

Nanometer-scale Science and Technology Division Room 19 - Session NS+SS+SU-WeM

Nanotechnology for Renewable Energy

Moderator: Robert Ilic, National Institute of Standards and Technology (NIST)

8:40am **NS+SS+SU-WeM-3 Can “Photovoltaic” Halide Perovskites (MAPbI₃ & MAPbBr₃) be Ferroelectric?**, *David Cahen*, Weizmann Institute of Science, Israel **INVITED**

Ferroelectricity, well-known in oxide perovskites, was suggested as possible reason for the outstanding solar-to-electrical energy conversion of MAPbI₃ & MAPbBr₃-based halide perovskite PV cells, esp. because ferroelectric domain wall conduction was thought to keep photogenerated charges separated. (à low carrier recombination rate à high photovoltage efficiency).

Contradicting experimental evidence, relevant to ferroelectricity, is based on structural diffraction, electric field vs. polarization plots, second harmonic generation and piezoelectricity measurements. To resolve this debate we first asked if

- the materials are pyroelectric, direct evidence for *spontaneous polarization*, a necessary condition for ferroelectricity.
- polar-domains exist in the structure, as often found in many ferroelectric materials.

Using home-grown, well-characterized single crystals, we find the cubic phases of MAPbI₃ (>330K) and MAPbBr₃ (>236K) phase to be non-polar, excluding ferroelectricity in them. The tetragonal phase of MAPbI₃, however, shows clear evidence of pyroelectricity when probing the potentially-polar, [001], crystallographic orientation, proving its polar nature. By adding low-temperature electric field vs. polarization and room temperature SHG studies and optical observations of polar domains, we arrive at a clear-cut conclusion that MAPbI₃ is ferroelectric in the tetragonal phase. I will briefly dwell on the remaining question, i.e., “does that really matter?”.

* work done by Yevgeny Rakita, Dr. David Ehre, Omri Bar-Eli, Elena Meirzadeh, Hadar Kaslasi, Yagel Peleg, with Profs. Gary Hodes, Igor Lubomirsky, Dan Oron, all from the Weizmann Inst.

9:20am **NS+SS+SU-WeM-5 NSTD-Recognition Award Talk: Mixed-Dimensional Nanomaterial Heterostructures for Electronic and Energy Applications**, *Mark Hersam*, Northwestern University **INVITED**

Layered two-dimensional (2D) nanomaterials interact primarily via van der Waals bonding, which has created new opportunities for heterostructures that are not constrained by epitaxial growth. However, it is important to acknowledge that van der Waals interactions are not limited to interplanar interactions in 2D materials. In principle, any passivated, dangling bond-free surface interacts with another via non-covalent forces. Consequently, the emerging layered 2D nanomaterials can be integrated with a diverse range of other materials, including those of different dimensionality, to form van der Waals heterostructures. This talk will explore mixed-dimensional combinations of 2D + n-D (n = 0, 1 and 3) materials, thus significantly expanding the van der Waals heterostructure concept [1]. In order to efficiently explore the vast phase space for mixed-dimensional heterostructures, our laboratory employs solution-based additive assembly [2]. In particular, constituent nanomaterials (e.g., carbon nanotubes, graphene, transition metal dichalcogenides, black phosphorus, and boron nitride) are isolated in solution, and then deposited into thin films with scalable additive manufacturing methods (e.g., inkjet, gravure, and screen printing) [3]. By achieving high levels of nanomaterial monodispersity and printing fidelity, a variety of electronic and energy applications can be enhanced including digital logic circuits [4] and lithium-ion batteries [5]. Furthermore, by integrating multiple nanomaterial inks into heterostructures, unprecedented device function is realized including anti-ambipolar transistors [6], gate-tunable photovoltaics [7], and neuromorphic memristors [8]. In addition to technological implications for electronic and energy technologies, this talk will explore several fundamental issues including band alignment, doping, trap states, and charge/energy transfer across previously unexplored mixed-dimensional heterointerfaces.

[1] D. Jariwala, *et al.*, *Nature Materials*, **16**, 170 (2017).

[2] J. Zhu, *et al.*, *Advanced Materials*, **29**, 1603895 (2017).

[3] J. Kang, *et al.*, *Accounts of Chemical Research*, DOI: 10.1021/acs.accounts.6b00643 (2017).

[4] M. Geier, *et al.*, *Nature Nanotechnology*, **10**, 944 (2015).

[5] K.-S. Chen, *et al.*, *Nano Letters*, **17**, 2539 (2017).

[6] D. Jariwala, *et al.*, *Nano Letters*, **15**, 416 (2015).

[7] D. Jariwala, *et al.*, *Nano Letters*, **16**, 497 (2016).

[8] V. K. Sangwan, *et al.*, *Nature Nanotechnology*, **10**, 403 (2015).

11:00am **NS+SS+SU-WeM-10 Magnetron Sputtered Nanostructured TiO₂ Thin Films for Dye Sensitized Solar Cells Applications**, *Pierre-Antoine Cormier*, *J Dervaux*, ChIPS, University of Mons, Belgium; *Y Pellegrin*, *F Odobel*, CEISAM, University of Nantes, France; *R Snyders*, ChIPS, University of Mons, Belgium

Among the many advantages of Dye Sensitive Solar Cells (DSSCs), their non-toxic and low cost components, their lightweight and their high performances under diffuse light and high temperatures are very interesting. DSSCs are therefore considered as a promising alternative to conventional Si and chalcogenide based solar cells. In DSSCs, the light is absorbed by dye molecules inducing an electron injection into a TiO₂ nanoparticles (NPs)-based photo-anode. Although this allows a high photon collection, the charge transport is limited by charge recombination at the NPs boundaries limiting the solar to conversion efficiency [1]. Many efforts have been devoted to rule this problem such as replacing NPs by nanofilms, nanotubes or hierarchical nanostructured thin films which offer a direct path way to electrons [1]. We previously shown that such hierarchical structure can be obtained by reactive magnetron sputtering (RMS) at grazing incidence which allows to tune the film morphology from slanted nanocolumns, to zigzag or pillars [2].

In this work, such films were synthesized and annealed during 2h at 773 K under atmospheric pressure in order to obtain nanocolumns composed by a single anatase crystal as verified by TEM. These films were used as photo-anode in liquid DSSCs, which were characterized under simulated AM1.5 Global spectrum and 1sun illumination. Different morphologies (slanted columns, zigzag and pillars) and different thicknesses of slanted columns based films were studied. In addition, the dye grafting efficiency on these structures was evaluated by absorbance measurements performed by UV-Visible spectrophotometry.

The slanted columns-based cells present the best performances followed by zigzag and pillar based ones. This result is directly related to the corresponding specific surface area which is the highest for the slanted columns films. By increasing the thickness of the slanted films from 1.2 to 4.3 μm, the cell efficiency increases from 1.2 to 2.6 %. As the short-circuit current density also increased while the open circuit voltage was not affected, it was concluded that the critical parameter limiting the cell efficiency is the adsorbed dye density, which is enhanced for thicker films

To overcome this limitation still using thin films, the slanted columns films were impregnated by TiO₂ NPs (~20nm). This allows for an enhancement of the cell efficiency by 2.2% attributed to a synergetic effect between: (i) a higher dye adsorption and (ii) the very good charge transport through the single crystalline columns.

[1] A. Hagfeldt *et al.* “Dye-Sensitized Solar Cells,” 2010

[2] J. Dervaux *et al.*, *Vacuum*, vol. 114, pp. 213–220, Nov. 2014.

11:20am **NS+SS+SU-WeM-11 Spectroscopic Evolution of Halide Perovskite Growth on Graphene Oxide Surfaces for Photovoltaics**, *Muge Acik*, Argonne National Laboratory; *G Lee*, Ulsan National Institute of Science and Technology, Korea; *R Rosenberg*, Argonne National Laboratory

High power conversion efficiency of perovskite-based solar cells offers promise for low-cost and scalable production of renewable energy. Hybrid organic-inorganic methylammonium lead halides, MAPbX₃ (X=I, Br, Cl)/mixed-halides (I_{3-x}Cl_x, I_{3-x}Br_x) have been reported as light harvesting layers with tunable bandgaps, long electron-hole diffusion lengths and high electron/hole mobility. Nevertheless, halide-based perovskites require *in situ* investigation for film growth mechanisms to overcome detrimental effects of incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, and weak cation-anion-solvent coordination (1). Graphene-derived hybrids has recently emerged as an ETL/HTL replacement in these devices. Graphene/perovskite structure-property relationships are, however, not well understood due to unclear chemistry at the ETL/perovskite/HTL interfaces (2). Moreover, effect of film thickness, lead content, stoichiometry control, and overlayer/underlayer morphology/composition ought to be examined for better charge transport at the graphene/perovskite interfaces. Stability factors also need to be

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studied for charge mechanisms to unravel device performance challenges. Indeed, underlayer ETLs ($\text{TiO}_2/\text{Al}_2\text{O}_3$) and overlayer HTLs (spiro-OMeTAD) were rarely studied with graphene. To address scalability and stability issues, we investigated degradation, nucleation and growth mechanisms in reduced graphene/graphite oxide (RGO) upon halide-based (I, Cl, Br) perovskite deposition. Chemical interactions were interpreted at perovskite/RGO interfaces for the grain size, orientation, boundaries, and surface/bulk effects using variable-temperature ($\leq 600^\circ\text{C}$, Ar(g)) *in situ* spectroscopy (infrared absorption and micro-Raman). Controlled perovskite formation was achieved at room temperature for bromide-based perovskites resulting in improved chemical stability (vs. iodide/chloride derivative). Perovskite decomposition was observed at $\geq 150^\circ\text{C}$ on RGO surfaces. Oxygen-induced chemical reactions occurred at $\leq 150^\circ\text{C}$, initiated at room temperature because of precursor interactions forming carbonyls upon perovskite deposition (3), and eliminated hydroxyls reducing GO during perovskite growth. Poor perovskite formation was observed on RGO due to varying electron affinity and reactivity of precursor halides, resulting in film degradation in air (O_2 , H_2O). Film morphology was explored by SEM, XRD, XPS, AFM, and the reaction mechanisms were studied by first principles calculations that bring insights for solar cell design principles.

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11:40am **NS+SS+SU-WeM-12 2D Material Laminates for Ultra-fast and Selective Molecular-scale Separation, Saeed Moghaddam**, University of Florida

Due to their intrinsic properties, 2D materials have provided a unique opportunity to develop membranes with ultrafast and highly selective permeation capability. Graphene oxide (GO) is among 2D materials that has garnered significant attention in the past several years and numerous studies have been conducted on transport characteristics of its laminates. However, a comprehensive understanding of the effect of synthesis conditions on physicochemical conditions of GO that dictate transport characteristics of its laminates is lacking. In this study, the effect of oxidation conditions during the synthesis process of GO flakes on transport characteristics of GO laminates are investigated. Transport properties of the GO laminates are observed to be significantly different. It is determined that i) mean-flake size, ii) surface defects, and iii) inter-layer spacing are the key parameters.

The fundamental knowledge gained has been utilized to develop membrane separators for energy and water applications. To enhance performance of DMFCs, it was determined that at a constant oxidation level methanol permeability decreases linearly with increasing the GO mean flake size while changes in proton conductivity remain insignificant. This behavior is attributed to difference in adopted conduction pathways of protons and methanol molecules. With increasing the oxidation level, proliferation of surface defects is deductively reasoned to be the dominant factor responsible for a large increase in the measured methanol permeability. The proton conductivity is also significantly increased with increasing the oxidation level because of greater number of ion exchange sites, shortened transport pathway and increased GO flakes inter-layer spacing. The observed transport characteristics are attributed to either different adopted conduction pathways or surface mobility of protons and methanol molecules. The findings imply that the GO nanoplatelets contain atomic formations that are more selective to protons than to methanol molecules.

We have also utilized the superior water selective transport properties of GO laminates as filtration membranes for Endocrine Disrupting Compounds (EDCs) with high permeate flux rates. A layer-by-layer (L-b-L) approach was utilized to prepare thin film composite membranes with a polymer support and a few layers of GO interlinked via poly(allylamine hydrochloride) (PAH).

The prepared membrane showed a fourfold increase in the permeate flux in comparison to the commercially available nanofiltration (NF) membranes. The rejection performance of the membrane was evaluated by studying the permeation of ibuprofen and a rejection rate of 75% was obtained.

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