium in planar LSCs. PVSK compounds are at the forefront of photovoltaic research, and their high refractive index, broad absorption spectrum, and superior QY make them theoretically ideal candidates for LSCs. In practice, however, the possibility of high self-absorption in a continuous film, coupled with the inherent instability of PVSK materials, have hindered their use. Our results display an impressive η_{opt} in the range 15%–29% despite high SA losses, and the devices remain operational for up to seven weeks in ambient conditions. We attribute this to the high QY and refractive pushed the efficiency to 34.7%. Further, using 3D Monte Carlo simulations that incorporate our experimental results, we have demonstrated the possibility of scaling these LSCs up to almost 100 cm, thereby providing a route toward optimizing thin film PVSK materials for these and other optoelectronic and photovoltaic applications. This work was supported by funds from the National Aeronautics and Space Administration grant no. NNX15AQ01A.

10:30 AM ET13.01.04

Light Scattering in Poly(methyl methacrylate) Doped with Functionalized Si Quantum Dots Samantha Hill¹, Ryan Connell², Vivian Ferry² and Uwe R. Kortshagen¹; ¹Mechanical Engineering, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States; ²Chemical Engineering & Materials Science, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

The near-infrared emission and large effective Stokes' shift of Si quantum dots (Si QDs) are attractive properties for light-management technologies like downshifting layers on photovoltaics or luminescent solar concentrating windows. In the case of the latter, the Si QDs must be finely dispersed in a transparent matrix, like a polymer, in order to achieve high light concentration factors. Our Monte Carlo models show that increasing the average light scattering length from 1 mm to 1 m in a 1 m² device would provide a 4-fold increase in collected light for devices using Si QDs with a quantum yield of 50%. This gain only increases in the case of more efficient Si QDs. However, obtaining low-scattering dispersions of Si QDs in relevant, cost-effective polymers remains a challenge, and few reports of Si QD / polymer composites exist. Here, we studied the effect of surface ligand choice on the light scattering properties of Si QDs incorporated within mass polymerized poly(methyl methacrylate). Nanocomposites were made using Si QDs capped with a typical, nonpolar ligand or an ester-ended analog. We find the two surface treatments lead to significantly different dispersion characteristics in methyl methacrylate: either a primarily singly dispersed mixture is achieved, or agglomeration produces strongly scattering Si QD clusters at least 10 times larger than a single QD diameter. Fully polymerized nanocomposites exhibit increased light scattering corresponding to the agglomeration state in the monomer, especially at higher QD loading fractions. UV-Vis measurements of these composites indicate that choosing ligands similar in structure to the composite monomer can help reduce scattering losses within the nanocomposites. These results offer a strategy to improve Si QD luminescent solar concentrator performances in a low-cost, structural polymer suitable for window applications.

10:45 AM ET13.01.05

Flexible Bragg Reflectors for Efficient Deformable Luminescent Solar Concentrators Mark Portnoj, Christian Sol, Tom S. Robbins, Johannes Schlaefer, Clemens Tummelshammer and Ioannis Papakonstantinou; Electronic and Electrical Engineering, University College London, London, United Kingdom.

Structural flexibility of photovoltaic devices can lead to an expanse of applications such as wearable technologies, flexible electronics, self-powered sensors and roll-to-roll manufactured smart facades.

Luminescent solar concentrators (LSCs) composed of flexible host matrices such as polydimethylsiloxane (PDMS) have been proposed as a means of providing this flexibility. The elastomer sheets doped with luminophores can be fabricated in a range of sizes, transparencies, colours and rigidities to the designer's needs.

This additional functionality can come at a cost to efficiency. Curvature results in increases in both reabsorption and escape cone losses. In this work we explore how curvature affects these losses and propose a solution for their mitigation. We investigate the effect of curvature on LSC efficiency by means of an experimentally verified Monte-Carlo model (MCM) for curved LSCs. We show that for large scale devices, the optimal concentrations of fluorophore concentrations at fixed thicknesses required to achieve the highest external optical efficiency differ for curved and flat LSCs.

To mitigate escape cone losses, we propose flexible distributed Bragg reflectors (DBRs) consisting of alternating PDMS and PDMS-titanium composite thin films with a refractive index contrast of ~0.3. These DBRs are designed to have omnidirectional reflectivity in the spectral region of the emission of the luminophores but high transmission in the absorption region. We fabricate prototype DBRs and compare reflectance to transfer matrix model (TMM) calculations. Combining our MCM and TMM into a hybrid package we optimise the application of such DBRs to Lumogen Red 305 doped flexible LSCs and demonstrate the DBR effect on their efficiency. We then use the model to predict the full potential of this pairing.

This work will pave the way for efficient and deformable LSCs. We plan to incorporate these into devices for use in everyday life.

11:00 AM *ET13.01.06

Powering Future Cities with Quantum Dot-Tinted Glass Luminescent Solar Concentrator Windows [Hunter McDaniel](#), Matt Bergren, Karthik Ramasamy, Aaron Jackson, Nikolay Makarov, Andres R. Velarde and Nicolai C. Archuleta; UbiQD, Inc., Los Alamos, New Mexico, United States.

In urban settings where demand (and price) for electricity is high, the space available for solar modules is minimal. Tall buildings utilize vast amounts of electricity that is transmitted from remote power stations on lossy transmission lines. Emerging competing sunlight-harvesting window solutions are expensive and have poor aesthetics. Competing quantum dot (QD) technologies are costly, toxic, and/or unstable. UbiQD invokes proprietary methods for low-cost manufacturing of stable, high performance, non-hazardous QD composites that are utilized in luminescent solar concentrators (LSCs). Partially transparent LSCs provide a simple method of harvesting sunlight wherein absorbed light is effectively redirected to small solar cells hidden in the frame of a window. The company has achieved a certified record performance for solar windows, and is close to its target of 50 W/m² of power output at 50% visible light transmittance, enough to turn an 80-story skyscraper into a >1GWh/yr urban power station. In this talk I will provide an overview to the market opportunity for solar windows, competitive landscape, and how our QD LSC technology compares. I will also provide a status update on UbiQD's best performing prototypes to date, and other recent milestones at the company.

SESSION ET13.02: Luminescent Solar Concentrating Windows II

Session Chair: Sayantani Ghosh

Monday Afternoon, November 26, 2018

Hynes, Level 3, Room 303

1:30 PM *ET13.02.01

Bottom-Up Design of Integrated Lumophore-Waveguide Materials for Luminescent Solar Concentrators [Rachel Evans](#)¹, Ilaria Meazzini², Niamh Willis-Fox², Adarsh Kaniyoor², Barry McKenna² and Lorcan Brennan²; ¹University of Cambridge, Cambridge, United Kingdom; ²Trinity College Dublin, Dublin, Ireland.

Single junction photovoltaic devices exhibit a bottleneck in their efficiency due to incomplete or inefficient harvesting of photons in the low- or high-energy regions of the solar spectrum. This can be overcome through the retro-fitting of a spectral converter to the device, which is used to convert solar photons into energies that are more effectively captured by the solar cell through a photoluminescence process. However, while a lumophore may show seemingly ideal optical characteristics for spectral conversion in an ideal solution (high emission quantum yield, strong absorption), disappointment frequently awaits on its translation to the solid-state, where aggregation and quenching effects lead to significantly reduced photoluminescence yields.

In an effort to overcome this limitation, our research focusses on the bottom-up design of integrated lumophore-host materials for solar spectral converters, in which materials chemistry design strategies are used to control the packing, orientation and placement of p-conjugated lumophores in solid-state host materials. Since the electronic properties depend explicitly on the arrangement and packing of the p-conjugated species, this approach provides a means of modulating the optical properties. In this talk, we will report our recent results on the design of Π -conjugated composite materials that utilise a family of organic-inorganic hybrid polymers known as the *ureasils* as the host. Ureasils are comprised of a siliceous skeleton that is chemically-grafted to poly(ethylene oxide) (PEO)/poly(propylene oxide) (PPO) chains through urea cross-linkages, the number of which depends on the degree of branching in the organic polymer precursor. Ureasils are intrinsically photoluminescent, exhibit high refractive indices and function as optical waveguides. Through judicious selection of the degree of branching and length of the organic backbone and the incorporation method (grafting vs immobilization vs permeation), we can control the packing, orientation and placement of the Π -conjugated species in the ureasil host. This in turn provides a means of modulating the optical properties. For example, a dramatic enhancement in the emission quantum yield to >60% is observed due to exciton localization at isolated nanodomains of a conjugated polyelectrolyte entrapped within the ureasil host. Similarly, Förster resonance energy transfer from the ureasil to embedded or grafted conjugated lumophores can be exploited to tune the emission color and even obtain white-light emission. These characteristics can be exploited to improve light-harvesting and trapping within the integrated material, which can be used to develop highly efficient LSCs to enhance the performance of silicon solar cells.

2:00 PM ET13.02.02

Polymer Formulation for Quantum Dot Luminescent Solar Concentrators [Aaron Jackson](#), Andres R. Velarde, Karthik Ramasamy, Nikolay Makarov, Matt Bergren and Hunter McDaniel; UbiQD, inc, Los Alamos, New Mexico, United States.

This work highlights key parameters required to make 12 inch square, and larger, quantum dot (QD) luminescent solar concentrators (LSC) for solar window applications. Our quantum dot solar windows are neutral in color and have a high optical power efficiency of 8% at 50% visible light transmittance (VLT). The windows use copper-indium-sulfide (CIS) quantum dots that are cheaper to make and less toxic than other QD materials. This makes them ideal for large area applications including safety inks and agricultural films in addition to solar windows. In an LSC, QDs absorb light and re-emit that light within the LSC. Due to total internal reflection (TIR), that re-emitted light channels to the edge of the LSC where the solar cells absorb and convert the light to electricity. Small defects in the LSC material reduce performance. This includes surface defects, defects in the polymer and QD aggregation in the polymer. A successful device must limit these defects.

High performance QDs, dispersing agents, and controlled resin curing are all important for manufacturing successful LSC materials and solar windows. Our CIS QDs have high QY and are stable in air at high temperatures. This allows formulation and curing of QD resins in air with minimum QY reduction. The high temperature stability also opens future opportunities for extrusion processes. In fact, we demonstrate that our CIS QDs can withstand 190°C for more than 10 minutes with minimal QY reduction. We incorporate QDs into windows as part of an interlayer in a glass laminate configuration where the laminate is made by a casting manufacturing technique. The glass has minimal surface defects which allows highly efficient TIR. Typically, the hydrophobicity of the QDs limits QD resin formulations to low viscosity, low adhesion, and low concentration formulations. However, by using dispersing agents and controlled curing techniques, we are able to formulate our resins with functionality similar to commercial polymers. For example, our resins use a variety of viscosity modifiers, plasticizers and adhesion promoters that allow scalable manufacture such as roll-to-roll coating and polymer casting. With these complex formulas, our QD LSCs with a VLT of 50% allow solar windows to be made with 29W/m² as certified with testing at NREL.

2:15 PM *ET13.02.03

Tuning Optical Properties in Composite Quantum Dots for Smart Windows [Alberto Vomiero](#); Luleå University of Technology, Luleå, Sweden.

Composite quantum dots (QDs) represent the forefront of both fundamental and applied research for smart windows. Specifically, the tunable absorption and emission properties of composite QDs make them ideal candidates for QD-based semitransparent and colored solar cells and luminescent solar

concentrators for application in building-integrated photovoltaics.

The optical properties of composite QDs can be finely tuned by proper adjustment of chemical composition, size and morphology of the single components and of the heterostructured systems, including symmetric and asymmetric core-shell and multiple shelled structures.

Key element for light emission is the modulation of the final electronic band structure of the composite, which will tune exciton dynamics in the final system, determining the functionality of the device.

We will illustrate different strategies to obtain the desired optical properties in different complexes to optimize the functionality in specific applications.

A few examples will include: (i) "Giant" composite core-shell QDs, in which modulation of core-to-shell interface induces a single-to double-color photoluminescence; [1-2] (ii) Near-infrared QDs with increased Stokes shift due to suitable electronic structure of the core and shell, to be applied in luminescent solar concentrators [3] and photoelectrochemical systems; [4] (iii) Composite TiO₂ mesoporous films sensitized by "giant" and composite QDs with high charge injection from the photoexcited QD to the TiO₂ anode, for excitonic solar cells [5] and hydrogen production [6].

[1] G. Sirigu et al. Phys. Rev. B 96, 2017, 155303

[2] H. Zhao et al. Small 12, 2016, 5354

[3] Y. Zhou et al. Adv. En. Mater. 6, 2016, 1501913

[4] L. Jin et al. Nano En. 30, 2016, 531

[5] A. Braga et al. J. Phys. Chem. Lett. 2, 2011, 454

[6] L. Jin et al. Adv. Sci. 3, 2016, 1500345

2:45 PM BREAK

3:15 PM *ET13.02.04

Visible-to-Near Infrared Sustainable Luminescent Solar Concentrators for Flexible Photovoltaics Rute Ferreira; Physics, Department of Physics, CICECO - Aveiro Institute of Materials, Aveiro, Portugal.

Luminescent solar concentrators (LSCs) appear as an intriguing way to cope with the mismatch between the photovoltaic (PV) cells absorption and the solar spectra, with the additional advantage of urban integration of photovoltaics [1,2]. We present LSCs based on bundles of triangular hollow-core plastic optical fibers (POFs) filled with amine-functionalized organic-inorganic hybrids (di- and tri-ureasils) doped with Rhodamine 6G, Rhodamine 800 or an Europium b-diketonate complex with visible-to-NIR tunable emission. The LSCs are characterized by optical conversion efficiency values up to $h_{opt} \sim 5.3\%$ and when coupled to commercial Si PV cells yield maximum power conversion efficiency values of PCE $\sim 0.74\%$ [3].

Aiming at following a sustainable route for the designing novel LSCs, photosynthesis was an inspiring natural mechanism and chlorophyll-based LSCs were processed and optically characterized. The chlorophyll molecules were extracted from *Spirulina maxima* which is an abundant cyanobacteria and an attractive natural source. To enable the easy and controlled processing of planar LSCs, the chlorophyll molecules were incorporated into di- and tri-ureasils with the added advantages of avoiding the formation of non-luminescent dye-aggregates, enhancing quantum yield and photostability. The chlorophyll-based LSCs were coupled to a Si-based PV device, revealing h_{opt} and PCE) values $\sim 3.70\%$ and $\sim 0.10\%$, respectively, demonstrating the huge potential of nature-inspired LSCs for sustainable PV energy conversion [4].

[1] M. J. Currie, J. K. Mapel, T. D. Heidel, S. Goffri, M. A. Baldo, Science, 2008, 321, 226-228.

[2] F. Meinardi, H. McDaniel, F. Carulli, A. Colombo, K. A. Velizhanin, N. S. Makarov, R. Simonutti, V. I. Klimov, S. Brovelli, Nat. Nanotechnol., 2015, 10, 878-885.

[3] S. F. H. Correia, A. R. Frias, L. Fu, R. Rondão, E. Pecoraro, S. J. L. Ribeiro, P. S. André, R. A. S. Ferreira, L. D. Carlos. 10.1002/adsu.201800002

[4] A. R. Frias, E. Pecoraro, S. F. H. Correia, L. M. G. Minas, A. R. Bastos, S. Garcia-Revilla, R. Balda, S. J. L. Ribeiro, P. S. André, L. D. Carlos, R. A. S. Ferreira, J. Mater. Chem. A, 2018, 6, 8712-8723.

3:45 PM ET13.02.05

Scalable, Power Efficient Luminescent Solar Concentrator Windows with Tailored Transparency David R. Needell¹, Haley Bauser¹, Megan Phelan¹, Colton R. Bukowsky¹, Ognjen Ilic¹, Brent A. Koscher², Junwen He³, Hanxiao Su³, Ralph Nuzzo³, A. P. Alivisatos² and Harry A. Atwater¹; ¹Applied Physics and Materials Science, California Institute of Technology, Pasadena, California, United States; ²Chemistry, University of California, Berkeley, Berkeley, California, United States; ³Chemistry, University of Illinois at Urbana-Champaign, Urbana-Champaign, Illinois, United States.

Since the inception of the luminescent solar concentrator (LSC) in the early 1970s for photovoltaic (PV) applications, tremendous research efforts continue to be directed toward harnessing LSC technology for power generation in large-area windows. Future energy-efficient buildings will ideally be equipped with windows that (i) provide for daylighting, (ii) enable flexible choice of colors, including transparent, grey and RGB values, (iii) manage thermal radiation to improve thermal efficiency, (iv) generate significant quantities of electrical power, and (v) have costs equal to or less than double-glazed windows. While LSCs represent an intriguing approach for such building integrated applications, current LSC technology does not maintain performance when scaled to module sizes comparable to current window areas.

To address this issue of sustained power efficiency with increasing module area, we introduce a scalable LSC form factor by patterning a grid of micro-cell, Si PV cells embedded within a layer of PLMA doped with InAs/InP/ZnS quantum dots (QDs). By fixing the waveguide to PV area factor (i.e. geometric gain), we demonstrate consistent photon travel lengths with increasing module size. We apply both a Monte Carlo ray-trace algorithm and an analytical closed form calculation of such power window performance for an arbitrarily large area, and evaluate visible transparency of such a re-engineered LSC device for building integrated PV applications. Such planar grid architecture represents a significant departure from traditional LSC geometries, which align the PV collector along the perimeter of the waveguide. Our analysis reveals how a grid-pattern arrangement for LSCs permits scalability, high power conversion efficiency, and tailored transparency.

4:00 PM *ET13.02.06

Advances and Challenges in Luminescent Solar Concentration for Building Integrated Photovoltaics Francesco Meinardi; Department of Materials Science, University of Milano-Bicocca, Bicocca, Italy.

Luminescent solar concentrators (LSCs) could facilitate the green architecture revolution by enabling the realization of semi-transparent photovoltaic (PV) systems, which could potentially convert the façades of urban buildings into distributed electrical power generators. LSCs were first proposed in 1976 as cost-effective alternatives to silicon solar cells. However, only after the recent breakthroughs in the realization of new classes of colloidal semiconductor nanocrystals, which combine suppressed reabsorption with broadband spectral coverage, the performances of the LSCs have been boosted to such a degree that they become the most promising technology for the next generation of PV glazing units. The LSC technology is now set on a clear path to become a PV technology that can be 'invisibly' integrated into the built environment without detrimental effects to the aesthetics of the building or the quality of life

of the inhabitants in the form of colorless and electrodeless solar windows or as other semi-transparent architectural elements. Nevertheless, this final integration step, and in particular the optimization of the power efficiency for devices on the meter scale, will require scientists and engineers to face new emerging challenges.

This talk will review the successful strategies that have allowed this historical change of pace, examining and comparing the different types of developed nanomaterials, and discuss the issues that remain to be investigated for further progress. On the materials side, the realization of high-quality optical waveguides will be the most demanding task. It will require a perfect dispersion of the nanocrystals inside the waveguide matrix to avoid detrimental light-scattering losses and, probably, also the adaptation to LSCs of highly transparent polymers or glass variants currently used in photonics and telecommunications will be necessary to produce very large LSCs. Finally, the optical-to-electrical conversion by the PV cells at the LSC edges will have to be suitably designed and optimized. This last step in the luminescent solar concentration process has not yet been fully investigated because of the challenges in the realization of highly performing optical waveguides. Together with the role of the waveguide absorption, this will soon be at the forefront of research into LSCs for real-world applications.

SESSION ET13.03: Electrochromic Windows
Session Chairs: Claes-Goran Granqvist and Alberto Vomiero
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 303

8:30 AM *ET13.03.01

Addressing the Problem of Black to Transmissive in Electrochromic Polymers for Switchable Windows [John R. Reynolds](#), Chi Kin Lo, Anna Österholm, Lisa R. Savagian and Dwanleen E. Shen; Georgia Institute of Technology, Atlanta, Georgia, United States.

Encouraged by the commercial utility of organic molecular electrochromes in electrochromic windows and mirrors, we are developing scalable and solution processable conjugated electrochromic polymers (ECPs), which provide a unique encompassing set of structurally tunable colorimetric and redox properties, stable over thousands and tens of thousands of redox switches. Processing of these materials is carried out using a variety of solution methods including spin-coating, spray-coating, blade-coating, slot die coating, and ink jet printing. In this lecture, we demonstrate how the optical absorbance spectra of ECPs can be tuned to yield materials of all colors that can be switched to highly transmissive forms as desired for absorptive/reflective (display type) and absorptive/transmissive (window type) devices. We will show how random copolymerization has been used to broaden spectral absorption yielding a family of black-to-transmissive ECPs. We have also developed a set of fast switching, high contrast, black and brown ECP blends, where the precise hues are readily tunable. We use these brown blends to showcase a practical application of ECPs in color changing eyewear. In addition to their aesthetic qualities, their optical memory in both the colored and colorless states allow these devices to be run at low power. Photo-oxidative stability will be addressed using encapsulated films and ECDs. Finally, we combine our ECP and OPV technologies into possibilities for solar powered electrochromic windows.

9:00 AM ET13.03.02

Digitally Inkjet Printed Electrochromic and Electrofluorochromic Polymer for Dual-Mode Display Applications [Manuel Pietsch](#)^{1,2}, Johannes Zimmermann^{1,2}, Tobias Rödlmeier^{1,2}, Stefan Schliske^{1,2}, Carlos Romero-Nieto³ and Gerardo Hernandez-Sosa^{1,2}; ¹LTI, Karlsruhe Institute of Technology, Karlsruhe, Germany; ²KIT, InnovationLab GmbH, Heidelberg, Germany; ³OCI, Ruprecht-Karls-University Heidelberg, Heidelberg, Germany.

Electrofluorochromic devices (EFCd) receive increasing attention in investigation in the past years, because they offer the possibilities for dual-mode display devices, which combine the advantages of reflective and emissive displays. Besides that, the low power consumption, the low voltage requirement and simple device architecture (i.e. electrochemical cell) provide the opportunity for low-cost display devices. To provide a cost-effective method with the freedom of design necessary for smart windows and display applications, inkjet printing can be used as a suitable method with high throughput, low material waste and upscaling capabilities to industrial fabrication.

Here, we report the synchronous electrochromic and electrofluorochromic switching of polyindeno[1,2-b]fluorene-8-tryarylamine (PIF8-TAA). The investigated devices consisted of a layer of PIF8-TAA and a polymer electrolyte gel (PEG), using poly(methyl methacrylate) (PMMA), tetrabutylammonium hexafluorophosphate (TBAPF₆) and propylene carbonate (PC), sandwiched between two indium tin oxide (ITO) electrodes. In its neutral state the polymer is transparent in the visible range and changes its color to deep red upon oxidation. Simultaneously, the blue colored fluorescence intensity is quenched. Besides its high stability in ambient conditions, the devices showed switching times of <2s, a coloration efficiency of 542±10cm²/C at 395nm, a fluorescence contrast ratio of 4,1±0,3 and an electrochromic contrast of 50±4% in the visible spectrum. These figures of merit ranking in the upper range of literature values make it a promising material for dual-mode display applications. Furthermore, by changing the working electrode to inkjet printed poly(3,4-ethylenedioxythiophene) (PEDOT) we demonstrate the fabrication of an electrofluorochromic device with independently addressable pixels to demonstrate the functionality of inkjet printed, structured EFCds. Thus demonstrating the potential of these devices in display and smart window applications.

9:15 AM ET13.03.03

Polymer Dispersed Liquid Crystal Optimization for Low Power DC Field Application [Caitlyn Cook](#), Elaine Lee, Brian Giera, Herbert Wakefield, Andrew Pascall, Marcus A. Worsley and Joshua Kuntz; Lawrence Livermore National Laboratory, Livermore, California, United States.

Polymer dispersed liquid crystals (PDLC) have been heavily researched for applications such as smart windows in buildings, displays, and automobiles. A large focus on improving smart window production is in the reduction of production cost and required power. Here, the developed PDLC provides transmittance contrast ratios up to 30, with required power on the order of micro-Watts. Our smart PDLC windows can maintain a steady state of high transparency in DC field application and does not require high power (milliWatt), high frequency AC fields like conventional PDLCs with similar contrast ratios. When using commercially available pre-polymer, significant relaxation of the transparent state back to a translucent or opaque state occurs when holding a voltage at a steady state for a few seconds. This phenomenon occurs increasingly so at lower voltages (10V), as determined via UV-VIS (transmission) and custom color difference quotient (reflection) characterization techniques. To further understand and improve relaxation with DC voltage application, a series of photosensitive acrylate-based pre-polymer chemistries similar to PN393 were formulated and tested. Each formulation component has been systematically modified and characterized via the aforementioned characterization techniques in conjunction with scanning electron microscopy and UV-Rheology in a trend towards decreasing the power requirements and reducing electro-optical relaxation with DC field application. With polymerization induced phase separation speeds completing within two seconds in response to 365nm light, such a formulation can be incorporated into a roll-to-roll production method and thus can be utilized for flexible electronics.

Prepared by LLNL under Contract DE-AC52-07NA27344.

9:30 AM BREAK

10:00 AM *ET13.03.04

Transparent Intelligence—Progress in Chromogenic Materials and Devices for Glazing Claes-Goran Granqvist; The Ångström Laboratory, Uppsala University, Uppsala, Sweden.

This paper outlines the essential properties of the radiation around us, and uses this information to specify a number of requirements for energy efficient glazing. Spectral selectivity, angular dependence, and time variability stand out as important concepts. Focus is then put on novel results for thermochromic and electrochromic materials and devices. In particular, I present a number of strategies for boosting the cycling stability of electrochromic thin films of tungsten oxide and nickel oxide by electrochemical pretreatment or post treatment in lithium-ion-conducting electrolytes, or by intermixing of several oxides.

10:30 AM ET13.03.05

Stretchable Array of Active-Matrix Based Poly(3-methylthiophene)/Prussian Blue Electrochromic Devices with Low Power Consumption Dong Sik Kim, Heun Park and Jeong Sook Ha; Korea University, Seoul, Korea (the Republic of).

We report on the fabrication of low power operated, stretchable array of active-matrix based electrochromic devices (ECDs). ECD consists of poly(3-methylthiophene) and prussian blue grown on indium tin oxide coated polyethylene terephthalate film, and mixed gel electrolyte of acetonitrile, poly(methyl methacrylate), propylene carbonate, and LiClO_4 . Upon application of a bias voltage at -1, 0, and 1 V, the ECD displays red, green, and blue colors, respectively. For the operation of the ECD, low powers of $373 \mu\text{W}/\text{cm}^2$ at -1.0 V and $378 \mu\text{W}/\text{cm}^2$ at 1.0 V are consumed but with a high coloration efficiency of $201.6 \text{ cm}^2/\text{C}$ at 1.0 V.

On a stretchable Ecoflex substrate, 4×4 array of ECDs with corresponding 4×4 n-type FETs as active-matrix elements for preventing the cross-talk, are integrated using patterned liquid metal, GaInSn interconnections. Such fabricated ECD array exhibits a mechanical stability under biaxial stretching by 30% and bending deformation. Finite element method analysis of the strain distribution also confirms that the strain is only concentrated onto the Ecoflex area between the active devices of ECD and FETs.

This work demonstrates the high potential of our fabricated stretchable ECD array in the application to full-color display associated with stretchable electronics, wearable devices, and electronic skin.

10:45 AM ET13.03.06

Hybrid Organic-Inorganic Materials for Multifunctional Window Application Elsa John and Aswani Yella; Indian Institute of Technology-Bombay, Mumbai, India.

Hybrid lead halide based perovskites have gained much interest as an absorber material in solar cells owing to its low cost, easy processing method and suitable optoelectronic properties like broad absorption, small exciton binding energy, long lived photogenerated carriers and ambipolar charge transport. The wide variety of the organic and inorganic moieties that can be incorporated into these perovskites not only make the structure very flexible but also enable fine tuning of the material specific to the application. Within a few years of its inception in the solar cells, the certified power conversion efficiency of these perovskite solar cells have increased from 3.8% to 22.1%, making it one of the most explored material in the field of photovoltaics. The most common general formula for these halide perovskites is ABX_3 , where A is a large monovalent cation (methylammonium CH_3NH_3^+ , formamidinium $\text{CH}(\text{NH}_2)_2^+$), B is usually Pb^{2+} and X is a halide ion. Three dimensional corner-sharing PbX_6 octahedra with the central site occupied by organic cations form the structure of these perovskites. Although these materials have most extensively been used in the solar cells, they have also garnered significant interest in other fields such as field effect transistors (FET), light emitting diodes (LED), laser diodes and photodetectors.

Changes in the structure of these hybrid materials induced by electrochemical changes bring about a change in the optical property making it a suitable material for multifunctional windows. This work highlights the structural changes in the material brought out by electrochemistry and the underlying phenomenon. The change in optical property is studied to optimize the device performance for window application, making it an environmentally sustainable material.

11:00 AM ET13.03.07

Designing Tunable On/Off Electrochromic Bragg Stacks Sungyeon Heo, Ankit Agrawal and Delia Milliron; Chemical Engineering, The University of Texas at Austin, Austin, Texas, United States.

Dynamic tuning of Bragg stacks with wide spectral range and reflection is desired for efficient energy-saving windows, camouflage platforms, and military purposes. Especially for window applications, color neutrality and efficient heat blocking can be achieved *via* visible or near-infrared reflection compared to dominant approach that utilizes light absorption. Previous approaches of designing dynamic electrochromic Bragg stacks used optical constants of thin films from *ex-situ* ellipsometry measurement. However this *ex-situ* method doesn't reflect dynamic reflection measurement condition and predicted reflection with simulation was missing. Moreover significant reflection at both charged and discharged states compromises its window applications, which is generally expected to show transparency in the discharged state. Here, we designed nanocrystals (NCs)-based Bragg stack films consisting of WO_x and ITO NCs, and demonstrated their on/off reflection tuning over visible and near-infrared ranges. We provide a complete analysis with a combined approach of *in-situ* ellipsometry and transfer matrix simulation to rationalize and predict the optical behavior of the Bragg stacks. Combining our novel processing approach with judicious material design, we show how an optimized 1-D Bragg stack can be implemented for electrochromic applications. First, Bragg stacks on the ITO-PET flexible substrates without any annealing process were demonstrated with the advantage of ligand stripped NCs. The Bragg stacks with annealing process gave more enhanced reflectance, predicted by the *in-situ* ellipsometry analysis. By adjusting the ITO film thickness, the reflectance was changed from visible to near-infrared range, and the each film's reflectance and peak position were tuned by changing the potential, matched with simulation. We expect this approach with simulation will guide us to rationally design the more enhanced NCs-based Bragg stack for efficient energy-savings in windows.

1:30 PM *ET13.04.01

Smart Materials Based on Multifunctional AIEgens Benzhong Tang; The Hong Kong University of Science and Technology, Hong Kong, China.

Chemists are always seeking new methods to obtain artificial smart materials with multiple on-demand functionalities. Although the responsive process of these smart materials can be monitored by various methods, such as NMR, IR, MS and electron microscopy, *etc.*, a problem associated with these methods is that they are all invisible to our naked eye. Fluorescence shows rich advantages such as superior sensitivity, high selectivity, fast response, and simplicity. More importantly, it can provide high spatiotemporal resolution for precise visualization into complicated processes in a noninvasive way. Another thing that needs to be considered is that most of the smart materials function in the condensed phase which show notoriously ACQ effect to result in compromised sensitivity. Diametrically opposed to conventional luminophores, AIEgens are nearly non-luminescent in the isolated state but luminesce strongly in the aggregate/clustered state. Based on different AIEgens, we have fabricated various intelligent materials which can respond to different stimuli, such as force, temperature, moisture, pH, electric, and light.¹⁻³ These smart materials show fascinating applications in sensors, actuators, and biological processes.^{4,5}

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2:00 PM ET13.04.02

Phase Transformation and Photophysical Properties of Silver Doped Copper Indium Sulphide Colloidal Quantum Dots for Solar Cell

Applications Shanna-Kay Spencer¹, Richard A. Taylor¹, Paul McNaughten² and Paul O'Brien²; ¹Chemistry, University of the West Indies, St. Augustine, Trinidad and Tobago; ²Chemistry and Materials, University of Manchester, Manchester, United Kingdom.

Ternary chalcogenide silver doped copper indium sulphide (Ag-CIS) quantum dots are currently being explored as promising materials for photovoltaic applications. Quantum dots <10 nm have been synthesized via a hot injection colloidal method using a unique combination of precursors and capping agents over a range of temperatures. Those synthesized at 140, 180 and 210 °C show quasi-spherical morphology with fairly narrow size distribution (5.6 ± 1 nm) exhibiting predominantly chalcopyrite structure. However, nanoparticles synthesized for 10 minutes at 180 °C have the narrowest size distribution with a wurtzite structure instead of chalcopyrite. Furthermore, structural data confirm a change from wurtzite to chalcopyrite structure and an increase in crystallinity with increasing content of silver ion dopants. It has been previously demonstrated that phase transformation from wurtzite to chalcopyrite for CIS nanoparticles occurs over a range of temperatures up to 600 °C but there are no reports to the best of our knowledge which employ the use of dopants or show an influence of synthesis duration on phase transformation.

These findings suggest an attractive route to tuning structure and optical properties and an effective means for possibly enhancing photoconductivity. To this end, we will be focused on making a plausible and crucial connection between the effect of synthesis duration and dopant content on phase transformation in colloidal Ag-CIS nanoparticles. Further we will discuss the effect of dopant concentration on the photo-physical properties including time-dependent luminescence and the role of the dopant Ag⁺ ion in these CIS quantum dots for tunable photovoltaic effects.

2:15 PM ET13.04.03

Chemical Solution Deposition Process of Advanced Multifunctional Transparent Thin Films—Inorganic Octahedral Metal Cluster and

Electrophoretic Deposition Process Fabien Grasset^{1,2}, Ngan T. Nguyen^{2,1}, Adele Renaud³, Maxence Wilmet^{3,1,4}, Giang T. Truong^{1,3,2}, Marion Dubernet^{1,2}, Noe Dumait³, Yann Molard³, Marian Amela-Cortes³, Stephane Cordier³, Naoki Ohashi^{2,1} and Tetsuo Uchikoshi^{2,1}; ¹UMI 3629 LINK, National Institute for Materials Science, Tsukuba, Japan; ²RCFM, National Institute for Materials Science, Tsukuba, Japan; ³UMR 6226 ISCR, Université de Rennes 1, Rennes, France; ⁴Saint-Gobain Recherche, Aubervilliers, France.

Transparent thin films or coatings, with thickness ranging from nanometers to few tens micrometers are playing a very important and indispensable role in daily life [1]. Recently, the demand of new robust, low cost and friendly-environmental functional hybrids thin films with high transparency for optical application is strongly increasing. The main targeted applications are lightening and color design [2], self-cleaning [3], photovoltaic luminescent solar concentrators [4-6] or window solar control [7-9]. Moreover, the use of solution processes are highly desirable in order to reduce the cost and waste and that can enable fabrication method for large area and even flexible devices.

This presentation will summarize our very recent works on the synthesis of multifunctional nanocomposites thin films or coatings on glass by chemical solution deposition processes (CSD) [10-18]. CSD processing of inorganic nanocolloidal solutions is generally acknowledged to be highly flexible in terms of precursor composition, targeted substrate and processing procedures (dip-spin coating, electrophoretic deposition process (EPD)...) in ambient pressures, and thus can be faster and less expensive than vapor based deposition routes while providing materials with matching or even superior properties. In this study, the EPD appears as an efficient process to fabricate highly transparent and functional nanocomposite thin films on glass for optical and energy applications. Several octahedral atom clusters were used to prepare thin films with high transparency in the visible. For instance, green, yellow, orange, red and brown colored and transparent films were successfully fabricated on an indium-doped tin oxide glass substrate. In addition, transparent films with prominent red-NIR luminescent properties were obtained by using specific Mo₆ clusters whereas UV and NIR filters were realized by using Ta₆ clusters.

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2:30 PM ET13.04.04

Transparent Electrodes for Multifunctional Windows—A Brief Overview [Daniel Bellet](#); LMGP, Grenoble Institute of Technology, Grenoble, France.

Both energy and material consumption of buildings are and will remain a major concern for the next decades. In every buildings, either residential or commercial, the overall energy use can significantly be lowered through optimization of heat accumulation and heat loss of façades and windows. This leads to research devoted to novel materials for smart windows which can be conceived as affordable multifunctional systems that offer enhanced energy control. Therefore development of materials for multifunctional windows is of huge importance. For instance electronically switchable windows, called as well smart windows, enable the alteration of their optical transparency thanks to an applied electric field. Generally speaking the topics of multifunctional windows concerns materials which can be photochromic, electrochromic, piezoelectric, transparent/semi-transparent etc. Very often these technologies required two parallel and opposite transparent electrodes: this is for example the case for creating an electric field to actuate an electrochromic material as well as for transparent/semitransparent photovoltaics to collect the photo-generated carriers. Therefore transparent electrodes should as well be thoroughly understood and optimized for an efficient integration into multifunctional windows.

The present contribution focuses on the different technologies associated to transparent electrodes. The various studied materials are for instance the classical transparent conductive oxides (TCO) and more recently metallic nanowire networks. We will describe and compare the main structural, optical and electrical properties of the different materials developed for transparent electrodes in multifunctional windows. The main scientific challenges associated with transparent electrodes for improving performance of multifunctional windows, as well as their stability, will be discussed. Stability can indeed be a crucial issue, involving electrical and/or thermal aspects, ageing or chemical degradation.

Some references of our team related to the study of transparent electrodes:

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2:45 PM BREAK

3:15 PM ET13.04.05

Improved TCO Process Stability Using *In Situ* 4-Point Probe Sheet Resistance Monitoring [Joshua Gurian](#) and James Colbridge; Telemark, Battle Ground, Washington, United States.

Increased interest in the production of transparent conductive oxides (TCO) thin films for the fabrication of multifunctional windows in optoelectronics has reduced allowable deposition process variation for TCO manufacturers. Here we present experimental results showing improved Indium-Tin-Oxide (ITO) run-to-run process stability using in-situ 4-point probe sheet resistance monitoring for process end-point determination versus traditional film thickness monitoring. The optical transmission and electrical properties of the resultant deposited thin films are compared.

3:30 PM ET13.04.06

Impact of Hydrogen on Optoelectronic Properties in a Variety of Binary and Ternary Transparent Conducting Oxides [Sebastian Huscain](#), Jianwei Shi, Zachary Holman and Mariana I. Bertoni; Arizona State University, Tempe, Arizona, United States.

As the push for zero-energy buildings and self-sustained smart cities advances, window materials with tunable optoelectronic properties become crucial for niche and widespread application. Transparent conducting oxides (TCOs) have played a large role as multifunctional windows in advancing display, energy generation, and energy management technologies, (e.g., LCDs, photovoltaics, and electrochromic windows). However, as these devices advance to meet needs of zero-energy building targets, fine control over carrier density (N_e), optical band gap ($E_{g,opt}$), work function (WF), and higher charge carrier mobility (μ) in TCOs is necessitated [1].

Recent work implicates hydrogen as a dominant donor in TCO materials [2-3], suggesting unintentional and intentional hydrogen incorporated into TCO layers during deposition may significantly impact these optoelectronic properties. We introduce hydrogen into a variety of sputtered TCO thin films by mimicking a portion of the fabrication process of silicon heterojunction (SHJ) solar cells, which rely on TCOs for charge extraction. Namely, hydrogenated amorphous silicon (a-Si:H) is deposited onto our substrates by plasma-enhanced chemical vapor deposition followed by sputtering of either indium oxide, zinc oxide, tin oxide, and indium tin oxide (ITO) targets. These film stacks of TCO/a-Si:H/substrate are subjected to varied time and temperature post-deposition annealing conditions, resulting in a broad range of N_e from $\sim 10^{15}$ cm⁻³ to $\sim 10^{19}$ cm⁻³, μ from ~ 2 -103 cm²/Vs, and WF from 4.40-4.84 eV. The a-Si:H layer acts as a source of hydrogen for the adjacent TCO films, and qualitative and quantitative measurements of hydrogen content in the TCOs before and after annealing show varying amounts of hydrogen incorporation into the TCOs. The resulting changes to measured μ , N_e , $E_{g,opt}$ and WF begin to elucidate hydrogen's role as a potential dominant donor defect in these materials.

Additionally, hydrogenated indium oxide films showing $\mu > 90$ cm²/Vs –roughly 3 times greater than state μ of the art ITO– were degraded by air exposure then exposed to UV irradiation. Observed changes to μ and N_e are strongly dependent upon the hydrogen content and annealing conditions that the films are subjected to, and suggest a threshold hydrogen amount of ~ 5.2 atomic % for hydrogen to be the dominant donor.

References:

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3:45 PM ET13.04.07

Sunlight Absorbing Metasurfaces for Superior Anti-Fogging [Christopher Walker](#), Efstratios Mitridis, Thomas Kreiner, Hadi Eghlidi, Thomas M. Schutzius and Dimos Poulikakos; ETH Zurich, Zurich, Switzerland.

Surface fogging is a common phenomenon that can have significant and detrimental effects on visibility. It affects a wide range of applications including windows, windshields, electronic displays, cameras, mirrors, goggles, and glasses. A variety of ongoing research is aimed at combating this problem by

understanding and developing stable and effective passive antifogging coatings that are capable of handling a wide range of environmental challenges. Common passive approaches range from creating superhydrophilic coatings, which turn the condensed droplets into a thin water film, to superhydrophobic surfaces, whose cleverly designed size and geometry allow condensed droplets to grow into the Cassie-Baxter state. In comparison to the normal case of surface fogging, both approaches improve transparent clarity; either by creating a thin water film or by shedding the condensate droplets as they form. Here we introduce an alternate passive approach, showing that by leveraging sunlight, one can use rationally engineered solar metamaterials to induce localized heating and significantly delay the onset of surface fogging and decrease de-fogging time. Importantly, this approach aims to, not only control, but inhibit condensate, and allows the surfaces to be partially transparent while also absorbing a significant fraction of the incident solar irradiation. The films are fabricated as a metal-dielectric nanocomposite of gold embedded in titania. Close to the percolation limit, this material system exhibits strong visible light absorption, due to localized surface plasmon oscillations in the nanometer-scale gold particles, which subsequently results in heat dissipation. Our research into solar metamaterials represents an environmentally friendly approach to passive anti-fogging and de-fogging. We expect its relevance to extend beyond environmentally-friendly applications, wherever transparency, material robustness or ultra-low thickness are a must.

SESSION ET13.05: Poster Session
Session Chairs: Jose Rajan and Karthik Ramasamy
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET13.05.01

Thermal Insulation via the Photothermal Effect of Chlorophyll Thin-Film Coating—An Energy Efficient “Green Window” Yuan Zhao and Donglu Shi; Dept of Mechanical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio, United States.

One of the critical components in energy saving is thermal insulation, especially for large-area high-rise public building windows in cold climates. The conventional approach mainly relies on optimization of the thermal insulators and window designs (double-pane). It has remained a great challenge, however, to implement single-panes due to conflicting intrinsic materials properties (i. e. thermal insulation vs transparency). In this study a new concept is developed to prevent heat loss without any insulating medium such as gases within double-panes and low-e coatings. A “Green Window” has been designed for single-pane applications that meet the U-factor specifications of Department of Energy for colder regions of the United States. The “Green Window” is structurally composed of a thin film window coating of naturally occurring chlorophyll that exhibits pronounced photothermal effect, while remaining highly transparent. Upon collecting solar light, considerable heat is created, effectively raising the window surface temperature, leading to a reduced U-factor less than $1.7 \text{ W m}^{-2} \text{ K}^{-1}$, even below the values of double-panes. As such we demonstrate of new concept in “thermal insulation” via optical means instead of sole dependence on thermal insulators. This concept lifts the dependence on insulating materials making single-pane window highly possible.

ET13.05.02

Joule-Heating-Induced Infrared Switching in Flexible VO₂ Nanoparticles Film Nan Shen and Chun Cheng; Southern University of Science and Technology of China, Shenzhen, China.

As a typical metal-insulator transition (MIT) material, vanadium dioxide has attracted much attention due to its distinct infrared and resistive switching characteristics. However, the relatively high phase transition temperature and uncontrollable thermally driven phase transition of VO₂ inhibited its practical applications. In our work, we fabricated flexible VO₂ nanoparticles films using a scalable printing method and investigated joule-heating-triggered infrared switching of VO₂ films by applying voltages. Well-matched luminous transmittance ($T_{\text{lum}}=57.3\%$) and solar energy modulation ability ($\Delta T_{\text{sol}}=13.8\%$) of VO₂ films can be achieved at 2.0 wt.% solid content. The infrared switching of VO₂ nanoparticles films is well controlled by input voltages and exhibits high stability. A quite small increase (<6.8%) after 10000 bending cycles is observed for normalized T_{lum} and ΔT_{sol} of VO₂ samples, reflecting excellent flexibility. Our results provide an alternative strategy to regulate the infrared switching performance of flexible VO₂ films, which would significantly promote the development of thermal-sensitive VO₂ devices.

ET13.05.03

Ladder-Structured Polysilsesquioxane/Al₂O₃ Nanocomposites for Transparent Wear-Resistant Windows Min Seon Kim¹, Yejin Ahn¹, Sunyoo Kim², Ji Ho Youk² and Bong-Gi Kim¹; ¹Department of Organic and Nano System Engineering, Konkuk University, Seoul, Korea (the Republic of); ²Department of Chemical Engineering, Inha University, Seoul, Korea (the Republic of).

As a protective layer for deformable displays, we synthesized ladder-type polysilsesquioxanes (LPSQs) containing cyclic epoxy as a curable unit. The mechanical properties after photo- and thermal-curing of LPSQs with a small amount of added Al₂O₃ nanoparticles were compared with those of the pure LPSQs. The prepared LPSQ-Al₂O₃ nanocomposites and the pure LPSQs exhibited comparable optical transparencies and thermal stabilities. In addition, the degree of conversion of the applied epoxy units in LPSQs and the resulting mechanical properties, as monitored by Fourier transform infrared spectroscopy and nanoindentation tests, indicated that the addition of nanoparticles to LPSQs moderately enhanced the epoxy conversion rate and remarkably improved the wear resistance, including hardness, after photo-/thermal-curing processes. The LPSQ-Al₂O₃ nanocomposites achieved higher wear resistance than epoxy-silica nanocomposites containing similar curable functional groups and reinforcing fillers (silica). The excellent mechanical properties of the LPSQ-Al₂O₃ nanocomposites could be attributed to three-dimensionally interconnected networks of organic-inorganic hybrid-type chemical structures in the LPSQ as well as additional reinforcement from amine-functionalized Al₂O₃ nanoparticles covalently interconnected with the LPSQ. We believe that the devised LPSQ-Al₂O₃ nanocomposites could serve effectively as a wear-resistant platform for deformable display windows.

ET13.05.04

Low Temperature Growth of Conductive SrVO₃ Thin Films on Various Substrates by RF Sputtering Deposition Daeho Jung, Hosun Lee, Hyeon Seob So and Sangbin Hwang; Kyunghee Univ, Yongin-si, Korea (the Republic of).

It is very important to improve the performance of transparent conducting oxide (TCO) for display applications. Recent studies have suggested a novel method of making transparent conductors. Perovskite metal oxides have correlated electrons, and become transparent in the visible spectral range due to the carrier mass renormalization. The effective mass becomes heavier, by the interaction between the electrons. To have high electrical conductivity and to be transparent in the visible light region, absorption and reflection of light must be minimized in the visible region, and high carrier concentration and small

carrier scattering are required. Particularly, strontium vanadates (SrVO_3) have been intensively studied due to high electrical conductivity as well as high optical transparency in the visible range.

SrVO_3 thin films were grown on various substrates using RF magnetron sputtering deposition with a commercial SrVO_3 target as low as at 400°C with a mixed gas of H_2 and Ar. Film thicknesses varied between 40 and 90 nm. We used $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT), LaAlO_3 , SiO_2/Si , a-, c-, m- and r-plane sapphires as substrates. The structural and morphological properties of SrVO_3 films were studied using grazing-incidence-angle X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoemission spectroscopy (XPS). The electrical properties of all samples were measured using Keithley 4200.

SrVO_3 films grown on LSAT substrates showed crystalline peaks of cubic phase SrVO_3 films at 53.3° (210) using GIXRD. SrVO_3 films grown on SiO_2/Si showed crystalline peaks of cubic and orthorhombic phases as well as $\text{Sr}_2\text{V}_2\text{O}_7$ phase. SrVO_3 films showed grain boundaries with the average grain size between 100 nm and 150 nm according to SEM. High-resolution TEM images of SrVO_3 thin films grown on LSAT showed high crystallinity and a well-ordered cubic phase.

We found the binding energy for multivalence state of $V_{2p_{3/2}}$ from V^{5+} (516.8 eV) to V^{4+} (516.3 eV) for SrVO_3 thin films on LSAT with increasing film thickness. We note that the insulating phase of $\text{Sr}_2\text{V}_2\text{O}_7$ (in V^{5+} state) films can be changed to SrVO_3 (in V^{4+} state) films as the growth times increased due to H_2 gas-induced reduction phenomenon.

The resistivity of the SrVO_3 films on LSAT was lower than other substrates because SrVO_3 films were nearly latticed-matched to LSAT substrates. XRD, TEM, and XPS depth profiles showed a good crystallinity of SrVO_3 thin films grown on LSAT substrates.

The transmission spectrum of SrVO_3 films with various film thicknesses grown on LSAT substrate were measured between 300 nm and 1000 nm of photon wavelength. The transmission was measured to be about 60% and 87% for film thickness of 40 nm and 70 nm, respectively, in the visible range.

This work demonstrates that high-quality cubic phase of SrVO_3 films can be grown using RF magnetron sputtering deposition with growth temperature as low as 400°C .

ET13.05.05

Electrochromic Perovskite Nickelate Windows Yifei Sun¹, Zhaoyi Li², Nanfang Yu² and Shriram Ramanathan¹; ¹Purdue University, West Lafayette, Indiana, United States; ²Columbia University, New York, New York, United States.

Electrochromic windows are of interest in energy efficient adaptive architectures as well as various tunable optical devices. In this work, we present a class of correlated perovskite nickelate thin films (such as SmNiO_3 (SNO) and NdNiO_3 (NNO)) as promising next generation electrochromic materials. We will discuss results from electrochromic devices comprising indium doped tin oxide (ITO) coated glass as transparent electronic conductors, NNO thin film as electrochromic layer and salt solution as liquid ionic conductor exhibiting quick response and excellent stability upon coloring and bleaching cycles. The mechanism of color change in perovskite nickelates is distinct from conventional electrochromic materials which are based on redox reactions and become more conductive upon electron doping. During ion intercalation, a colossal phase transition in nickelate occurs that is an effect of strong electron-electron correlation, which makes them highly insulating and transparent due to charge carrier localization. We further show that the nickelate films allow for continuous and large tuning of optical transmissivity across the entire visible, near-infrared and mid-infrared spectra, which is of interest for control of sunlight transmission and variable emissive coatings.

ET13.05.06

High Transparency and Self-Healing Liquid-Infused Surfaces for Optical Devices Meiling Zhang¹, Qi Liu¹, Jun Wang^{1,2} and Rongrong Chen¹; ¹Key Laboratory of Superlight Material and Surface Technology, Ministry of Education, Harbin Engineering University, Harbin, China; ²Institute of Advanced Marine Materials, Harbin Engineering University, Harbin, China.

High transparency is one of the basic requirements for optical devices, such as smart windows, solar cell panels and optoelectronic devices, to function well. However, frequent exposure of these devices to different outdoor environments, inevitably stains their outermost surfaces, which might diminish their performance. Superhydrophobic surfaces have anti-adhesion properties with water contact angle greater than 150° and slide angle below 5° . However, during the process of droplet condensation on a rough surface, the droplets on the surface can transform from the Wenzel-Cassie state to the Wenzel state, leading to the failure of superhydrophobic effect. Aizenberg et al. [1] first proposed the concept of a slippery liquid-infused porous surface (SLIPs). They poured lubricating oil into the porous surface for the preparation of super-slippery surfaces, along with the formation of a dynamic oil film, solving the problem of super-hydrophobic failure efficiently. Silica is often chosen as the alternate material because of its low refractive index and low absorbance of visible light. Herein, we propose to use tube-like SiO_2 textures for trapping a lubricant liquid inside, and choose this liquid for allowing a drop of another liquid to float on this mixed substrate. A micro-mesoporous hollow tubular material with a wall thickness of about 100 nm and an inner diameter of about 1 μm was prepared successfully. Inspired by Yao Lu et al. [2], they use glue to make the coating robust on the surface, in this paper, glutaraldehyde was chosen as an adhesive to adhere the porous hollow tube-like SiO_2 on the glass substrate and then a lubricant oil is poured into the surfaces after modification with FAS. As a consequence, these surfaces have remarkable slip properties: drops hardly pin on them, which makes them roll off readily and continuously retract as evaporating, contrasting dramatically with usual solids. It should be a promising candidate for long-term transparent optical devices.

Keywords: transparency surfaces; self-healing; SiO_2 ; mechanical robust

Acknowledgements

This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.

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ET13.05.07

Composition and Structural Characterization of Photochromic Gd-Based Oxy-Hydrides Thin Films Giorgio Colombi², Steffen Cornelius², Alessandro Longo¹, Herman Schreuders², Fahimeh Nafezarefi² and Bernard Dam²; ¹Institution Netherlands Organization for Scientific Research (NWO), The European Synchrotron, Grenoble, France; ²Chemical Engineering, Delft University of Technology, Delft, Netherlands.

On average 30-40% of the energy consumption in the developed world is in the building sector. In this context, smart energy saving windows are envisaged to play an important role in bringing this number down and help with the urban air-pollution that is typical of the warm season.

The recently discovered Rare Earth-based metal oxy-hydrides (MH_xO_y) are a particularly promising class of inorganic materials which show photochromic properties under ambient condition. The optical transmittance in these materials can be decreased reversibly by exposure to sunlight. The largest contrast change is observed between 400 and 1000 nm, however, the photochromic contrast extends up to the MID-IR region. Therefore these materials are not only

suitable for the light-modulation in the visible range (where the darkening is colour-neutral) but they also act as a barrier to the heat irradiated by the sun at longer wavelengths.

Despite the efforts of the last years, the darkening and bleaching mechanism is still under debate and it remains unclear which parameters affect its amplitude, speed and persistence upon several illumination cycles. In the interest of this open question, this work attempts to tackle the somehow elusive chemical nature of this materials.

The focus is given to Gd-based oxy-hydrides, a case-study chosen for its high optical contrast and for its sensitivity to several scattering techniques. Phase purity, Gd lattice and long-range order are probed by XRD, while XAS gives information on the local coordination of the Rare Earth and on the position of the lighter atoms within the lattice. The hydrogen to oxygen ratio and the exact composition are measured by RBS and ERD. These compositional and structural information can serve in future computational works to depict the band structure of the material: a first step to shed light on the chemical interplay of oxygen and hydrogen and on their effect on the electronic structure of the Gd oxy-hydrides.

ET13.05.08

Reversible Responsive Multifunctional Porous Particle by Chemical Vapor Deposition Wenny Wenny and Hsien-Yeh Chen; Chemical Engineering, National Taiwan University, Taipei, Taiwan.

A challenging fabrication of porous particle with reversible responsive functions is being approached by chemical vapor deposition (CVD). The compatible poly-para-xylylenes are utilized to cloak chemicals without changing their characteristics. Solidified droplets of solution is carried out to undergo the process of sublimation and used for the vapor deposition. The sublimation process also allows the polymer to go through vapor deposition. Remarkably, it is able to imitate the shape of the droplets and maintaining their specialities such as reversible magnetic, temperature responses, etc. This study is demonstrated by ferroferric oxide (Fe₃O₄), which is well known for its magnetic response and poly(N-isopropylacrylamide) (PNIPAM), that is renowned for its temperature response. It is capable to be applied in biomedical materials to support chemicals with specific roles and expectantly may lead to an excellent drug carrier with detection, targeting and delivering abilities.

ET13.05.09

Field Effect Smart-Glass for Near Infrared Reflection and Transmission Mark C. Altwerger, Iulian Gherasoiu and Harry Efsthadiadis; SUNY Polytechnic Institute, Albany, New York, United States.

We report the development of a versatile and robust, metamaterial that can reflect near infrared heat radiation (NIR) in the range 0.7-2.5 μm while transmitting more than 90% of the visible light intensity. Metal oxides can be used to manage the light reflectance over the long wavelength range. However, to obtain high reflectivity starting at shorter wavelengths, the doping concentration of the metal oxide must be increased above the level of $1 \times 10^{21}/\text{cm}^3$. At these concentrations the dopant incorporates not only substitutionally, but large amounts will also be found interstitially. Interstitial dopants have been shown to produce carriers with heavier effective mass, decreased mobility, and deeper donor states that significantly decrease the transmittance. Ultimately substitutional dopants degrade the crystallinity of the host material, generating compensating defects that limit the achievable carrier density. To circumvent the need for excessive dopant incorporation we deposited a multilayer structure that alternates insulating and conducting layers of silicon dioxide (SiO₂) and silicon doped zinc oxide film (ZnO:Si). This structure is deposited by RF magnetron sputtering from Si and ZnO targets at low temperature. The structure uses the electric-field enhancement of carrier density to regulate the bandwidth of the NIR and in turn the amount of heat reflected. This is achieved through the formation of a quasi 2-dimensional electron gas in a thin layer at the dielectric/ZnO:Si interface. In this paper, the synthesis conditions as well as the results of the electro-optical and structural characterization of the device, through Hall effect measurements, x-ray diffraction (XRD), scanning and transmission electron microscopy (SEM, TEM), atomic and conductive force microscopy (AFM/CAFM), Rutherford Back Scattering (RBS), as well as transmittance measurements in the range from 0.3 μm to 1.3 μm are presented. The fabrication challenges are discussed and a path for improving the performance of the device is outlined.

ET13.05.10

Hydrothermal Synthesis and Characterization of Mn-Doped VO₂ Nanowires Gen Long, Mostafa Sadoqi, Asher Suissa and David Matatov; Saint John's University, Jamaica, New York, United States.

Monoclinic VO₂ is a known polymorph of vanadium dioxide that has received much attention due to its layered structure, high energy storage capacity, moderate work potential and promising applications in functional windows. VO₂ can usually be obtained through a hydrothermal method under high pressure. In this work we report a study of synthesis and characterization of VO₂ doped with Manganese using a rapid single-step hydrothermal process with V₂O₅, Mn-Acetate and citric acid as precursors. Different syntheses were carried out in which the concentration of V₂O₅ and citric acid remained constant whereas the concentration of Manganese (II) Acetate was varied. The reactants underwent a stirring phase for 30 minutes before being loaded into a hydrothermal reactor for 2.5 hours at 200°C. The resultant was washed three times to remove the residual precursors. Imaging and spectroscopy characterizations such as TEM, SEM, XRD, EDS and UV-VIS-NIR have been performed on different doping concentration and the results display a dependence on doping concentrations. The successful doping of Mn in VO₂ provides another possible approach of tuning (through magnetic field) in the relevant applications.

ET13.05.11

A Novel Viologen-Based Electrochromic Device Containing All-in-One Self-Healing Polymer Electrolyte Yi Wang, Rongzong Zheng and Chunyang Jia; School of Electronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, China.

Electrochromism refers to a phenomenon where materials undergo electrochemical reactions accompanied by the change of their optical characteristics from a bleaching to a coloration state through the manipulation of potential biases. This technology enables several useful applications, including smart windows, antiglare rear view mirrors and electrochromic (EC) displays. The efforts in recent years were mainly focused on development of various EC materials, while less attention has been paid to the problems arises in practical application of these ECDs. These devices not only require excellent EC performance, but also reliability and resistivity against various external forces (such as repeated bending) and irreversible physical damages unavoidable during practical applications. Hence, excellent self-healability and renewability are important for the development of ECDs aiming for extending lifetime and lower cost of materials and devices. Here, a novel viologen derivative has been synthesized to perform as chromophores and dissolved in the self-healing polymeric electrolyte for the fabrication of ECDs. The self-healing polymer electrolyte has been synthesized containing acrylic acid, 1-vinylimidazole and vinyl hybrid silica nanoparticles copolymerizing. A type of hybrid ECDs was fabricated containing the self-healing electrolyte with viologen EC materials and polyaniline film counter electrode. The devices shown higher optical contrast (over 45%), fast switching time (2.0 s for coloring and 1.8 s for bleaching), coloration efficiency (406.96 cm²/C) and cycling stability (>5000 cycles). The self-healing polymer electrolyte shows excellent

mechanical properties (tensile strength 11 kPa, elongation at break 210%), and noticeable self-healing performance with healing efficiency of 90.5% within 20 min. This work highlights the important of self-healing property for the ECDs and opens up a new strategy for manufacturing ECDs to further development of the devices for advanced smart windows.

ET13.05.12

Microcapsule Display Based on Polyurethane Acrylates Jihong Bae, Kyung Seok Kang, Chanhyuk Jee, Hyo Jin Jung, WonBin Lim, Byeongjoo Kim and PilHo Huh; Pusan National University, Busan, Korea (the Republic of).

The different molecular weight of polyurethane (PU) prepolymer were successfully prepared using polycaprolactone diol (PCL) and Isophorone diisocyanate (IPDI) as soft segment of prepolymer, dimethylolbutanoic acid (DMBA) as emulsifier, and trimethylamine (TEA) as neutralizer. Synthesized prepolymer and liquid crystals (LC) were stirred at the constant rate. And de-ionized water (DI) containing bis-hexamethylenetriamine (BHMT) was added in the reaction mixture for the polyurea reaction. LC contains photo-curable acrylate, which allows to have a certain oriented direction in the micro droplet by UV irradiation. Generally, the study of polymer isolated liquid crystal (PILC) are founded on the combination of UV epoxy and liquid crystal or the mechanical dispersion using membrane filters. The most problem of these studies is the lack of capsule size control and the aggregation of polymer. In this study, it is possible to control the microcapsule size by the molecular weight of the prepolymer in the waterborne polyurethane form. We measured the molecular weight and the peak of the functional group of the polyurethane through the GPC and FT-IR. Various properties to apply as opto-electronic device were also evaluated the response time, contrast ratio and voltage-transmittance curves. These microcapsule LC research using polymer matrix is being applied to the variety fields of next-generation display such as 3D printer material, smart window and flexible display.

ET13.05.14

Colorful Semitransparent Organic Photovoltaics Using Solution Process Color Filter Electrodes Norshafidah Binti Abu Shafian, Youngji Kim, Jieun Son, Jerome Hyun and Kyungkon Kim; Ewha Womans University, Seoul, Korea (the Republic of).

Recently, colorful and semitransparent organic photovoltaic (OPVs) are growing due to their demand in aesthetically power generating windows. Traditionally, different colors in OPVs has been fabricated by employing different active layer materials exhibiting distinct absorption spectra, while semitransparent OPV mainly focus from less opaque top electrodes. Thus, this will complicate the process of fabrication and cause deviations in device performance among differently colored OPVs. Herein, colorful semitransparent OPVs with a single active layer material are demonstrated using Ag-TiO₂-Ag Fabry-Perot resonant cavity color filters (CFs) electrodes. Thermal evaporation of Ag layer and spin coating technique of solution process TiO₂ layer will help to restore the active layer material from damage. The CF enables the OPV to transmit spectrally pure colors with peak transmission efficiencies surpassing 25% average transmission for window application, and allows the colors to be freely tuned by changing the thickness of TiO₂ layer. Besides being effective color electrode, this CF works as a mirror to reflect the absorption light thus enhance the short-circuit current. It is shown that when compared to a transparent OPV consisting of the same active layer material and thickness, CF-integrated OPVs generate more short circuit current. With this current result, simple and convenient fabrication technique is needed to achieve pure color, high transmission and higher efficiency compare to only semitransparent OPVs.

ET13.05.15

Phonon and Magnetoelastic Coupling in Multiferroic Al_{0.5}Ga_{0.5}FeO₃ Karuna K. Mishra, Alvaro Instan, Mohan K. Bhattarai, Sita Dugu and Ram Katiyar; University of Puerto Rico, San Juan, Puerto Rico, United States.

Multiferroic materials that exhibit coexistence of both magnetic and ferroelectric order parameters are of research interest because of the intriguing coupling phenomena among spin, phonon, and charge degree of freedoms. Al_{0.5}Ga_{0.5}FeO₃(ALF) is a lead-free multiferroics exhibits ferrimagnetism near room temperature. We report phonons and magnetic ordering in ALF using our experimental findings involving temperature dependent Raman scattering and magnetization measurements. A single phase polycrystalline sample was prepared by solid-state reaction method and its phase purity was confirmed from the XRD analysis. Energy dispersive X-rays analysis and X-ray photoelectron spectroscopic results indicate nearly stoichiometry of the elemental compositions. Temperature dependent magnetization studies in both field-cooled and zero-field-cooled conditions identify the Neel's temperature T_N around ~220 K. ALF stabilizes in orthorhombic (*Pna2*) phase with eight formula units which translate into a total of 117 Raman active optical phonons. However 30 modes are experimentally observed in our measured Raman spectra. The temperature dependence of phonon frequencies are analyzed based on the standard anharmonicity model in the paramagnetic phase. In the low temperature ferromagnetic phase, a large departure of phonon frequencies from the extrapolated theoretical curve which essentially represents the normal phonon behaviors, suggests the existence of spin-phonon coupling in this system. In addition to lattice modes, several bending modes of octahedral are found to be strongly affected by the magnetic ordering. Further studies on ALF thin films are in progress. The detail experimental results will be presented in the meeting.

SESSION ET13.06: Dye and Perovskite Solar Cells
Session Chair: Richard Lunt
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 303

8:30 AM *ET13.06.01

Electrical Control of Photoluminescence in Hybrid Perovskite Films Juan Bisquert; University of Jaume I, Castello, Spain.

The development of organic-inorganic lead halide perovskites with very large efficiency requires us to understand the operation of the solar cell. These materials have excellent semiconductor and optoelectronic properties, but they are ionic as well as electronic conductors. The motion of ionic defects can regulate the number of nonradiative recombination centers, hence electrical control of planar devices with lateral contacts can give a switch of PL. This property may be exploited to extract information on transport and recombination and for the realization of new of new applications. Finally we adress new methods of characterization of the optical response by means of light modulated spectroscopy.

9:00 AM ET13.06.02

Hybrid Nanowires and 3D Nanoflowers on a Large Scale for Dye-Sensitized and Perovskite Solar Cells Jose Rajan¹, Zinab Bakr¹, Bhupender Pal¹, Naveen Kumar Elumalai² and Mashitah Mohd Yusoff¹; ¹Faculty of Industrial Sciences & Technology, University of Malaysia Pahang, Kuantan, Malaysia; ²School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney, New South Wales, Australia.

Optical transparency and workability at low light conditions enable the dye-sensitized solar cells (DSSCs) and the perovskite solar cells (PSCs) as desirable choice as smart windows in modern buildings for adding aesthetics with diverse choice of colours while producing clean electricity so as to realize zero-energy buildings. In both of these solar cells, the photoactive material is chemically developed from solutions on a wide bandgap material, known as photoelectrode. The photoelectrode influence the performance of the solar cells in many ways as they are either the charge separation medium or the charge transport medium or both. Commercially available mesoporous TiO₂ has been a widely investigated material; but its sluggish charge kinetics due to the surface states and intrinsic poor electrical conductivity triggered an intensive search on new materials worldwide. As a result many materials and materials architectures are developed with superior properties than the commercial choice; however, most of new materials are hardly scalable to the industrial levels. Among them, nanowires and 3D nanostructures such as flowers offer many advantages such as anisotropic charge dynamics, large surface area, and high crystallinity. Again, most of the materials synthesized thereby are through hardly scalable chemical processes. We have now developed nanowires and 3D nanoflowers as a composite of two binary wide bandgap metal oxide semiconductors (SnO₂-TiO₂) in large quantities (100 g scale) using multineedle electrospinning technique by controlling the nucleation and growth of inorganic species in a polymeric nanofibrous growth vessel. In the conventional electrospinning to synthesize inorganic nanowires, the metal precursor dispersed in the polymeric fiber is allowed to nucleate and grow at appropriate conditions – which took place at equilibrium conditions, i.e., the growth vessel (the polymeric fiber) is large enough to accommodate the nuclei. On the other hand, to synthesize composite nanoflowers a non-equilibrium situation is produced such that the nuclei developed could not be located within the growth vessel such that growth requires an expansion of space. The electron microscopic investigations show that this strategy is successful and the large scale electrospinning could be applied to produce the two type of materials architectures. The composite formation, surface properties, and electrochemical properties of the composite materials are systematically investigated and compared with their single component counterparts. Finally, DSSCs and PSCs were fabricated using the composite nanowires and 3D nanoflowers. The devices fabricated using the 3D nanoflowers showed superior photovoltaic properties than those of the nanowires; the best performing device in this study is a perovskite solar cell with a photo conversion efficiency of 17.25%, open circuit voltage of ~1 V, short circuit current density of ~23.73 mA/cm² and fill factor 73.07%.

9:15 AM DISCUSSION TIME

9:30 AM BREAK

SESSION ET13.07: Other Windows
Session Chair: Richard Taylor
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 303

10:00 AM *ET13.07.01

Highly Transparent Solar Cells for Distributed Applications Richard R. Lunt; Michigan State University, East Lansing, Michigan, United States.

Solar energy offers a viable solution to our growing energy demand, but adoption has been hindered by cost, aesthetics, and difficulties with integration. Excitonic materials offer new opportunities for unique solar harvesting science and applications that can help accelerate solar deployment in new areas previously inaccessible. In the first part of this talk I will introduce our work on developing highly transparent photovoltaics (TPVs) that can maximize the product of the transparency and efficiency for seamless solar harvesting around buildings, automobiles, mobile electronics, and greenhouses. These devices are enabled by the manipulation of excitonic semiconductor materials with selective harvesting in the invisible components of the solar spectrum. I will describe key photophysical properties, outline the thermodynamic and practical limits for a range of TPVs, and discuss their commercial impact for a variety of applications. I will also discuss new figures of merit necessary to characterize and test TPVs. In the second part, I will describe the development of several new classes of materials for TPV integration including: 1) organic salts that allow selective photoresponse beyond 1600nm; 2) luminescent nanoclusters with massive downconversion; and 3) halide perovskites with ideally tuned bandgaps and transparencies above 70%. TPVs ultimately represent a new paradigm for solar energy harvesting that could generate nearly half of the US electricity demand when deployed at full-scale, while also creating additional functionality in managing solar heat.

10:30 AM ET13.07.02

100 cm² Dynamic Windows Based on Reversible Metal Electrodeposition with Sub-Minute Switching Speeds Michael Strand¹, Tyler S. Hernandez¹, Christopher Barile² and Michael D. McGehee^{1,3,4}; ¹Stanford University, Stanford, California, United States; ²University of Nevada, Reno, Reno, Nevada, United States; ³University of Colorado Boulder, Boulder, Colorado, United States; ⁴National Renewable Energy Laboratory, Golden, Colorado, United States.

While the demand for optically tunable windows is paramount in today's residential and industrial communities, traditional electrochromic windows have not yet been commercialized on a large scale. Dynamic windows based on reversible metal electrodeposition (RME) have emerged as an exciting, undeveloped class of electrochromic devices posed to overcome the challenges inherent to conventional technologies. Metals are ideal light-modulators for dynamic windows because they can be color-neutral, inert, IR-reflective, and opaque at 20-50 nanometer thicknesses. Our team has demonstrated metal-based dynamic windows that boast cheap processing, fast switching, and stable performance over thousands of cycles on the 25 cm² scale. Several technical challenges hinder further scalability of the technology. Common transparent electrode materials like indium tin oxide (ITO) have relatively high sheet resistance. By Ohm's Law, maintaining a uniform current density through resistive electrodes necessitates a voltage drop proportional to the electrode area. Large-scale dynamic windows must be engineered with a tolerance to the non-uniform potential distribution across the electrode surface in order to maintain optical uniformity during switching. Additionally, undesired side reactions like the hydrogen evolution reaction (HER) set strict limits on the potentials that may be applied in aqueous electrolytes. The ideal system will enable uniform nucleation and growth of metal films over the potential range set by side reactions inherent to aqueous electrolytes, and the voltage drop inherent to transparent conductors. Prudent design of electrode structure enables uniform and reversible electrodeposition over large areas. Using a scalable process, we fabricate transparent electrodes coated with Pt nanoparticles for dynamic windows. The Pt nanoparticles serve as preferred nucleation sites for the electrodeposition reactions. By controlling the nanoparticle surface density, we have direct control over the active site density for nucleation, and thus the subsequent growth of the metallic film. This nucleation control enables transparent electrodes that exhibit uniform transmission versus time relationships over a large range of applied potentials. Finally, we demonstrate 100 cm² dynamic windows based on reversible metal electrodeposition that switch uniformly despite the voltage drop across the working electrode. The devices switch reversibly from a clear state (60% transmission) to a color-neutral, opaque state (<5% transmission) in less than one minute.

10:45 AM ET13.07.03

Dynamic Windows with High Contrast, Neutral Color and Excellent Durability Using Metal Electrodeposition and Dissolution Christopher Barile¹, Michael McGehee^{2,3}, Shakirul Islam¹, Tyler S. Hernandez^{2,3}, Michael Strand^{2,3} and Daniel Slotcavage³; ¹University of Nevada, Reno, Reno, Nevada, United States; ²University of Colorado Boulder, Boulder, Colorado, United States; ³Stanford University, Stanford, California, United States.

Optoelectronically tunable windows have applications in buildings, automobiles, and switchable sunglasses. By controlling solar lighting and heating, dynamic windows significantly improve the energy efficiency, comfort, and aesthetics of spaces as compared to traditional window technologies. The majority of research on switchable windows over the last several decades has focused on transition metal oxides and polymers as the optically-active materials. In contrast, we are developing dynamic windows based on the reversible electrodeposition and dissolution of metals. These windows display clear-to-black transitions with ~80% optical contrast in 1 minute. 25 cm² device prototypes cycle thousands of times without significant deterioration.

The transparency of these windows is controlled via the electrochemical movement of metal between a transparent conducting working electrode and a counter electrode metal frame. To enable uniform electrodeposition over a large working electrode area, transparent conducting oxides are modified with a self-assembled monolayer of Pt nanoparticles, which serves as an inert metal seed layer for metal nucleation and enhances electrodeposition morphology. An aqueous electrolyte separates the two electrodes and consists of Ag⁺, Cu²⁺, and/or Bi³⁺ ions.^{1,2} We interrogated several electrodeposition chemistries and derived relationships between electrolyte composition and device performance. Through the use of electrolyte additives, we have designed dynamic windows with good durability at cycling temperatures as low as -40°C.³ Finally, we discuss how improvements in electrode design such as coupling metal-based working electrodes with more traditional counter electrodes will increase the scalability and functionality of these devices.

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11:00 AM ET13.07.04

Electrolyte and Electrode Engineering for Dynamic Windows Based on Reversible Metal Electrodeposition Tyler S. Hernandez^{1,3}, Michael Strand^{1,3}, Christopher Barile², Dan Slotcavage¹ and Michael D. McGehee³; ¹Stanford University, Menlo Park, California, United States; ²University of Nevada, Reno, Reno, Nevada, United States; ³University of Colorado Boulder, Boulder, Colorado, United States.

Optically tunable dynamic windows demonstrate many advantages over static lighting controls, such as blinds and shades. This technology allows users to control both heat and light flow into and out of buildings, without sacrificing their comfort or view. Despite both the aesthetic and energetic appeals of these reversibly tinting windows, existing electrochromic technologies have yet to perform ideally. Dynamic windows based on reversible metal electrodeposition (RME) offer an exciting alternative to traditional electrochromic technologies. The use of metals is an attractive option for electrochromic applications due to their high optical extinction coefficients, color neutral metallic state, chemical inertness, and high solubility in aqueous electrolytes. Our group has recently designed 25 cm² RME dynamic windows that demonstrate color-neutral, fast switching speeds over thousands of cycles with minimal degradation.¹

These windows operate by the reversible, electrochemical movement of metallic ions from a transparent conducting electrode to a metal counter electrode frame through an aqueous electrolytic medium, usually consisting of Bi³⁺ and Cu²⁺ ions.² Despite a promising initial design, indium tin oxide (ITO) working electrodes degrade under the acidic environments necessary for aqueous Bi-Cu halide electrolytes.³ Furthermore, the counter electrode frame design will be problematic at a larger scale due to the voltage drop associated with increasing ionic diffusion lengths. We address both the durability and scalability issues associated with these initial devices by designing RME dynamic windows with an acid stable working electrode, a halide-free Bi-Cu electrolyte, and a plane-parallel counter electrode.

Barile, C. J.; Slotcavage, D. J.; Hou, J.; Strand, M. T.; Hernandez, T. S.; McGehee, M. D. *Joule*, **2017**, *1*, 133.

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11:15 AM ET13.07.05

Color Degradation of Organic Semiconductors in Power Generating Windows Bharati Neelamraju, Michael Anderson and Erin L. Ratcliff; The University of Arizona, Tucson, Arizona, United States.

Organic Photovoltaics (OPVs) have incredible prospects for next-generation, flexible opto-electronic energy harvesting and storage devices. Their unique properties of being semi-transparent, flexible, light-weight, low cost and scalable with customizable color perception makes them an ideal candidate for energy generating windows technology for buildings and green houses. Their tunable transparency and color selectivity gives them an aesthetic edge over conventional technology while maintaining the power conversion efficiencies. In green houses, this tunable wavelength approach of OPVs allows maximum usage of the photosynthetically relevant light to reach the plants, while using the unused wavelengths for generating electricity. Yet challenges still exist in terms of degradation of organic semiconductors in these devices which could affect both the efficiency and the color of the OPVs in the long run for use in power generating windows. This effort considers the following "How does degradation of organic semiconductors effect the color and power conversion efficiency (PCE) of the OPV devices in a given architecture". Electronic properties and color measurements in CIE coordinates are analysed using spectroscopy and correlated with density of states. Transport properties are analyzed using mobility, conductivity and PCE measurements. Collectively, these measurements allow us to design organic semiconductor systems with controllable behaviors for next-generation of organic photovoltaic technologies.

1:45 PM ET13.08.01

A Combined Experimental and Theoretical Study into the Performance of Multilayer Vanadium Dioxide Nanocomposites for Energy Saving Applications Christian Sol¹, Johannes Schlaefer¹, Tao Li¹, Ivan P. Parkin² and Ioannis Papakonstantinou¹; ¹Electronic & Electrical Engineering, University College London, London, United Kingdom; ²Chemistry, University College London, London, United Kingdom.

In the built environment there is an increasing issue of heat management, with buildings expending significant energy resources to maintain comfortable living temperatures. In many parts of the world, this entails the use of both heating and cooling during daylight hours depending on ambient temperatures. Due to the variation in the desired temperature control classical solutions can become counterproductive in their aim of maintaining comfortable temperatures, therefore it is important to employ adaptive solutions that vary their functionality based on circumstance. In recent years vanadium dioxide (VO₂) has generated a broad range of interest due to its heat-mediated structural phase transition from a semiconductor to a metal, which occurs at a critical temperature that may be tuned via doping. The phase transition of VO₂ significantly modulates its optical properties, with the high temperature metallic state absorbing and reflecting considerably more infrared radiation than the lower temperature monoclinic state due to the presence of free electrons; a window coated with a VO₂ film may passively vary its transmission of infrared radiation based on the ambient temperature, in doing so reducing the temperature management energy-load.

Here, we present a theoretically optimised design for a thermochromic smart window film based on a multilayer stack of silica, titania and vanadium dioxide (VO₂) on a glass substrate and use the simulations to guide the fabrication process. The design makes use of coherent interference within the multilayered structure to suppress reflection of visible light and improve the reflective component of solar modulation. In doing so, we are able simultaneously improve the visible transmission and solar modulation of the film above what would be possible with a single layer film. Additionally, the use of thin film VO₂ also acts to reduce the detrimental transition hysteresis typically seen in small domain sized nanoparticulate VO₂ films. The multilayer structure is fabricated via spin coating of sol-gel based precursors and subsequent annealing. After which the structure is optically characterised and results are compared with simulation along with standard single layer VO₂ films and other nanoparticulate based VO₂ films.

2:00 PM ET13.08.03

Interdependence of Molecular Precursors, Morphology and Phase Transitions in Thermochromic VO₂ Nanostructured Thin Films David Graf, Lasse Jürgensen, Michael Frank, Axel Klein and Sanjay Mathur; University of Cologne-Inorganic Chemistry, Cologne, Germany.

In recent years, monoclinic/rutile vanadium dioxide VO₂ (M1/R) has attracted attention as a promising candidate for energy saving window applications due to its unique thermochromic reversible metal-insulator transition (MST) at 68°C. Phase selective chemical vapor deposition of nanostructured vanadium dioxide (VO₂) and sesquioxide (V₂O₃) was achieved by deploying [V(OR)₄]_n (R = tBu, n = 1 (1), R = Et, n = 3 (2), R = Me, n = 4 (3)). Use of [V(OⁱBu)₄] (1) produced thin films of monoclinic VO₂ (M1) at 700 and 800 °C consisting of anisotropic nanostructures with high crystallinity and small hysteresis in the metal-to-semiconductor transition (MST). Film morphologies manifested strong dependence on growth temperatures and exhibited pronounced texturing effects at high temperatures (>700 °C). The microstructure of the films was found to significantly affect the MST behavior of VO₂ films. DTA measurements of VO₂ films showed MST at 63 °C (700 °C) and 65 °C (800 °C), much lower than the transition temperature observed in single crystal material (68 °C). Precursors were characterized in the solid-state (XRD) and solution-state (temperature dependent EPR, NMR) to reveal a thermochromic association-dissociation equilibrium in solution (complex 2 and 3), involving monomeric, dimeric and oligomeric species. Use of 2 and 3 as single precursors produced thin films of crystalline conductive V₂O₃ consisting of nanosheets (5 nm) with a flower-like morphology. Preliminary electrochemical performance investigation of V₂O₃ samples presents superior behavior for supercaps application.

2:15 PM ET13.08.04

Fabrication and Spectral Properties of Textured Phase Change VO₂ Nanostructures Obtained via Oxidation of Thermally Evaporated Metallic Vanadium Films Merve Ertas Uslu^{1,2}, Ibrahim B. Misirlioglu^{1,2} and Ibrahim Sendur^{1,2}; ¹Faculty of Engineering and Natural Sciences, Sabanci University, Istanbul, Turkey; ²Nanotechnology Research and Application Center, Sabanci University, Istanbul, Turkey.

We demonstrate the growth of highly textured VO₂ nanocrystals via annealing of amorphous e-beam deposited metallic V. Temperature dependent ellipsometry results reveal the pronounced reflection near the IR spectrum above the transition and an almost temperature independent weak reflection in the visible spectrum. The infrared reflection displays a strong hysteresis during heating and cooling near the transition temperature at 68°C, indicating a first order transition and a strain-free structure. Our work demonstrates the feasibility to obtain high quality phase change nanostructures that transmit the visible spectrum but reflect infrared and is suitable for large scale fabrication.