

PCSI

Room Ballroom South - Session PCSI-1WeM

Hybrid and Mixed-Dimensional Interfaces I

Moderator: A. Alec Talin, Sandia National Laboratories

8:30am PCSI-1WeM-1 Nanoimaging and Spectroscopy of Emerging Photovoltaic, Marina Leite, University of Maryland INVITED

Solar energy can deliver the >184 000 TWh per annum required to meet the current worldwide energy needs. Yet, High-performance and low-cost photovoltaics (PV) are still required to successfully substitute fossil fuel-based technologies. Hybrid perovskites and thin-film polycrystalline materials are promising options for high-performance and low-cost PV. These materials present mesoscale constructs, with nano- and microscale grains and boundaries that individually contribute to the devices' optoelectronic behavior [1,2]. For hybrid perovskites, their stability is the primary limiting factor towards commercialization. Thus, we resolve the dynamic optical [3] and electrical [4] responses from the macro- to the nanoscale, as these materials are exposed to: water, oxygen, temperature, bias, and illumination. We further propose a machine learning (ML) tactic to deconvolute the individual and combined effects of each parameter on device stability. We elucidate ion motion within the perovskite grains by a fast scanning probe microscopic new method that enables us to spatially (<20 nm) and temporally (msec) resolve the devices' open-circuit voltage (Voc) (Fig 1) [4,5]. In the realm of polycrystalline materials, we demonstrate a novel AFM-based approach to image local Voc variations, based on illuminated Kelvin-probe force microscopy [6]. Our functional imaging paradigm provides a new platform to map device performance with nanoscale spatial resolution.

[1] E. M. Tennyson, J. M. Howard, M. S. Leite. ACS Energy Letters 2, 1825(2017).

[2] E. M. Tennyson, J. A. Frantz, J. M. Howard, W. B. Gunnarsson, J. D. Myers, R. Y. Bekele, S.-M. Na, M.

S. Leite. ACS Energy Letters 1, 899(2016).

[3] J. M. Howard, E. M. Tennyson, S. Barik, R. Szostak, E. Waks, M. Toney, A. F. Nogueira, B. R. A.

Neves, and M. S. Leite. J. Physical Chemistry Letters 9, 3463(2018).

[4] J. L. Garrett, E. M. Tennyson, M. Hu, J. Huang, J. N. Munday, M. S. Leite. Nano Letters 17, 2554(2017). [5] E. M. Tennyson, C. Gong, M. S. Leite. ACS Energy Letters 2, 2761(2017).

[6] E. M. Tennyson, J. L. Garrett, J. A. Frantz, J. D. Myers, R. Y. Bekele, J. S. Sanghera, J. N. Munday, M.

S. Leite. Advanced Energy Materials 5, 1501142(2015).

9:05am PCSI-1WeM-8 Electronic Charge Transport in Solution-processed Vertically Stacked 2D Perovskite Quantum Wells, H Tsai, Rice University; R Asadpour, Purdue University; M Kanatzidis, Northwestern University; M Alam, Purdue University; A Mohite, Rice University; Wanyi Nie, Los Alamos National Laboratory

State-of-the-art quantum well based devices such as photovoltaics, photodetectors and light emission devices were enabled by understanding the nature and the exact mechanism of electronic charge transport. Ruddlesden-Popper halide perovskites are two-dimensional solution-processed quantum wells and have recently emerged as highly efficient semiconductor for solar cell approaching 13% in power conversion efficiency. However, further improvements will require an understanding of charge transport mechanisms, which are currently unknown and further complicated by the presence of strongly bound excitons. In our study, we discovered that the carrier transport is closely related to the structure and stacking of those quantum wells. Combining systematic device characterization and simulation, we conclude that the photo generated electron-hole pairs need to overcome the multiple internal potential barriers for collection to occur. The potential barriers that block the efficient separation of electron-hole pairs are attributed to the misalignment between crystalline slabs. Both of those properties are unfavorable for photovoltaic cell operation. Here we elucidate the critical role of field-assisted charge carrier separation that overcomes these bottlenecks leading to the efficient photocurrent collection. On the other

hand, the structure of the 2D perovskites could promote the radiative recombination by spatially localizing the electrical injected carriers, which makes them an excellent material for light emitting diodes.

9:10am PCSI-1WeM-9 N-type Doping in Organic Semiconductor Thin Films by using a Dendritic Oligoarylamine-substituted Benzimidazole Dopant, Yuji Yoshihashi, Keio University, Japan

Organic n-type doping with donor dopants has not been established well because of air instability of conventional donor dopants. With this background, we have focused on imidazole-based compounds as solution-processable and pure organic n-type dopants. These compounds are known as strong single-electron reductants. However, these dopants are quickly oxidized in solution phase in ambient condition. In this work, we report an approach for increasing the stability of benzimidazole dopant molecule in solution phase by attachment dendritic oligoarylamine (N,N-bis[4-(di-4-anisyl-amino) phenyl]amine) at the 2-position of the imidazole ring (N3-DMBI-H shown in Fig. 1)[1].

N3-DMBI-H was newly synthesized by ourselves. N3-DMBI-H solution in chlorobenzene (CB) revealed much better stability in ambient air than solutions of other benzimidazole dopants. [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) solution (in CB) was dropcast onto Si substrates covered with 200 nm-thick SiO₂ layer. Doping concentrations of N3-DMBI-H were 0, 0.5, 2 and 5 wt%. After that, the dropcast films were dried and heated at 100°C overnight to activate the dopants. The above processes were performed in a N₂-filled glovebox. After Au electrodes (thickness: 25 nm) were deposited onto the PCBM film surfaces by vacuum evaporation, we measured two-terminal current-voltage (*I-V*) characteristics of PCBM films under a vacuum condition (10⁻² Pa).

Figure 2 shows two-terminal *I-V* characteristics of undoped and N3-DMBI-H doped PCBM films. The gap distance between the two contact electrodes was 50 μm. As shown in Fig. 2, doping N3-DMBI-H into PCBM increased the current value by more than five orders of magnitude. The electrical conductivity of the N3-DMBI-H-doped PCBM thin film was reported to be 6.39 × 10⁻⁴ cm⁻¹(undoped PCBM: 6.62 × 10⁻⁹ S cm⁻¹). This result suggests that the electric resistance of PCBM thin films considerably decreased by N3-DMBI-H doping, due to carrier (electron) doping effects.

[1] M. Uebe, Y. Yoshihashi, K. Noda, M. Matsubara, A. Ito, *J. Mater. Chem. C* 2018, 6, 6429-6439

9:15am PCSI-1WeM-10 Multi-scale Modeling of Molecule-Surface Interactions for Improved Charge Transfer across Photoelectrochemical Interfaces, A Iyer, K Kearney, University of Illinois at Urbana-Champaign; A Rockett, Colorado School of Mines; Elif Ertekin, University of Illinois at Urbana-Champaign INVITED

The design of efficient, stable photoelectrochemical devices requires the use of complex heterojunctions composed of semiconducting, protective, and catalytic layers. Understanding the nature of charge transport across these interfaces is challenging, due to the complexity of the interfaces and possibility of competing charge transfer mechanisms. We present our recently developed multiscale approach that combines first-principles density functional theory (DFT) and solid-state drift/diffusion device scale modeling to give insights into the nature of charge transport across photoelectrode interfaces [1-3], Fig. 1. DFT is used to estimate the surface dipole induced by the functionalization, and the device software wxAMPS is used to predict experimentally measurable features such as the JV curve and the open-circuit voltage. Using this approach, we are able to identify the mechanism of hole transfer across *n*-Si(111)-R|TiO₂ photoanodes where -R is a series of mixed aryl/methyl monolayers containing an increasing number of methoxy units (mono, di, and tri). In collaboration with experiment, we find that hole transport is limited at the *n*-Si(111)-R|TiO₂ interface and occurs by two processes—*thermionic emission* and/or *intraband tunneling*—where the interplay between them is regulated by the interfacial molecular dipole. Finally we will highlight how molecule/surface interactions can be used to model doped silicon slabs at experimental doping densities in a computationally tractable manner.

9:45am PCSI-1WeM-16 Scanning Electrochemical Microscopy of Graphene-based Hybrids: Insights into Physicochemical Interfacial Processes and Electroactive Site Density Distribution, Sanju Gupta, Western Kentucky University

Surface (and interfacial) science is found in various environments of scientific significance including biomembranes, ocean and atmospheric chemistry, applied electrochemistry and at the grand challenges of *energy-water-nexus* [1]. Molecular redox behavior on the surface and at the interface is drastically different than bulk counterparts.

Wednesday Morning, January 16, 2019

In this talk, we demonstrate scanning electrochemical microscopy (SECM) is a powerful tool to investigate dynamic physical-chemical processes at surfaces and buried interfaces. This technique helps to determine ion (or electron) transfer kinetic rate, diffusion coefficient, imaging electrochemical redox reactions and activity. The significant advantage offered by SECM is its capability of probing chemical information at the solid/liquid interfaces. A constant potential is applied to the tip and electrochemical working electrode (*i.e.* the substrate in electrolyte) to drive reaction of redox species (or mediator) in bulk electrolyte solution to probe the surfaces of graphene-based hybrids, relevant for electrochemical energy systems. The micro-configured cyclic voltammograms, probe approach (current versus tip–substrate distance) curves in feedback and imaging modes, for graphene/CNT, graphene/transition metal oxide and aerogels are chosen as case examples to probe ion adsorption, charge transfer dynamics and to map highly electroactive ('hot spots') edge sites. The SECM setup has a resolution of ~40 nm and can locate and relocate areas of interest precisely after a coarse image. The heterogeneous electrode surfaces comprised of graphene nanosheets (conducting)/other nanomaterials (semiconducting) exhibit peak and valley tip current behavior and site distribution and the data is analyzed in terms of reactive basal plane and edge plane sites distribution, and help to determine heterogeneous rate constant using modeling and fitting experimental data. The findings reinforce the available electron density of states in the vicinity of the Fermi level contributing to higher electroactivity, faster interfacial diffusion, and shorter distances for electron transfer, facilitated through molecular and chemical bridges [1].

[1] S. Gupta and S. B. Carrizosa, Appl. Phys. Lett. **109**, 243903 (2016).

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Author Index

Bold page numbers indicate presenter

— A —

Alam, M: PCSI-1WeM-8, **1**
Asadpour, R: PCSI-1WeM-8, **1**

— E —

Ertekin, E: PCSI-1WeM-10, **1**

— G —

Gupta, S: PCSI-1WeM-16, **1**

— I —

Iyer, A: PCSI-1WeM-10, **1**

— K —

Kanatidis, M: PCSI-1WeM-8, **1**
Kearney, K: PCSI-1WeM-10, **1**

— L —

Leite, M: PCSI-1WeM-1, **1**

— M —

Mohite, A: PCSI-1WeM-8, **1**

— N —

Nie, W: PCSI-1WeM-8, **1**

— R —

Rockett, A: PCSI-1WeM-10, **1**

— T —

Tsai, H: PCSI-1WeM-8, **1**

— Y —

Yoshihashi, Y: PCSI-1WeM-9, **1**