

Nanomaterials

Room Naupaka Salon 5 - Session NM-MoM

Nanocharacterization

Moderator: Roya Maboudian, University of California at Berkeley

8:00am NM-MoM1 Identification of Point Defects in Transition Metal Dichalcogenides by Combining Atomic Resolution Force Microscopy, STM/STS and Density Functional Theory: Missing Vacancies in MoSe₂ and WS₂, Frank Ogletree, Lawrence Berkeley National Laboratory; *S. Barja*, UPV/EHU-CISC Ikerbasque, Spain; *S. Refaely-Abramson*, University of California Berkeley; *B. Schuler*, Lawrence Berkeley National Laboratory; *D. Qiu*, University of California Berkeley; *S. Wickenberg*, Lawrence Berkeley Laboratory; *J. Neaton*, *A. Weber-Bargioni*, Lawrence Berkeley National Laboratory

Point defects can strongly influence material properties of 2D materials including Transition Metal Dichalcogenides (TMDs), where they can modify optical and transport properties, catalytic activity, and act as single photon emitters. It has been difficult to directly correlate specific defects with macroscopic measurements of TMD optical and transport properties. Scanning transmission electron microscopy (STEM) investigations have provided significant structural information, but STEM cannot directly probe electronic structure. In addition radiation damage is a significant problem for TMDs, making it difficult to determine intrinsic defect concentrations [1].

Here we report on the first applications of atomic resolution AFM to TMD point defects [2,3]. Cryogenic AFM/STM/STS studies using a CO molecule tip, when combined with advanced density functional excited-state theory, provide sufficient information for detailed point defect characterization. The experimental methods can resolve:

1. defect location through AFM, including local strain with ~ 30 pm lateral and 3 pm vertical resolution. This is difficult to do with STM alone due to the strong convolution of geometric and electronic structure [4]
2. electronic structure, through scanning tunneling spectroscopy (STS), which identifies localized resonances and in-gap states, and STM spatial maps of localized states and orbitals
3. charge state, through Kelvin-probe AFM and STS charging peaks
4. radial and reflection symmetry breaking, for example defects in the chalcogen plane appear very different in AFM if located on the upper or lower TMD surface, while the STS maps and spectra are similar. Defects localized in the metal plane have one AFM signature for a given STS structure.

The detailed information from scanning probe studies strongly constrains geometric structural models for theoretical simulations, and the results of these simulations can be directly compared to STS maps and local spectra, allowing detailed understanding of defects.

We will report on studies on MBE-grown MoSe₂ and CVD-grown WS₂. Based on STEM studies, chalcogen vacancies have been identified as the most common point defects, and have been predicted to have in-gap states. While our AFM/STM studies show chalcogen site defects whose AFM contrast is consistent with Se or S vacancies, they do not show any electronic in-gap states. In combination with theory, we identify these sites as substituted oxygen, which has very low STEM contrast.

[1] Wang, Robertson, Warner, *Chem Soc Rev* 2018.

[2] Barja, Refaely-Abramson, Schuler, Qiu et al, submitted.

[3] Schuler, Kastl, Chen et al, submitted.

[4] Barja et al, *Nature Physics* 2015.

8:20am NM-MoM2 CO-tip AFM Identification and STM-induced Luminescence of Point Defects in Monolayer WS₂, Bruno Schuler, Lawrence Berkeley National Laboratory; *D. Qiu*, University of California Berkeley; *S. Refaely-Abramson*, *C. Kastl*, *K. Cochran*, Lawrence Berkeley National Laboratory; *S. Barja*, Lawrence Berkeley Lab, USA; *C.T. Chen*, *N. Borys*, *R. Koch*, *F. Ogletree*, *S. Aloni*, *A.M. Schwartzberg*, Lawrence Berkeley National Laboratory; *S. Louie*, University of California Berkeley; *J. Neaton*, *A. Weber-Bargioni*, Lawrence Berkeley National Laboratory

The advent of transition metal dichalcogenides (TMDs) and other two-dimensional (2D) materials has attracted considerable attention due to

unique material properties emerging from their reduced dimensionality. Because of this strong confinement, structural defects greatly modify such properties and have therefore become of increasing interest to the 2D materials community. Particularly the creation of in-gap defect states is decisive for their optoelectronic properties and catalytic activity.

Using low-temperature scanning probe microscopy with CO functionalized tips we identified and characterized common point defects in monolayer WS₂ (see Fig. 1).

Contrary to previous reports, we suggest that the most abundant defect is an O substitution at a S site, not a S vacancy, with a distinctively different electronic structure.

In contrast to O decorated S vacancies, a W substitutional defect and pristine S vacancies create distinct defect states within the band gap of WS₂. Interestingly, both types of point defects exhibit spin-orbit split defect states with a large splitting of 80 meV and 280 meV, respectively. Moreover, these defects exhibit electron-induced luminescence with a characteristic bias dependence. Spectrally integrated luminescence maps resemble the defect orbitals.

The same sample was also characterized with nano-ARPES and photoluminescence spectroscopy, which shows that thermally grown graphene on SiC constitutes a suitable platform for cross-correlation microscopy of TMD materials (and potentially other van der Waals materials) in both, UHV and ambient conditions.

The atomic-scale characterization allows an unprecedentedly detailed picture on the structure and functionality of point defects in 2D-TMDs.

8:40am NM-MoM3 Intermolecular and Molecule-Substrate Interactions in Surface-Supported Nanostructures Characterized by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy, J. Schultz, P. Whiteman, S. Mahapatra, Nan Jiang, University of Illinois at Chicago

In order to fully characterize molecular assemblies at the single molecular scale, advanced analytical surface techniques have to be employed. We carried out scanning tunneling microscopy (STM) experiments on two molecules (N,N'-bis(2,6-diisopropylphenyl)-perylene-3,4,9,10-bis(dicarboximide) (PDI) and subphthalocyanine (SubPc)), which are both self-assembled on noble metal substrates. The STM experiments were complemented by tip-enhanced Raman spectroscopy (TERS), surface-enhanced Raman spectroscopy (SERS) and density functional theory (DFT) calculations. In particular, we have interrogated the lifting of an accidental vibrational degeneracy of a mode of PDI on Ag(111) and Ag(100) surfaces, with the most strongly perturbed mode being that associated with the largest vibrational amplitude on the periphery of the molecule. In the other hand, the alignment between experimental TERS of SubPc on surface and DFT calculated Raman spectrum of gas phase SubPc was quite good, which indicates that the interaction between SubPc molecules in the monolayer is very weak. New two-dimensional molecular superstructures were discovered to consist of several distinct molecular binding configurations. Both TERS and SERS experiments of SubPc yielded nearly identical vibrational spectra for both binding configurations, consistent with their small adsorption energies (<0.2 eV) as calculated by DFT. Our results demonstrate the necessity of advanced Raman techniques such as TERS when precisely probing molecule-molecule and molecule-substrate interactions.

9:00am NM-MoM4 Quantifying the Thermodynamics of Ligand Binding to CsPbBr₃ Quantum Dots via Solution ¹H NMR Characterization, Sara Smock, R.L. Brutchey, University of Southern California

The characterization of surface ligand binding to quantum dots is important to fully understand their behavior, such as photoluminescence quantum yield. One of the most promising recent classes of quantum dot materials is the CsPbX₃ halide perovskites (where X = Cl⁻, Br⁻, I⁻) because of their growing applications in LEDs, X-ray detectors, and lasers. These CsPbX₃ quantum dots possess bright photoluminescence and narrow emission line widths over a wide color gamut. Using the hot-injection synthesis first reported by Protesescu et al. (*Nano Lett.* 2015, 15, 3692), the ligand shell supporting the resulting CsPbBr₃ quantum dots has been reported to be highly dynamic and primarily comprised of oleylammonium bromide binding to the surface in an NC(X)₂ fashion without accompanying oleate X-type coordination. To date, however, the characterization of ligand binding has been qualitative in nature. Herein, we will report on quantifying the thermodynamics of *n*-alkyl carboxylic acid and amine ligand binding to CsPbBr₃ quantum dots via ¹H NMR spectroscopy. ¹H NMR is a powerful characterization tool for organic ligands on the surfaces of nanocrystals to observe ligand binding and gain insight into the thermodynamics of ligand

exchange processes. In agreement with previous studies, we find the supporting ligands to be fluxional in nature; however, both ammonium and carboxylate binding to the purified nanocrystal surface is unequivocally observed. *n*-Alkyl carboxylic acids undergo an exergonic exchange equilibrium with bound oleate ($K_{eq} = 1.97$) at 25 °C, while *n*-alkyl phosphonic acids undergo an irreversible ligand exchange. *n*-Alkyl amines exergonically exchange with oleylamine ($K_{eq} = 2.52$) at 25 °C. Exchange occurs with carboxylic acids, phosphonic acids, and amines on CsPbBr₃ quantum dots without etching the nanocrystal surface; increases in steady-state PL intensities are correlated with more strongly bound conjugate base ligands.

9:20am **NM-MoM5 Nanomaterials for Creating Sensitive and Selective Biosensing Interfaces**, *Leyla Soleymani*, McMaster University, Canada
INVITED

Biosensors bring together biorecognition and signal transduction to analyze biologically relevant targets. The performance metrics of biosensors, such as limit-of-detection and speed, are strongly influenced by their structure. Designing material architectures that increase the sensor sensitivity, decrease background signals, and reduce analysis time is critical for entering biosensors into clinical decision making and health monitoring. Through this work, we have developed strategies for creating three-dimensional electrodes, combining them with biorecognition and self-cleaning interfaces, and translating biorecognition into electrochemical signals.

Porous and wrinkled hierarchical electrodes are created through self-assembly, electroless deposition, and bulking enabled by shape memory polymer substrates. Biorecognition is achieved by combining functionalized electrodes with molecular machines created using DNA nanotechnology. Self-cleaning is achieved using strategies that transform electrodes to omniphobic surface. Signal transduction is performed by electrochemical and photoelectrochemical readout using photo-active electrodes.

Three-dimensional electrodes, biorecognition elements, and signal transduction components are integrated into microfluidic networks for sensing small molecules, nucleic acids, and proteins. This integrated biosensing platform is used for analyzing clinical samples, and a test with a clinically-relevant limit-of-detection is achieved for diagnosing endometriosis.

10:20am **NM-MoM8 Effects of Defects on Band Structure and Excitons in WS₂ Revealed by Nanoscale Photoemission Spectroscopy**, *Adam Schwartzberg, C. Kastl, S. Aloni, A. Weber-Bargioni, C.T. Chen*, Lawrence Berkeley National Laboratory

Two-dimensional materials with engineered composition and structure will provide designer materials beyond conventional semiconductors. However, the potentials of defect engineering remain largely untapped, because it hinges on a precise understanding of electronic structure and excitonic properties, which are yet not predictable by theory alone. Here, we introduce correlative, nanoscale photoemission spectroscopy to visualize how the local introduction of defects modifies electronic and excitonic properties of two-dimensional materials at the nanoscale. As a model system, we study chemical vapor deposition grown monolayer WS₂, a prototypical, direct gap, two-dimensional semiconductor. By cross-correlating nanoscale angle resolved photoemission spectroscopy, core level spectroscopy and photoluminescence, we unravel how local variations in defect density influence electronic structure, lateral band alignment and excitonic phenomena in synthetic WS₂ monolayers. Our results not only provide a unified picture of nanoscale heterogeneity, but they also open up the possibility to precisely understand and tailor lateral heterointerfaces in such two-dimensional materials.

10:40am **NM-MoM9 4D Nanocharacterization by Spectro-ptychography Tomography of Alumina Aerogels Coated with Zinc Oxide by Atomic Layer Deposition**, *Adam Hitchcock, J. Wu, X. Zhu*, McMaster University, Canada; *D.A. Shapiro*, Lawrence Berkeley National Laboratory; *J.R.I. Lee, M.M. Biener, S.A. Gammon, T.T. Li, T.F. Baumann*, Lawrence Livermore National Laboratory

Highly porous materials with nanoscale functional coatings are of increasing technological interest in the areas of energy conversion and storage, catalysis, and sensing [1,2]. 3D nanocharacterization with explicit chemical speciation capability is important for their optimization. Here the new method of soft X-ray spectro-ptycho-tomography [3] is used to characterize Al₂O₃ aerogel samples coated with ZnO by atomic layer deposition (ALD). 4D imaging (chemical mapping in 3D by spectro-tomography) of an Al₂O₃ aerogel coated with ZnO by atomic layer

deposition (ALD) was performed using both scanning transmission X-ray microscopy (STXM) and ptychography [4]. 2D and 3D spatial resolution was significantly increased by ptychography, relative to STXM. A 2D spatial resolution of 14 nm was achieved with ptychography while the spatial resolution of the 2D STXM maps was only 24 nm. The degree of ZnO coverage of the surface of the Al₂O₃ aerogel framework in 3 different samples was estimated and compared to the ALD targets. Quantitative analysis showed that the ZnO ALD coatings are non uniform. Comparisons are made to Electron microscopy imaging and X-ray fluorescence analysis results were performed, confirming the results. Other analyses of the 4D results, including 3D thickness distributions of each species and measurements of the degree of contact between Al₂O₃ and ZnO, were extracted from the reconstructed 3D data. Together the results provide useful feedback for optimization of the nanostructure of ALD coated alumina aerogels.

STXM performed using BL10ID1 at CLS and BL 5.3.2.2 at ALS. Ptychography performed using BL 11.0.2 and 5.3.2.1 at the ALS. Research supported by NSERC and the Department of Energy, Basic Energy Sciences under contracts DE-AC02-05CH11231 and DE-AC52-07NA27344. CLS is supported by the Canada Foundation for Innovation.

References

- [1] J. Biener *et al.*, *Energy Environ. Sci.* **4** (2011) 656.
- [2] M.M Biener *et al.*, *ACS Appl. Mater. Interfaces* **5** (2013) 13129.
- [3] Y. Yu *et al.*, *Nature Communications* **9** (2018) 921.
- [4] A.P. Hitchcock, *J. Electron Spectrosc. Rel. Phenom.* **200** (2015) 49.

Nanomaterials

Room Naupaka Salon 5 - Session NM-MoE

NanoCatalysis

Moderator: Fumitaro Ishikawa, Ehime University

6:20pm NM-MoE3 Nanostructured $\text{MoO}_3/\text{Al}_2\text{O}_3$ Powders and Films for Chemical-Looping Oxidative Dehydrogenation of Ethane, H. Henry Lamb, P. Novotný, S. Yusuf, F. Li, North Carolina State University

Ethylene, a major petrochemical building block, is produced industrially by endothermic steam cracking of ethane and petroleum naphtha at 800–850°C. Catalytic oxidative dehydrogenation (ODH) of ethane offers huge potential for reductions in energy consumption and greenhouse gas emissions; however, ethane ODH using co-fed O_2 also requires costly cryogenic air separation [1]. As an alternative, we are investigating redox catalysts that operate in a cyclic mode (chemical looping, CL) and utilize lattice oxygen (O^{2-}) as the sole oxidant [2–3]. One monolayer (1 ML) equivalent $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts prepared by conventional impregnation and calcination methods contain highly dispersed supported molybdate species and exhibit high ethylene selectivity (>95%) in CL-ODH at 500–550°C. In contrast, at higher MoO_3 loadings the $\text{Al}_2(\text{MoO}_4)_3$ bulk phase predominates, as evidenced by Raman spectroscopy and x-ray diffraction (XRD); these catalysts have somewhat higher activity albeit 10–12% lower ethylene selectivity under equivalent conditions. X-ray photoelectron spectroscopy (XPS) studies indicate that high ethylene selectivity correlates with reduction of Mo^{+VI} to Mo^{+IV} . The presence of Mo in lower oxidation states (+V, +IV) triggers H_2 and CH_4 generation resulting in selectivity loss. Interaction of molybdate species with the Al_2O_3 support appears to decrease reducibility and enhance ethylene selectivity in CL-ODH. Even after extended reduction in ethane at 550°C, the monolayer catalyst retained about 25% Mo^{+VI} . In contrast, for 3 ML equivalent catalysts, surface Mo^{+VI} is rapidly consumed, and its concentration eventually approaches zero. To better elucidate the nature of the catalytically active sites, model catalysts consisting of nanostructured MoO_3 films on c-plane sapphire were deposited at 580°C by molecular beam epitaxy using a conventional Knudsen cell. The sapphire substrate after annealing at 700°C in UHV exhibited a streaky reflection high-energy electron diffraction (RHEED) pattern. Films deposited at short times (<1 min) were polycrystalline with relatively smooth surfaces (1.1 nm RMS roughness by atomic force microscopy). XPS revealed that MoO_3 films deposited *in vacuo* were oxygen-deficient. Surface asperities grew with deposition time and with annealing at 700°C in UHV. The catalytic properties of the films are currently under investigation using molecular beam methods.

References:

1. C.A. Gärtner, A.C. van Veen, J.A. Lercher, *ChemCatChem* 5 (2013) 3196–3217.
2. S. Yusuf, L. Neal, V. Haribal, M. Baldwin, H.H. Lamb, F. Li, *Appl. Catal. B* 232 (2018) 77–85.
3. P. Novotný, S. Yusuf, F. Li, and H.H. Lamb, *Catal. Today* (2018) in press.

6:40pm NM-MoE4 Fabrication of Visible Light Active Nanostructured $\text{TiO}_2/\text{Cu}_2\text{O}$ Heterojunction Thin Films, Anna Patricia Cristobal, M.G.K. Ramos, A.D. Montallana, University of the Philippines; L.B. Zhang, J.P. Chu, National Taiwan University of Science and Technology, Taiwan, Republic of China; M.R. Vasquez, University of the Philippines

Designing multiphase or multicomponent semiconductor heterojunctions is a promising strategy to enhance the performance of photocatalytic materials. Titanium dioxide (TiO_2) is a material of interest as a photocatalytic material because of its availability, stability, and cost-effectiveness. However, one major drawback of TiO_2 is its wide band gap resulting to photocatalytic activity in the UV region only. Through heterojunction coupling of TiO_2 with a lower band gap semiconductor such as cuprous oxide (Cu_2O) with a direct band gap of 2.17 eV, visible light active photocatalytic activity can be achieved. $\text{TiO}_2/\text{Cu}_2\text{O}$ heterojunction thin films were assembled in a configuration wherein the junction of the coupled semiconductors is exposed to light irradiation for photocatalysis. This design ensures that photocatalytic reaction can occur in both semiconductors since they are exposed to the light source. A layer of TiO_2 thin film was deposited on (100) silicon (Si) substrate via reactive RF magnetron sputtering coupled with post deposition thermal annealing at 500°C. To form the heterojunction, ordered Cu clusters were patterned on top of the TiO_2 layer through a mask. The deposited Cu were transformed

into Cu_2O by thermal oxidation at 200°C in air atmosphere followed by slow cooling at a rate of 0.48°C/min. The $\text{TiO}_2/\text{Cu}_2\text{O}$ heterojunction films were characterized using XRD and FE-SEM with EDS mapping. Photocatalytic performance was evaluated by visible light photodegradation of methylene blue dye as the test analyte. The XRD pattern of the $\text{TiO}_2/\text{Cu}_2\text{O}$ heterojunction film indicated the existence of rutile and anatase phases of TiO_2 as well as the existence of mostly Cu_2O phase. SEM image of the $\text{TiO}_2/\text{Cu}_2\text{O}$ showed a patterned thin film design composed of a TiO_2 thin film layer decorated with grain-like Cu_2O clusters that are approximately 500 μm in diameter. At higher magnification, the TiO_2 thin film exhibited a porous columnar structure while the Cu_2O is characterized by terraced grain-like structures. Using an effective thin film surface area of 1.0 $\text{cm}^2 \times 2.5 \text{ cm}$, around 50% removal rate of methylene blue was observed in 6 h of visible light irradiation. This promising approach of designing immobilized heterojunction thin films offers a potential for wastewater treatment applications using visible light irradiation.

7:00pm NM-MoE5 Enhanced Photocatalytic Activity of Plasma-modified Electrospun PVA/ TiO_2 Nanocomposites, Arantxa Danielle Montallana, A.P. Cristobal, University of the Philippines; B.Z. Lai, J.P. Chu, National Taiwan University of Science and Technology, Taiwan, Republic of China; M.R. Vasquez, University of the Philippines

Poly(vinyl alcohol)/titanium oxide (PVA/ TiO_2) nanocomposites were successfully synthesized using the electrospinning method. 1% (w/v) <25 nm TiO_2 nanoparticles (NP) were dispersed in 12% (w/v) PVA solution and was electrospun using the following parameters: $V = 15 \text{ kV}$, tip-to-collector distance = 15 cm, and flow rate = 0.5 mL/hr. The nanofibers were collected on an aluminum foil mounted to a 3 in diameter grounded electrode rotating at ~850 rpm. Scanning electron microscopy images revealed a smooth and continuous fiber morphology with average fiber diameter of $281.84 \pm 53.47 \text{ nm}$. Energy dispersive x-ray spectroscopy maps showed the dispersion of TiO_2 NPs in the nanofiber mats (NFM). Raman spectral analysis showed TiO_2 peaks at 142.76, 394.64, 515.42, and 639.07 cm^{-1} confirming the integration of the NPs in the NFM. No changes were observed in the PVA peak at 2911.7 cm^{-1} after TiO_2 NP loading, implying that the addition of TiO_2 NPs did not alter the chemical composition of PVA and TiO_2 . The NFMs were irradiated with a 13.56 MHz radio frequency plasma system using oxygen gas for 1 min exposure time. Plasma exposure allowed the controlled etching of the nanofiber to expose the TiO_2 NP on the surface. Using a $3 \times 3 \text{ cm}^2$ NFM, photodegradation of methylene blue (MB) as the test analyte under UV irradiation was conducted. UV-vis spectral analysis was used to monitor the change in concentration of MB. After 9 hr irradiation, pristine samples showed 83% removal of the dye while plasma-treated samples showed 90% removal rate. Using only TiO_2 NP, 95% removal efficiency was achieved after 4 hr UV irradiation. However, use of NPs only for photodegradation is not advisable since it becomes difficult to collect and reuse the NPs. Thus, immobilizing the TiO_2 NPs would allow reusability of the photocatalytic nanocomposites.

7:40pm NM-MoE7 Large Scale Production of Nanoparticle Catalysts for Biomass Conversion Processes, E.J. Roberts, L. Wang, University of Southern California; F. Baddour, D. Ruddy, S. Habas, National Renewable Energy Laboratory, USA; N. Malmstadt, Richard Brutchey, University of Southern California

In order to realize more sustainable routes for the conversion of biomass into useful liquid fuels, the use of lower-cost and more Earth-abundant catalysts is required. This necessitates the development of advanced catalysts that promote the desired transformations (e.g., hydrogenation, deoxygenation), while resisting deactivation, and that can be produced cost-effectively at relevant scales. Advances in the controlled synthesis of colloidal nanoparticle catalysts have resulted in the demonstration of promising catalytic performance for these materials, with Earth-abundant transition metal and transition metal carbide nanoparticles representing two such examples. Research by our team has focused on developing chemistry that enables precise control over nanoparticle catalyst phase and/or morphology. This presentation will focus on recent developments regarding the translation of these chemistries to continuous flow reactors for nanoparticle catalyst scale up. A key metric for scale up is ensuring that the resulting nanoparticles synthesized in flow are functionally equivalent to those produced in small (mL) batch reactors. The catalytic performance of these nanoparticles will be compared between those produced in batch and continuous flow, and further compared to their “bulk” material equivalents, for key transformations of model biomass compounds.

Monday Evening, December 3, 2018

8:00pm **NM-MoE8 Influence of a Tailored Nanoparticle Composite Cathode on Electrochemical Properties of Anode-Supported Solid Oxide Fuel Cells**, *Jong-Eun Hong*, *H.A. Ishfaq*, *T.H. Lim*, Korea Institute of Energy Research (KIER), South Korea; *S.-B. Lee*, Korea Institute of Energy Research (KIER), South Korea; *K.T. Lee*, DGIST, South Korea; *R.H. Song*, Korea Institute of Energy Research (KIER), South Korea

Application of nanocatalysts to a solid oxide fuel cells cathode is expected to increase triple phase boundary (TPB) density and electrocatalytic reactivity to oxygen reduction reaction, resulting in performance improvement. Thus a conventional Sr- and Fe-doped LaCoO_3 (LSCF) based composite cathode was tailored with nanoparticles of a multi doped ceria that has an enhanced ionic conductivity and evaluated for electrochemical properties. In this study, Sm- and Nd-doped ceria (SNDC) nanoparticles were successfully prepared on the composite cathode via an in situ sol-gel process, which was confirmed by field emission scanning electron microscopy analysis. The tailored nanoparticle cathode indicated an increase in power density for a reduction of polarization resistance in anode supported SOFCs. It was attributed that more conductive nanoparticles led to enlarge the specific surface area and promote the reactivity for the cathode reaction.

Nanomaterials

Room Naupaka Salon 5 - Session NM-TuM

Nanofabrication and Nanodevices

Moderator: Adam Hitchcock, McMaster University

8:00am NM-TuM1 High-throughput, Continuous Flow Synthesis of Colloidal Nanoparticles as a Safe and Sustainable Nanofabrication Method, Emily Roberts, R.L. Brutchey, University of Southern California

In the past two decades, flow chemistry methodologies have been recognized as a step towards more green and sustainable chemical and material production. As an industrial demand for colloidal nanoparticles increases, there will be an increasing need to scale up and process intensify typical small-scale bench-top reactions. In respect to nanofabrication, continuous flow reactors have efficient heat and mass transport, excellent control of local mixing conditions, improved safety, decreased solvent waste, and are automatable. These advantages address green chemistry values by decreasing or preventing waste, improving the atom economy by increasing production yields, offering less hazardous synthetic methods, increasing throughput, and enhanced energy efficiency.

We will present our recent results on the development of high-throughput, continuous flow reactors for the synthesis of various colloidal nanoparticles. Reactor designs for a wide range of temperatures (150-320 °C), using various heating methods (conventional oven, microwave heating, and sand bath), reusable solvents, and one- and two-phase flow will be discussed. The differences between resulting products in terms of yield, morphology, and functionality will also be evaluated. Lastly, the continuous flow methods will be compared to analogous batch reactions to assess the viability of continuous flow nanofabrication methods.

8:20am NM-TuM2 Nanoporous Oxide Memristive System & Artificial Synapses for Next Generation Electronic Device Application, Gunuk Wang, Korea University, Republic of Korea

The two-terminal oxide-based memristive switch is garnering enormous interest for the development of next-generation nonvolatile memory beyond current Si-based memory technology and is concurrently considered as an artificial synapse candidate for the neuromorphic computing hardware. In this talk, I will introduce a breakthrough and attractive approach, that is utilized a nanoporous oxide structure as a switching medium, for fabricating simple and cost-efficient high-density memory arrays with acceptable switching performances, low power consumption, and low electroforming voltage (or forming-free). I will talk a topic about the single nanopore (SNP)-based SiO_x memories that enable unipolar switching through its internal vertical nanogap, which outperforms the switching ability of any other unipolar memory [1-3]. As a second part, I will briefly introduce our recent approaches and achievements for the neuromorphic device technology using two-terminal self-rectifying memristor synapse employing a Pt/Ta₂O_{5-y}/nanoporous (NP) Ta₂O_{5-x}/Ta layers [4,5].

References :

- [1] S. Kwon et al., *Nano Lett.* 2017, 17, 7462.
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- [4] W. Huh et al., *Adv. Mater.* In press 2018.
- [5] S. Jang et al., under review 2018.

8:40am NM-TuM3 Synaptic Plasticity and Learning Behaviors Mimicked in Electromigrated Au Nanogaps, Keita Sakai, K. Minami, S. Tani, T. Sato, M. Ito, Tokyo University of Agriculture & Technology, Japan; M. Yagi, National Institute of Technology, Ichinoseki College, Japan; J. Shirakashi, Tokyo University of Agriculture & Technology, Japan

For many years, neuromorphic devices that can mimic functions of biological brains have been studied in the field of neuromorphic engineering. The synaptic functionality of neuromorphic hardware originates in a gradually modified resistance. Previously, we have investigated simple methods for controlling the tunnel resistance of the nanogaps called activation. In this technique, electromigration is induced between nanogap electrodes by a field emission current, resulting in the reduction of the gap width. The tunnel resistance of the nanogaps also decreases after activation. In this study, we apply the activation procedure for Au nanogaps and demonstrate the experimental implementation of

synaptic functions in Au nanogaps. First, Au nanogaps were fabricated by electron-beam lithography and lift-off process. Then, a fixed width and height voltage pulse was loaded to Au nanogaps periodically. After the applied pulse was removed, current decayed rapidly at the beginning of the time followed by a gradual fading to a stable level. By increasing the number of stimulations, the relaxation time increased, implying a slow fade in forgetting process time. Meanwhile, it was observed that current level was clearly elevated, showing a potentiation of synaptic weight. These phenomena confirm the STP-to-LTP transition in our device. These results indicate that inorganic synapses are successfully achieved using Au nanogaps controlled by the activation.

9:00am NM-TuM4 Preparation and Corrosion Properties of Bulk Nanocrystalline Two-phase Ag-25Cu Alloys, Zhongqiu Cao, X.T. Yin, Q.Y. Tian, Y. Wang, K. Zhang, J. Lu, Shenyang Normal University, China

In this paper, two bulk nanocrystalline LPRAg-25Cu and MAAG-25Cu (at.%) alloys were prepared by liquid phase reduction and mechanical alloying methods, respectively, and afterwards hot pressing process. Fig. 1 depicts the X-ray diffraction (XRD) pattern (a) and the transmission electron microscopy (TEM) photograph (b) of LPRAg-25Cu alloyed powders. These alloyed powders have no impurities with about 10 nm average grain sizes. The densities of two bulk nanocrystalline Ag-25Cu alloys exceed 99%. The average grain size measured by XRD is about 13 nm after liquid phase reduction and about 27 nm after hot pressing, about 8 nm after mechanical alloying and about 19 nm after hot pressing.

Fig. 2 depicts the microstructures of two nanocrystalline alloys and a coarse grained counterpart (PMAG-25Cu). They all are composed of two phases. One is α phase rich in Ag, the other is β phase rich in Cu. The microstructure of coarse grained PMAG-25Cu alloy is extremely inhomogeneous. The microstructure of nanocrystalline LPR or MAAG-25Cu alloys is more homogeneous than that of coarse grained PMAG-25Cu alloy, while the microstructure of nanocrystalline LPRAg-25Cu alloy is most homogeneous.

Fig. 3 depicts Open Circuit potential (a), polarization (b), EIS (c), and Mott-Schottky (d) curves of three Ag-25Cu alloys. Corrosion rates of three Ag-25Cu alloys increase in the range of PMAG-25Cu, MAAG-25Cu and LPRAg-25Cu alloys. The corrosion rate of nanocrystalline alloy is faster than that of corresponding coarse grained alloy. The faster corrosion rates are attributed to the different microstructures of three Ag-25Cu alloys prepared by the different processes including the grain size as well as phase distribution and compositions. EIS plot of coarse grained PMAG-25Cu alloy is composed of a single capacitive loop. The corrosion process is controlled by electrochemical reactions. EIS plots of nanocrystalline MAAG-25Cu and LPRAg-25Cu alloy are composed of a single capacitive loop with diffusion tail. The corrosion processes of two nanocrystalline Ag-25Cu alloys are controlled by diffusion. The passive films formed on three Ag-25Cu alloy surface exhibit n-type semiconducting properties. The passive current density of LPRAg-25Cu alloy is lower than that of PMAG-25Cu alloy, but higher than that of MAAG-25Cu alloy. Thus, the chemical stability of passive films on MAAG-25Cu alloy surface is highest.

Acknowledgements

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9:20am NM-TuM5 Nanomaterials-enabled Advances in Microfabricated Sensors for Environmental and Health Monitoring, Roya Maboudian, University of California at Berkeley

INVITED

Accurate detection of toxic and flammable gases is critical to public health and the environment, and to the safe operation of many industrial processes. This presentation will discuss our efforts in low-power gas sensing for health, environmental and process monitoring. The core technology is a suspended polycrystalline silicon microheater functionalized with a number of nanotechnology-based sensing materials, targeting various analytes. Our microheater platform will be described and the latest results in sensitive, selective, and stable detection of several target gas molecules (including H₂, propane, CO and NO₂) will be presented. The talk will end with plans for future directions.

10:20am NM-TuM8 Nature-Inspired Approaches to Nanotechnologies, Jong-Souk Yeo, Yonsei University, Republic of Korea

Biomimetics, Biomimicry, Nature-Inspired, or Biologically Inspired technologies are all referring to the emerging fields where innovations are strongly influenced by the wisdom from nature or biological systems.

Biomimetics is the scientific approach of learning new principles and processes based on systematic study of living organisms, plants, or animals in order to develop novel engineering systems through the convergence of biology, materials science, cognitive science, robotics, and nanotechnology. Especially, the multi-functionality offered by nature can enable various applications with the help of nanotechnology. Multiple levels of approaches are feasible from nature-inspired – adaptation of how nature works, adoption of what nature provides, or replication of natural processes and functionalities for eco-friendly, sustainable, and highly efficient technologies. In this talk, nature-inspired approaches to nanotechnology will be introduced for next generation technologies in omniphobic surfaces, color reflective displays, neuromorphic semiconductors, stretchable electronics, biomaterials and biosensors enabled by biomimetic surface, optical, electronic, or bio functionalities.

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10:40am NM-TuM9 A Reproducible Assay for Versatile Biosensing by Surface-enhanced Raman Scattering. *M. Al Mamun, N.A. Cole, S. Juodkazis, Paul Stoddart*, Swinburne University of Technology, Australia

Over the forty years since its discovery, surface-enhanced Raman scattering (SERS) has attracted significant attention as a sensitive technique for surface analysis. The high sensitivity of SERS and compatibility with microfluidic techniques makes it an attractive option for point-of-care sensing applications. However, we are not aware of any routine analytical applications of SERS that have emerged to date. In particular, SERS substrates are subject to variability due to high sensitivity to nanometre scale structure, complex surface interactions in real-world samples, susceptibility to environmental contamination, and a limited substrate shelf life. Here we report a versatile biosensing technique, where the target analyte is labelled with biotin, and is in turn reliably captured by a streptavidin-coated substrate. Subsequent exposure to an excess of biotin saturates the remaining binding sites and provides an internal intensity reference to assist quantification. Once the analyte has been immobilized via the biotin-streptavidin interaction, a photochemical reduction process is used to deposit silver nanoparticles over the surface. This generates a SERS substrate on demand, with high sensitivity and high reproducibility, while protecting the surface from environmental contamination. Using atto-488 as a model analyte, it has been shown that the process can deliver nanomolar sensitivity. The fluorescent emission of the atto-488 was used to confirm the surface immobilization, but is quenched by the presence of the metal coating in the SERS measurements. With appropriate extensions to an integrated microfluidic platform, the developed technique has the potential to be used to detect a wide range of small molecule targets of interest in body fluids.

11:20am NM-TuM11 Molecular Dynamics Investigation for Chemical Effects of Nanobubble Collapse on Precision Polishing. *Yoshimasa Aoyama, N. Miyazaki, Y. Ootani, N. Ozawa, M. Kubo*, Tohoku University, Japan

For manufacturing high-performance semiconductor devices, the fabrication of a highly-planar surface is important. As the planarization method, chemical mechanical polishing (CMP) is used for efficient processing. The efficient process leads cost-savings. Therefore, the design of more efficient and more precise CMP process is required. Then, Aida et al. have recently reported that the nanobubble contributes to CMP process[1]. In this polishing process, the water hammer shock is regarded as the elemental process, which brings the jet stream when the nanobubble collapses[2]. From their study, effects of the jet would depend on the solvents around the nanobubble and the inner gaseous species of the nanobubble. However, the details of chemical relationship among CMP process, solvents, and gaseous species are unclear. Therefore, understanding the atomistic CMP mechanism with nanobubble and the chemical effects of solvents and gaseous species in nanobubble collapse phenomenon are required to establish more efficient CMP process. In this study, we performed nanobubble collapse simulation by molecular dynamics method using reactive force field, which is possible to simulate the formation and dissociation of chemical bonds.

First, we prepared the simulation model with vacuum nanobubble in the water solvent and the simulation model without nanobubble. A vacuum nanobubble is modeled by removing the water molecules as the spherical shape. Then, we performed nanobubble collapse simulation and applied a shock for the substrate surface by using “momentum mirror”[3]. From these simulations, we found that the jet was generated in the model with a nanobubble, and this jet brought larger plastic deformation on the substrate, indicating that the nanobubble increased the efficiency of CMP process. Second, in order to investigate the effects of gaseous species in the nanobubble, we prepared nanobubble models with various gaseous species. By determining the density of gas molecules in the nanobubble to satisfy the Young-Laplace law, we succeeded in creating oxygen and nitrogen nanobubble stably. By this procedure, we got to be able to fabricate various gaseous nanobubbles stably and simulate nanobubble collapse process under various solvents and gaseous species. In the conference, we are going to report the atomistic CMP mechanism and chemical effects of solvents and gaseous species in nanobubble collapse simulation.

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11:40am NM-TuM12 Determination of Anisotropic Diffusion Ratio on Si(110)-16×2. *Masahiro Yano, T. Terasawa, S. Yasuda, S. Machida, H. Asaoka*, Japan Atomic Energy Agency, Japan

Establishing bottom-up nanofabrication-techniques are required to develop electronic devices and create novel functional devices because further miniaturization using top-down techniques is becoming hard due to fundamental physical and technological limitation. The anisotropic material-diffusion, which dominates the formation of the nanostructures, should be clarified to control the nanofabrication using template surface more precisely. Si(110)-16×2 reconstructed structure has been used as a template for fabricating several types of nanowires and nanodots due to the one-dimensional structure in which the one-atomic-layer steps are arranged at a period of 2.5 nm. However, the influence of the anisotropic material-diffusion on the Si(110)-16×2 surface has not been clarified because of difficulty determining the anisotropic material diffusion ratio on the reconstructed structure.

In this study, we focused on a nano-hole, called as “void”, formed during the thermal decomposition of oxide layer on Si, where the pure Si was exposed due to the desorption of the oxide layer to determine the anisotropic Si diffusion rate ratio on the Si(110)-16×2. The void is grown by the Si atoms which was created and diffused on the void bottom decomposed the oxide layer following the reaction, $\text{Si} + \text{SiO}_2 \rightarrow 2\text{SiO}\uparrow$. The voids were observed by scanning tunneling microscope (STM) at room temperature because the oxide layer is decomposed by STM at high temperatures.

The void sidewall exposed the (17, 15, 1) plane, meaning that the void is surrounded by crystallographically equivalent planes. This indicated that the anisotropic void growth rate ratio depends on only the density ratio of diffusing Si supplied to oxides between the void edges because the reaction and desorption rate of oxide were uniform around the void. The length of the voids along to the step rows of the 16×2 reconstructed structure was longer than that of perpendicular to the step rows. We found that the anisotropy of the void shape decreased as the void became deeper, indicating the reduction of the Si density ratio during the diffusion on the sidewall. Taking the migration of diffusing Si atoms between the adjacent sidewalls and the creation of diffusing Si atoms on sidewalls into account, we determined that the diffusion parallel the step rows of the reconstructed structure at the void bottom was 7 times faster than that perpendicular to the step rows. This diffusing ratio will help to realize the precise control of the nanodots and nanowires formation on the Si(110)-16×2 reconstructed structure.

Tuesday Afternoon Poster Sessions, December 4, 2018

Nanomaterials

Room Naupaka Salon 1-3 - Session NM-TuP

Nanomaterials Poster Session I

Moderator: Shintaro Fujii, Tokyo Institute of Technology

NM-TuP1 alginate based Nanocomposite for Microencapsulation of Probiotic: Effect of Cellulose Nanocrystal (CNC) and Lecithin, *Monique Lacroix*, INRS-Institut Armand-Frappier, Canada

Lactobacillus rhamnosus ATCC 9595 were encapsulated in alginate-CNC-lecithin microbeads for the production of nutraceutical microcapsules. The concentration of CNC and lecithin in alginate microbeads was optimized by monitoring the viability of *L. rhamnosus* after stabilization of the microbeads by freeze-drying. Results showed that alginate microbeads (AC-0) reduced by 0.95 log CFU/g whereas addition of 13 wt% CNC in alginate microbeads (AC-3) reduced ($P > 0.05$) by 0.01 log CFU/g of bacterial viability after freeze drying. Incorporation of 2 wt% lecithin in alginate-CNC microbeads (ACL-1) also revealed a protective effect during free drying same as alginate-CNC microbeads (AC-3). The compression strength of the freeze-dried ACL-1 microbeads improved 40% compared to alginate microbead alone. Swelling studies revealed that addition of CNC and lecithin in alginate microbead decreased (around 47%) the gastric fluid absorption but increased the dissolution time by 20 min compared to alginate microbeads (A-0). During complete transition through the gastric passage, the viability of *L. rhamnosus* in dried ACL-1 microbeads was 52% higher as compared to *L. rhamnosus* encapsulated in A-0 based beads. The viability of *L. rhamnosus* was also evaluated during storage at 25 and 4°C. It was found that at 25 and 4°C storage conditions, the viability of *L. rhamnosus* encapsulated in ACL-1 microbeads decreased by 1.23 and 1.08 log respectively, whereas the encapsulation with A-0 microbeads exhibited a 3.17 and 1.93 log reduction respectively.

NM-TuP2 In-situ Low Energy Electron Microscopy at Near Ambient Pressures, *Thomas Schulmeyer*, SPECS-TII, Inc.

Low-energy electron microscopy (LEEM) is a spectromicroscopy technique, which allows the study of dynamic processes at surfaces and interfaces, such as thin-film growth, surface reactions, and phase transitions. With the FE-LEEM P90 from SPECS, which is based on the instrument design by Rudolf Tromp from IBM, lateral and energy resolution of below 5 nm and 250 meV, respectively, can be achieved. Depending on the excitation source and the settings on the instrument a variety of different imaging modes are possible: mirror electron microscopy, low energy electron diffraction (LEED), phase contrast imaging, reflectivity contrast, dark field imaging and bright field imaging, as well as photoelectron emission microscopy and spectroscopy. As a new development the technical capabilities of LEEM and PEEM have been extended towards near ambient conditions by developing a special objective lens concept and sample chamber geometry. This enables the analysis of materials and devices under near ambient conditions and even in situ during operation. For this a Laser heater allows for sample temperatures up to 800°C during the measurements. The technical realization will be presented in detail. Furthermore experimental results will be shown on Graphene, Silicon under Nitrogen atmosphere. First results from real surface reactions will be discussed.

NM-TuP8 Surface Nanostructures Composed of Thiolated Cyclodextrin/Au and Fe Species: Gas- and Liquid-Phase Preparation, *S. Kotorova*, Institute of Nuclear and Physical Engineering, FEI STU, Slovakia; *Monika Jerigova*, Comenius University, Bratislava, Slovakia; *D. Lorenc*, International laser center, Bratislava, Slovakia; *M. Prochazka*, Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia; *D. Velic*, Comenius University, Bratislava, Slovakia

Supramolecular surface nanostructures have application potential as functional devices. Studied system consists of a host molecule of monothiolated β -cyclodextrin chemically adsorbed on an Au surface through a S-Au bond (assigned as Au-S-CD) and of Fe species incorporated as the guest. Secondary-ion mass spectrometry (SIMS) is used to study the formation and composition of these surface supramolecular nanostructures.

The Fe species were prepared by pulsed laser ablation in water and thermal effusion in vacuum. Using laser ablation in water, the solution of Fe species was dropped on Au-S-CD. The relevant mass peaks were observed at 1227 m/z, 1243 m/z and 1260 m/z and were assigned to $C_{42}H_{68}O_{34}SNa-Fe^+$, $C_{42}H_{68}O_{34}SKFe^+$, $C_{42}H_{68}O_{34}SNa-FeO^+$ and $C_{42}H_{68}O_{34}SK-FeO^+$,

which can be interpreted as supramolecular complexes with Fe as $C_{42}H_{68}O_{34}SNa-Fe$ and $C_{42}H_{68}O_{34}SK-Fe$ or adducts with FeO as $C_{42}H_{68}O_{34}SNa-FeO$ and $C_{42}H_{68}O_{34}SK-FeO$, respectively. The comparison of isotope distributions with the experimental data supported the presence of a supramolecular host-guest complex between Au-S-CD and the Fe species and an adduct between Au-S-CD and FeO. The Fe species were presumably the first product of the ablation, so the formation of a supramolecular CD-Fe complex was preferential. Presumably, the second product of the ablation were the FeO species. Thermal effusion, even with a cooled surface, was negative with respect to the complex observation, no mass peaks corresponding to supramolecular complexes were observed. Nevertheless, a glucopyranose unit of the CD-S molecule and a variety of molecular fragments corresponding to CD-S associated with Fe and FeO were observed. One can assume that supramolecular complex formation is in this case also dependent on the surface diffusion of the Fe species. Since the surface diffusion of the Fe species at this low temperature might be minimized, the probability of complex formation might be close to zero.

This work was supported by VEGA 1/0400/16.

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NM-TuP9 Controlled Pore Arrangement of Silicon Nanoparticles Having Mesoporous Structure, *Taisuke Kuga*, *K. Sato*, Tokyo Denki University, Japan

In recent years, semiconductor nanoparticles (NPs) having mesopores have been applied in a wide range of environment, energy and medicine fields, such as sensors, rechargeable batteries and drug delivery systems. The NPs can produce inexpensively by using electrochemical etching. However, they are confronting some serious problems, such as complicated preparation techniques and low production yield of mesopores. Therefore, it is necessary to develop new synthesis approaches for realization of facile preparation of the NPs with mesopore structures and large-scale production of the mesopores. We have prepared silicon nanoparticles (SiNPs) with mesopore structures using an inexpensive chemical route with good productivity. In this presentation, we propose a new way to fabricate SiNPs with mesopore structures by simplified procedures based on a chemical approach, and investigate the size distribution, depth and density of the mesopores by scanning electron microscopy (SEM). The features of our synthesis technologies are to adopt the simplified synthesis system in which only commercially available SiNPs with mean diameter of approximately 100 nm and redox agent were used. The size, depth and density of the mesopores on the SiNP surfaces strongly depends on the redox reaction time. When the redox reaction time was 1 min, the shallow mesopores with mean size of approximately 24 nm were formed on the SiNP surfaces. As the redox reaction time increased from 1 min to 5 min, the depth of the mesopores deepened without change of mean size. SEM images of SiNPs with mesopores obtained by redox reaction time for 10 min were shown in Figure 1. The mesopores with mean size of approximately 29 nm were densely formed on the SiNP surfaces, and also their depths became increasingly deeper. Therefore, our suggested synthesis technologies can provide a new chemical route for high production yield of mesopores.

NM-TuP10 Nanobiosensor Comprising Conductive Polymer Enclosed with Polymer Vesicles for Selective Detection of Influenza A Virus, *Geunseon Park*, Yonsei University, Republic of Korea; *H.O. Kim*, Korea University, Republic of Korea; *J.-W. Lim*, *C. Park*, *S. Haam*, Yonsei University, Republic of Korea

Nanobiosensor has been selected as a method for detecting wide range of pathogens to prevent pandemic emergence. As one of promising platform, conductive polymer based nanobiosensor has a distinct advantage in the way that its ability to sensitive and rapid detection. In this study, we designed a detection system which is conductive poly aniline based on polymersome conjugated with peptide for specific recognition of influenza A virus. We synthesized poly aniline polymerized within a polymersome consisting of methoxy polyethylene glycol-block- polyphenylalanin copolymer (mPEG-b-pPhe). Then we conjugated the polymersome with peptide binding to hemagglutinin located on the surface of influenza virus. In the presence of Influenza virus, the nanoparticle aggregated with the virus, exposing absorption wave length change. These results indicate that this nanobiosensor could be a potential candidate in terms of detecting influenza virus.

Tuesday Afternoon Poster Sessions, December 4, 2018

NM-TuP11 Efficient Antiviral Delivery Polymersomes by Optimization of Surface Density of Cell-targeting Groups for Virus Treatment, Chaewon Park, H. Chun, Yonsei University, Republic of Korea; M. Yeom, H.-O. Kim, Korea University, Republic of Korea; J.-W. Lim, Yonsei University, Republic of Korea; W. Na, Korea University, Republic of Korea; G. Park, Yonsei University, Republic of Korea; A. Kang, Korea University, Republic of Korea; D. Yun, Yonsei University, Republic of Korea; J. Kim, Yonsei University, Republic of Korea; D. Song, Korea University, Republic of Korea; S. Haam, Yonsei University, Republic of Korea

Influenza A virus (IAV), which causes one of the most contagious diseases is a global health concern, and is responsible for seasonal epidemics and pandemics. Despite laudable advances in antiviral agents and drugs, the vast majority of them have shown limited efficacy due to non-specificity and low viability in physiological or endosomal environment, especially in the case of intracellular drug. A nano platform, consisting of phenylboronic acid (PBA) pendant group polymer which has sialic acid-targeting property, gained greater access to the intracellular space transporting antivirals within the host cell. Amphiphilic copolymers made of pPhe-b-mPEG-PBA formed polymersomes which encapsulated hydrophilic antiviral agents in the core and hydrophobic drugs in the exterior layer. Combination of antiviral drug delivery using amphiphilic nanocarrier and cell-targeting functional group gives a better chance to improve transfection and intracellular distribution efficiency of therapeutic substances.

NM-TuP12 Photovoltaic Performance of Inorganic/Organic Hybrid Solar Cells using Boron-doped Silicon Nanoparticles, Kuniaki Furuya, K. Sato, Tokyo Denki University, Japan

Solar cells using silicon nanoparticles (SiNPs) have attracted attention as one of highly-efficient cells because they not only widen the absorption bands of solar light but also enable the light harvesting via excitonic energy transfer [1]. In order to enhance the transfer efficiency of photogenerated charge carriers between the SiNPs region, we have fabricated boron (B)-doped p-type SiNPs of single nanometer in size by combining thermal diffusion at high temperature with redox reaction of the surface regions of the Si powders (100 nm in size) in etchant containing hydrofluoric acid/nitric acid. Additionally, we have also prepared the inorganic/organic hybrid solar cells consisting of the B-doped p-type SiNPs and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) so as to reduce the production cost. In such hybrid solar cells, the arrangement of the B-doped p-type SiNPs and PEDOT:PSS in the active layer is critical to improve the power conversion efficiency (PCE). In this presentation, we focus on the position of the B-doped p-type SiNPs, such as the stacking structures consisting of n-type Si substrate/blend layer of B-doped p-type SiNPs and PEDOT:PSS and the stacking structures consisting of n-type Si substrate/B-doped p-type SiNPs/PEDOT:PSS, and discuss the photovoltaic performance of these inorganic/organic hybrid solar cells. The *J-V* characteristics of the hybrid solar cells consisting of n-type Si substrate/blend layer of B-doped p-type SiNPs/PEDOT:PSS (cell 1) and n-type Si substrate/B-doped p-type SiNPs/PEDOT:PSS (cell 2) were shown in Figure 1. The photovoltaic performance of these hybrid solar cells strongly depends on the arrangement of the stacking structures. The cell 1 constructed from the blend layer of B-doped p-type SiNPs/PEDOT:PSS obtained PCE of 3.85% with open circuit voltage (V_{oc}) of 0.36 V, short circuit current density (J_{sc}) of 26.5 mA/cm² and fill factor (FF) of 0.40. The value of the PCE increased to 5.27% for the cell 2 stacked individually the B-doped p-type SiNPs and the PEDOT:PSS, showing the V_{oc} of 0.34 V, J_{sc} of 29.6 mA/cm² and FF of 0.52. This result demonstrates that the control of arrangement of B-doped p-type SiNPs is beneficial for obtaining the higher PCE because of the efficient transport of the charge carriers between the NPs region.

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Nanomaterials

Room Naupaka Salon 5 - Session NM-TuE

Magnetic Properties and Nanocomposites

Moderator: H. Henry Lamb, North Carolina State University

5:40pm **NM-TuE1 Voltage-Assisted Magnetic Switching in MgO/CoFeB-Based Magnetic Tunnel Junctions by Way of Interface Reconstruction**, J. Ko, **Jongill Hong**, Yonsei University, Republic of Korea **INVITED**

Engineering of interfacial structures has become important to find new scientific observations and to create novel applications more than ever before. In this presentation, we show that the interface reconstructed by sub-monolayer-thick Mg insertion improved the magneto-electrical properties of perpendicular magnetic tunnel junctions essential for modern spintronic applications. The 0.2–0.4 nm-thick Mg inserted between MgO tunnel barrier and CoFeB ferromagnet restructured the interface in such ways as to protect the CoFeB from over-oxidation, to strengthen the texture, to make the interfacial roughness smooth, and to relax the mechanical stress. Observed were great increases in the perpendicular magnetic moment and perpendicular magnetic anisotropy of the CoFeB by 2.1 and 1.8 times, respectively, which can be ascribed to the optimum interfacial condition because of the least possible chemical damage. Furthermore, strong enhancement of (010) in-plane and (001) out-of-plane texture and of interfacial roughness led to a significant increase in the tunnel magnetoresistance by 4.4 times from 13.2 to 57.6% by the insertion. Most importantly, the electric field-controlled magnetic anisotropy coefficients became *symmetrically bipolar* to the electric field, which is essential for device applications, and they were increased over 100 fJ/V·m, which is 6 times larger than one found before the Mg insertion owing to optimum chemical and physical structures at the interface. As a result, we could successfully demonstrate the voltage-induced magnetization switching for the perpendicular magnetic tunnel junctions with the help of an external magnetic field. We strongly believe that our findings will ignite further study on the new way of electrical control over magnetic switching and provide an essential ingredient to realize electric field-driven energy-effective magneto-electronic devices.

6:20pm **NM-TuE3 A Theoretical Outlook on the Exotic Properties of Spin Ice and Other Magnetic Pyrochlore Thin Films**, **Michel Gingras**, University of Waterloo, Canada

Frustrated magnetic materials and strongly correlated electron systems are a forefront of research in modern condensed matter physics and materials science. Despite almost three decades of investigations, the theoretical understanding of these fascinating systems remains incomplete. The most prominent theoretical frameworks used to tackle these systems take the form of an *emergent gauge theory* akin to the gauge theory that describes conventional electromagnetism.

Spin ice is an unusual substance in which the magnetic moments of individual atoms behave very similarly to the protons in conventional water ice — hence the name spin ice — failing to align even at very low temperatures and displaying the same residual entropy that Linus Pauling calculated for water ice and which is measured experimentally. Spin ices, which belong to the broad class of compounds called magnetic pyrochlores, actually have something in common with electromagnetic fields; both can be described by a gauge theory. Many aspects of conventional electromagnetism are sensitive to constraints from enclosure boundaries, such as total internal reflection used in communication with optical fibers. It is then reasonable to wonder if spin ices have similar sensitivities to boundary effects and confinement. Motivated by the recent experimental realizations of spin ice and other magnetic pyrochlore thin films, I will explore in this talk some of the exotic physical phenomena that arise when considering spin ice thin films such as, for example, a novel magnetic charge crystallization on the film surface while the bulk remains thermally disordered [1]. From a broader context, magnetic pyrochlore thin films offer a natural platform to study the confinement of emergent gauge fields describing strongly correlated systems and the evolution of nontrivial magnetic correlations as one moves from three to two dimensional spin textures [2].

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6:40pm **NM-TuE4 Extending Compound Semiconductor Nanowire Functions by the Introduction of Additional Elements**, **Fumitaro Ishikawa**, Ehime University, Japan **INVITED**

Semiconductor nanowires are promising as building blocks in nanoelectronics and nanophotonics. The introduction of III–V compound semiconductor heterostructures into NWs provides dynamic control for the electronic band structure of these systems. On the other hand, oxides displaying advantageous dielectric, thermal, and resistive properties, which cannot be achieved in semiconductors, make their combination with semiconductors appealing. GaAs and related heterostructure have realized various optical and electronic devices with high speed and efficiency, e. g., transistors, lasers, and solar cells. To extend the functions of the materials system, diluted nitride and bismide has been paid attention over the past decade. They can largely decrease the band gap of the alloys, providing the greater tunability of band gap and strain status, eventually suppressing the non-radiative Surface and/or Auger recombinations. Selective wet oxidation for Al-rich AlGaAs is a vital technique for vertical surface emitting lasers. That enables the introduction of precisely controlled oxides in the system, enabling the optical and electrical confinement, heat transfer, and mechanical robustness.

We introduce the above materials into GaAs nanowires.[1] GaAs/GaAsN core-shell nanowires showed clear redshift of the emitting wavelength toward infrared regime. Further, the N introduction passivates non-radiative surface recombination, demonstrating laser emission from the single nanowire.[2,3] GaAs/GaAsBi core-shell structure was also obtained, showing a characteristic modification of the nanowire morphology.[4] Selective and whole oxidations of GaAs/AlGaAs core-shell nanowires produce semiconductor/oxide composite GaAs/AlGaOx. Possibly sourced from molecular species, the oxide shell shows white luminescence. [5,6]

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7:40pm **NM-TuE7 Single-molecule Study on Nanocarbon Materials**, **Shintaro Fujii**, Tokyo Institute of Technology, Japan **INVITED**

Understanding charge transport through nanocarbon materials across the metal–molecule interface is a fundamental issue in organic devices. In recent years, single-molecule scale studies on charge transport through the metal–molecule interface have been made possible by break junction techniques. Here, we present our recent single-molecule transport studies on nanocarbon materials using scanning tunneling microscopy (STM) and break junction techniques in combination with current-voltage measurements and first principle simulations [1–4].

Bowl-shaped π -conjugated nanocarbons, or buckybowl, are a novel class of sp^2 -hybridized nanocarbon materials. In contrast to tubular carbon nanotubes and ball-shaped fullerenes, the buckybowl feature structural flexibility. Bowl-to-bowl structural inversion is one of the unique properties of the buckybowl in solutions. Bowl inversion on a surface modifies the metal–molecule interactions through bistable switching between bowl-up and bowl-down states on the electrode surface, which makes surface-adsorbed buckybowl a relevant model system for elucidation of the mechano-electronic properties of nanocarbon materials. We demonstrate that the bowl inversion can be induced by approaching the STM tip toward the molecule. By tuning the local metal–molecule interaction using the STM tip, the sumanene buckybowl exhibits structural bistability with a switching rate that is two orders of magnitude faster than that of the stochastic inversion process.

Aromaticity of nanocarbons is a fundamental concept in chemistry. Antiaromatic nanocarbons are predicted to exhibit remarkable transport properties and high redox activities. However, it has only been possible to measure compounds with reduced aromaticity but not antiaromatic nanocarbons due to their energetic instability. We addressed these issues by investigating the single-molecule charge transport properties of a genuinely antiaromatic nanocarbon, showing that antiaromaticity results in an order of magnitude increase in conductance compared with the aromatic counterpart. Single-molecule I - V measurements and first principle transport calculations reveal that this results from a reduced energy gap

and a frontier molecular resonance closer to the electrode potential in the antiaromatic species. The conductance of the antiaromatic complex is further modulated electrochemically, demonstrating its potential as a high-conductance transistor.

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8:20pm NM-TuE9 Interfacial Defect Vibrations Enhance Thermal Transport in Amorphous Multilayers with Ultrahigh Thermal Boundary Conductance, Ashutosh Giri, J. Braun, J. Gaskins, University of Virginia; S. King, Intel Corporation; A. Henry, Massachusetts Institute of Technology; W. Lanford, University at Albany; P. Hopkins, University of Virginia

The role of interfacial nonidealities and disorder on thermal transport across interfaces is traditionally assumed to add resistance to heat transfer, decreasing the thermal boundary conductance (TBC). However, recent computational works have suggested that interfacial defects can enhance this thermal boundary conductance through the emergence of unique vibrational modes intrinsic to the material interface and defect atoms, a finding that contradicts traditional theory and conventional understanding. By manipulating the local heat flux of atomic vibrations that comprise these interfacial modes, in principle, the TBC can be increased. In this work, we provide experimental evidence that interfacial defects can enhance the TBC across interfaces through the emergence of unique high frequency vibrational modes that arise from atomic mass defects at the interface with relatively small masses. We demonstrate ultrahigh TBC at amorphous SiO₂:H/SiC:H interfaces, approaching 1 GW m⁻² K⁻¹ and are further increased through the introduction of nitrogen defects. The fact that disordered interfaces can exhibit such high conductances, which can be further increased with additional defects, offers a unique direction to manipulate heat transfer across materials with high densities of interfaces by controlling and enhancing interfacial thermal transport.

8:40pm NM-TuE10 Icephobic and Hydrophobic Behaviour of Laser Patterned Polyurethane Nanocomposite Coatings, Bartłomiej Przybyszewski, Warsaw University of Technology, Poland; R.K. Kozera, Technology Partners Foundation, Poland; A. Boczkowska, Warsaw University of Technology, Poland; A.G. Gonzalez-Elipe, A.B. Borrás, Instituto de Ciencia de Materiales de Sevilla, Spain

Laser Patterning (LP) is a versatile tool for the fabrication of micro and sub-micropatterns on different materials. Inspired by typical plant surfaces with super-hydrophobic character such as lotus leaves and rose petals, structured hydrophobic surfaces have been prepared to discuss the wettability properties. In this work, LP was used to produce periodic surface structures on modified polyurethane (PU) coatings with periods ranging from 10 to 30 µm. The influence of the different modifications of PU as well as topographical characteristics of the produced micropatterns on coatings' wettability and icephobicity was investigated. The morphologies of structured samples include linear, square and rhombic protuberances. 2024 Al alloy and commercially available polyurethane topcoat, an extensively used materials in aircrafts and marine vessels, were employed as the substrates. To characterize the surface topography of the produced structures Scanning Electron Microscopy and Laser Profilometry were utilized. Static contact angle (SCA) and contact angle hysteresis (CAH) have been determined using standard wettability tests. Ice accretion, ice adhesion and freezing delay time tests have been carried out to assess icephobic properties of investigated coatings. It was found that prepared structured surfaces showed hydrophobic property with a WCA as high as 170° and CAH lower than 10°. Measurements of the contact angle of water on the treated surfaces allowed to identify a wetting behavior depending mainly on the laser period, surface roughness and chemical composition of investigated surfaces.

Wednesday Afternoon Poster Sessions, December 5, 2018

Nanomaterials

Room Naupaka Salon 1-3 - Session NM-WeP

Nanomaterials Poster Session II

Moderator: Paul Stoddart, Swinburne University of Technology

NM-WeP1 Fabrication of Morpho Butterfly Structure using Standing Wave Effect, Tomoki Nishino, H. Tanigawa, Ritsumeikan University, Japan; A. Sekiguchi, Litho Tech Japan Corporation, Japan

In recent years, biomimetic technologies have been extensively studied. Morpho butterflies are representative examples of structural colors, and many scientists have done research. On the wing, small thin plates called scales with a size of 70 x 150 μm and a thickness of a few microns are spread like roof tiles. When one scaled powder is enlarged, it has a streaky structure on the scale, this streak is called ridge. It is a characteristic of morpho butterfly that each of the ridges (lid interval: 1 μm) appears blue.

In this paper, the morpho structure can be fabricated by using lithography technology. The standing wave effect is exposure unevenness generated in the resist film when the photoresist on the Si substrate is exposed with monochromatic exposure light. Two reflected lights of the resist surface and the Si substrate cause interference waves. It strengthens and weakens according to the film thickness. No interference wave is generated by the reflected light of the Si substrate, and constant reflection intensity of light is always obtained.

Patterning was performed on the resist, cross-sectional development was performed, and the standing wave effect in the resist film was confirmed.

We propose that the morpho structure can be fabricated by using lithography technology.

NM-WeP2 Photovoltaic Performance of Organic Polymer Solar Cells using Silicon Nanoparticles with Various Phosphorus Contents, Naoki Ikeda, K. Sato, Tokyo Denki University, Japan

Silicon nanoparticles (SiNPs) are used for solar cell applications because they not only enhance light absorption efficiency of the photoelectric conversion layer but also expand the absorption bands of sunlight. We have fabricated the phosphorus (P)-doped SiNPs using an electroless chemical etching, which is inexpensive and simple techniques. When the P powders was used as n-type dopant, it was difficult to uniformly incorporate the P atoms in the SiNP core. To overcome this challenge, we performed the P doping into SiNPs using P dispersed solvent. In this presentation, we report the photovoltaic performance of the organic polymer solar cells using SiNPs with various P contents. The P-doped SiNPs were fabricated by etching the Si powders with a diameter of 100 nm in a hydrofluoric acid/nitric acid mixture solution using high-speed mixer and by thermally diffusing the P atoms at high temperature. The P contents in the SiNPs were controlled by varying the annealing temperature. The solar cells were prepared by individually coating the P-doped SiNPs and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) on the micro-pyramidal structured Si substrate. The current density-voltage characteristics of undoped SiNPs/PEDOT:PSS solar cells and the P-doped SiNPs/PEDOT:PSS solar cells were shown in Figure 1. The solar cell using undoped SiNPs showed a power conversion efficiency (PCE) of 4.81% with a short circuit current density (J_{sc}) of 27.7 mA/cm^2 , an open circuit voltage (V_{oc}) of 0.361 V and a fill factor (FF) of 0.482. On the other hand, these cell parameters dramatically increased by doping the P atoms into SiNPs; that is, the values of J_{sc} , V_{oc} , FF and PCE were 29.7 mA/cm^2 , 0.349 V, 0.560 and 5.79%. These results are attributable to the uniform incorporation of P atoms into SiNPs by the use of the P dispersed solvent and the improvement of transport efficiency of photogenerated charge carriers between the SiNPs.

NM-WeP3 Effect of Phosphorus-doping on Photovoltaic Performance of Si Nanoparticles/Polymer Hybrid Solar Cells, Masataka Takase, K. Sato, Tokyo Denki University, Japan

Semiconductor nanoparticles (NPs) are increasingly gaining attention as suitable materials to enhance photovoltaic performance for solar cell applications because the absorption regions of solar light can control by tuning the band gap due to quantum confinement effect. We have investigated the photovoltaic performance of solar cells using phosphorus (P) doped n-type silicon NPs (SiNPs) so as to improve the transport efficiency of photogenerated charge carriers, and we have compared to that of the undoped SiNPs. In this presentation, we report the effect of P-doping on the photovoltaic performance of solar cells using n-type silicon NPs (SiNPs). The n-type SiNPs were prepared by doping P dopant in commercially available NPs of 100 nm in size using thermal diffusion

process at high temperature. The doping states of P atoms in the obtained n-type SiNPs were confirmed by X-ray photoelectron spectroscopy (XPS), indicating that the P atoms exist as the P-Si bonds at the substitutional sites of Si atoms in the crystalline core of n-type SiNPs. We prepared the solar cells in which the undoped SiNPs layer or n-type SiNPs layer applied on the micro-pyramid-shaped Si substrate was covered with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), which is p-type conducting polymers. The solar cells using the undoped SiNPs showed the low power conversion efficiency (PCE) of 1.44% with open circuit voltage (V_{oc}) of 0.318 V, short circuit current density (J_{sc}) of 10.1 mA/cm^2 and fill factor (FF) of 0.451. When the active layer in the solar cells replaced the undoped SiNPs by the n-type SiNPs, the values of PCE, J_{sc} and FF dramatically increased to 4.79%, 22.3 mA/cm^2 and 0.520, respectively. These improvements are because the reduction in the value of the series resistance (R_s) (0.23 $\Omega\cdot\text{cm}^2$ for the solar cells using the n-type SiNPs) due to the increase in the number of photogenerated charge carriers by P doping. This result demonstrates that the P-doped n-type SiNPs is beneficial for obtaining the higher PCE.

NM-WeP4 Effect of Amino Modification on Photovoltaic Performance of Silicon/Polymer Solar Cells with Porous Desert Structures, Kento Saito, K. Sato, Tokyo Denki University, Japan

Various micro-texture structures have been reviewed in silicon (Si)/polymer solar cells. Our research group have suggested a facile approach to forming micro-desert structure (MDS) on the Si substrate surface by enclosing Si substrate, phosphorus (P) powders and hydrofluoric acid (HF)/nitric acid (HN) mixed solution in a sealed container. However, the MDS is confronting serious problem for antireflection effect, which affects the power conversion efficiency (PCE) of the solar cells, showing the reflectance of 29.8 % in the incident wavelength range of 500-1000 nm. To drop the reflection of the MDS, we fabricated a porous desert structure (PDS) with ordered cylindrical mesopore in the MDS by treating in a mixed solution containing silver perchlorate (AgCl)/sodium hydroxide (NaOH). Additionally, the inside wall of the mesopore of the PDS was modified with amino group to infiltrate the polymer into the mesopore. In this presentation, we report the effect of the amino modification on the photovoltaic performance of the Si/polymer (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)) solar cells with PDS. The PDS with the pore diameter of approx. 20 nm and the depth of approx. 500 nm was confirmed by scanning electron microscopy (SEM). Such PDS showed the low reflectance of 1.93 % or less in the incident wavelength range of 500-1000 nm, indicating an excellent antireflection effect. When the PDS was modified with amino group, the photovoltaic performance was dramatically improved. The Si/ PEDOT:PSS solar cells with the amino-modified PDS attained the PCE of 4.53% with a short-circuit current density (J_{sc}) of 27.9 mA/cm^2 , an open-circuit voltage (V_{oc}) of 0.362 V and a fill factor (FF) of 0.450 compared to the solar cells having the unmodified PDS with the values of J_{sc} of 22.9 mA/cm^2 , V_{oc} of 0.261 V, FF of 0.375 and PCE of 2.24 %. This is due to the fact that affinity between the Si with the PDS and the water-soluble PEDOT:PSS enhanced by the modification of hydrophilic amino group.

NM-WeP6 Indoor Light Photocatalytic Performance of Graphene Quantum Dot-TiO₂-PAN Composite based on Electrospinning Matrix, Hyonkwang Choi, W. Yang, KwangWoon University, Korea, Republic of Korea

TiO₂ is one of the most promising catalysts owing to its relatively low cost, superior photocatalytic performance, long-term stability, low cost, and low toxicity under UV illumination.

However, the inherent drawbacks of the TiO₂, e.g. the poor response to visible light due to its large bandgap of 3.2 eV, and the fast recombination of photogenerated electron-hole pairs, have significantly impeded the photocatalytic application. To address these matters, the absorption of TiO₂ has been extended into the visible range using chemical doping. Nitrogen doping, especially, can alter the band structure or suppress the recombination efficiency of the photogenerated electron-hole pairs, resulting in an enhanced photocatalytic capacity of TiO₂ in the visible light region.

We present a facile method to the fabrication of nitrogen-doped GQDs/TiO₂ via polyacrylonitrile (PAN)-based carbon fibers (PAN-CFs). Electrospun PAN-CFs have here been selected to produce an electrochemically-active carbon-network matrix containing in-frame incorporated nitrogen, because of its high carbonization yield and high controllable residual nitrogen content. Also, an improvement in visible light absorption is enabled at the GQDs/TiO₂ heterostructure due to bandgap narrowing of TiO₂ by Ti-O-C bond formed between GQDs and TiO₂. PAN

Wednesday Afternoon Poster Sessions, December 5, 2018

plays a dual role, nitrogen doping during its cyclization as well as acting an electrical conducting substrate of a support that enhances the performance of other decorated active catalysts. Thus, nitrogen-doping process of GQDs/TiO₂ heterostructure and its corresponding structural and optical properties were investigated through a series of experiments (SEM, TEM, FTIR, XPS, XRD, UV-Vis, PL). We also demonstrate that GQDs/TiO₂/PAN electrodes exhibit enhanced photochemical and electrochemical activities advantageous by indoor light methylene blue test and solar-driven hydrogen evolution reaction.

NM-WeP7 Multispectral Optical Imaging Retrofitted to XPS and SIMS Instruments, *Peter Cumpson, I. Fletcher, N. Sano*, Newcastle University, UK
All X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToFSIMS) instruments have optical cameras to image the specimen under analysis, and often to image the sample holder as it enters the system too. These cameras help the user find the appropriate points for analysis of specimens. However they seldom give as good images as stand-alone bench optical microscopes, due to the limited geometry, source/analyser solid angle and Ultra-High-Vacuum (UHV) design compromises. This often means that the images displayed to the user necessarily have low contrast, low resolution and poor depth-of-field.

To help identify the different regions of the samples present we have found it useful to perform multispectral imaging by illuminating the sample with narrow-wavelength-range light emitting diodes (LEDs). By taking an image under the illumination of these LEDs in turn, each at a successively longer wavelength, one can build-up a set of registered images that contain more information than a simple Red-Green-Blue image under white-light illumination. We show that this type of multispectral imaging is easy and inexpensive to fit to common XPS and ToFSIMS instruments, using LEDs that are widely available. In our system we typically use 14 LEDs including one emitting in the ultraviolet (so as to allow fluorescent imaging) and three in the near infra-red. The design considerations of this system are discussed in detail, including the design of the drive and control electronics, and three practical examples are presented where this multispectral imaging was extremely useful in XPS and SIMS.

NM-WeP8 Synthesis of Small Cubic Metal Nanoparticles of Fe⁰, Co⁰ and Ni⁰ by using Calcium Hydrate as Reducing Agent, *Maria Volokhova, A. Boldin, L. Seinerberg*, National Institute of Chemical Physics and Biophysics, Estonia

Metal oxide nanoparticles (NPs) are widely used in different biomedical fields, such as tissue engineering [1], MRI contrast enhancement [2] and detection of proteins [3]. In the current study we are focusing on synthesizing metal nanoparticles (size ~20 nm). In comparison with their oxide counterparts, metal NPs with improved magnetic properties could be used as a MRI contrast agent. Our metal NPs were synthesized using metal oxide NPs, which have been synthesized beforehand by using simple one-pot pyrolysis [4]. Metal hydrate salt and polyvinylpyrrolidone (PVP) in DMF were used as starting materials. The reaction is carried out in a teflon tube that is heated in a furnace (< 200°C). The metal oxide NPs were covered with SiO₂ and reduced using CaH₂ in a vacuum sealed tube [5]. Therefore, NPs with a cubic metal core and a SiO₂ shell coating were obtained. The crystal structure and morphology of the NPs were analyzed using X-ray diffraction (XRD) and transmission electron microscope (TEM). Using the physical properties measurement system (PPMS), we have studied the magnetic properties of the NPs at the room temperature. As far as biomedical applications are concerned, we improved the solubility of the NPs in water. For this purpose zwitterionic dopamine sulfonate (ZDS) [6] was synthesized and used as a coating material for the NPs. Preliminary toxicology experiments of the NPs confirmed their suitability for biomedical application.

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NM-WeP10 Control of Fluorescence Color and Magnetic Intensity of Magnetofluorescent Microparticles, *Takafumi Yasuzawa, K. Sato*, Tokyo Denki University, Japan

In recent years, magnetofluorescent materials have attracted attention as one of a powerful tool to provide simultaneously diagnosis and treatment of cancer cells such as image diagnosis using fluorescence property and thermotherapy using magnetism property. We have developed the magnetofluorescent microparticles in which fluorescent ammonium silicon fluorides ((NH₄)₂SiF₆) were formed on the surface of the ferromagnetic magnetite (Fe₃O₄) layer, which applied on the Si substrates. This microparticles have some serious challenges; for instance, emission of only single light (red-orange color) and poor magnetic response due to the formation of the diamagnetic ferric fluoride (FeF₃) by the chemical reaction between the Fe₃O₄ and hydrofluoric acid/nitric acid mixture solution during the preparation process. To overcome these challenge, we suggest the approach to combine the phosphorus (P)-doped (NH₄)₂SiF₆, as a novel fluorescent materials, with Fe₃O₄ without the formation of FeF₃. In this presentation, we report the fluorescence color and chemical composition of the magnetofluorescent microparticles. The P-doped (NH₄)₂SiF₆ microparticles were linked with the Fe₃O₄ using ultrasound cleaner. To vary the fluorescent color of the P-doped (NH₄)₂SiF₆ microparticles, they were immediately treated in vacuum or in atmospheric environments. The fluorescence properties and chemical composition of the obtained microparticles were investigated by using photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS) measurements. The fluorescent color varied from yellow to green light due to the oxidation of the P-doped (NH₄)₂SiF₆ in atmospheric environment. Furthermore, the magnetic component in the microparticles was composed of only Fe₃O₄ without the formation of FeF₃. Therefore, we suggest that the particles become a highly effective tool of diagnosis and treatment of cancer cells as a novel magnetofluorescent materials.

NM-WeP11 Nonideality in Atomic Layer Deposition and Its Implication in Efficient Electrolysis, *Changdeuck Bae, T.A. Ho, H. Shin*, Sungkyunkwan University, Korea, Republic of Korea

We describe the spontaneous formation of a composite chalcogenide materials that consist of two-dimensional (2-D) materials dispersed in bulk and their unusual charge transport properties for application in hydrogen evolution reactions (HERs). When MoS₂ as a representative 2-D material is atomic layer deposition-deposited on transition metals such as Cu in a controlled manner, the sulfidation reactions also occur with the metal. This process results in remarkably unique structures, i.e., bulk layered heterojunctions (BLHJs) of Cu-Mo-S that contain MoS₂ flakes inside, which are uniformly dispersed in the Cu₂S matrix. The resulting structures were expected to induce asymmetric charge transfer via layered frameworks and tested as electrocatalysts for HERs. Upon suitable thermal treatments, the BLHJ surfaces exhibited the efficient HER performance of approximately 10 mA/cm² at a potential of as low as -0.1 V versus a reversible hydrogen electrode (RHE). The Tafel slope was approximately 30 to 40 mV/dec. The present strategy was further generalized by demonstrating the formation of BLHJs on other transition metals such as Ni. The resulting BLHJs of Ni-Mo-S also showed the remarkable HER performance and the stable

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Wednesday Afternoon Poster Sessions, December 5, 2018

operation over 10 days without using Pt counter electrodes by eliminating any possible issues on the Pt contamination.

NM-WeP12 Stretchable Temperature Sensor Based on Elastomeric rGO/PU Nanocomposite Fiber, *Tran Quang Trung, N.-E. Lee*, Sungkyunkwan University, Republic of Korea

Developing fiber-based sensors and integrating them with textile to develop smart textile smart clothes, and smart gloves for monitoring physiological and biological signals of human body are promising for next generation of wearable electronic platform. In recent, there have been many efforts on development of stretchable temperature sensors. However, they still presented some limitations such as requirement of complicated fabrication process, high cost, low yield, and unstability in output performances under mechanical deformation. Herein, we proposed a stretchable temperature sensor with simple fabrication process based on elastomeric rGO/PU nanocomposite fiber. By incorporating high thermal-responsive material (reduced graphene oxide (rGO)) into outstanding mechanically stretchable elastomer polymer (polyurethane (PU)), we generated a free-standing rGO/PU elastomeric composite fiber with high thermal responsivity and good mechanical deformation via a simple fiber spinning method. The fiber with outstanding mechanical deformation helps it easily moulded in serpentine shape and encapsulated by polydimethylsiloxane (PDMS) to generate a free-standing stretchable temperature sensors. Fabricated device presented high responsivity, stretchability, and stability in sensitivity under applied stretching. The free-standing stretchable temperature sensor can be embedded on PDMS substrate, sewn on stretchable fabric and bandage, and laminated on human body to monitor the temperature changes of skin during doing exercise. These results demonstrate that the free-standing, fiber-based, stretchable temperature sensor has great potential for development of smart textile for personal healthcare.

NM-WeP14 Au Nanoparticle Decorated rGO/MoS₂ Sandwich Catalyst for Photodegradation, *Jyh-Ming Ting*, National Cheng Kung University, Republic of China

With the development of industry and the rapidly innovative technology progress, various pollution issues have thus occurred. For example, management of wastewater is one of the critical issues. Therefore, waste water purification by semiconductor or semiconductor composite photocatalyst has been attracting much attention. In the study, we have investigated a novel catalyst for use as photocatalyst. The photocatalyst is a novel visible light response Au nanoparticle decorated rGO/MoS₂ material. The synthesis of such photocatalyst involves the use of a supercritical fluid carbon dioxide process. The processing conditions were studied to obtain desired characteristics of the photocatalyst. The obtained photocatalyst was for the degradation of MB.

NM-WeP15 Surface Modification of CFRP by CNT-Doped Buckypapers, *Bartłomiej Przybyszewski, K. Dydek, P. Latko-Duralek, A. Boczkowska*, Warsaw University of Technology, Poland

One of the latest trends in the development of new materials is to improve the electrical and thermal conductivity of Carbon Fiber Reinforced Polymers (CFRP). Instead of metallic meshes, lightweight structures are searching as more promising candidates that decrease the total weight of composite laminates and are electrically conductive in order to be able to provide electromagnetic shielding.

Thin sheets made from an aggregate of carbon nanotubes (so called buckypapers) are novel CNT-based materials which mainly consist of carbon nanotubes that are bonded together by thermal treatment. They can improve the electrical conductivity of CFRP composites due to the presence of carbon nanotubes (CNTs), which are known to be highly conductive nanoparticles.

In order to investigate the effect of surface modification of CFRP by CNT-doped buckypapers on the electrical and thermal conductivity of CFRP, two types of laminates were fabricated with different buckypaper types. All panels were made from carbon prepregs using a vacuum bag (Out of Autoclave method). Electrical conductivity was measured in three directions of the fabricated panels. The differences in the results were explained by microscopic observations. In addition, the effect of CNT-doped buckypapers on the thermal properties of the panels was analyzed.

NM-WeP16 Characterizing the Quality of Molten Al Alloys with Hydrogen, Porosity and Bifilm Content, *H. Jang, P. Youn, H. Kang, G. Lee, J.B. Jeon, J. Park, E. Kim, Sunmi Shin*, Korea Institute of Industrial Technology, Korea

In response to the recent strengthened environmental regulations, high strength aluminum alloys have been actively studied as a substitute for

steel material for light weight of vehicle. In particular, Al-Mg alloy is a typical high-strength aluminum alloy, and it is used as a structural material with excellent strength and deformation resistance. Mg alloying element induces solid solution hardening and precipitation hardening depending on coexistence of Si and Zn. On the other hand, Mg element weakens the fluidity of the molten alloy and increases the amount of inclusions due to the strong bonding force with oxygen. In order to reduce the internal defects and improve the mechanical properties of Al-Mg alloys, the quality of molten Al-Mg alloys should be precisely controlled. In this study, the melt quality of Al-Mg alloys was characterized by measuring hydrogen, porosity and bifilm content and the effect of Mg content and melting process parameters on the melt quality was discussed.

NM-WeP17 Molecular Confinement on Nanostructured Polymer Surfaces, *Sara Heedy, A.F. Yee*, University of California, Irvine

Polymers have a characteristic size (lamella thickness, molecular orientation, etc.) which may depend on processing, especially when fabricated into structures that range from 10's to 100's of nm. These dimensions may be important in certain properties such as electrical or thermal conductivity. These properties will be strongly affected when fabricated polymer nanostructures have dimensions comparable to the critical length scale of physical phenomena (unconstrained radius of gyration, mean free path of charge carriers, mass transport, etc.). Enhanced mechanical, optical, and electrical properties of nanostructures, including arrays of nanopillars and nanolines less than 1 μm tall, have been well documented. Scientists and engineers who desire to control such properties are often unable to characterize and predict the nanoscale surface chemistry change due to surface topography. This research aims to significantly update the current knowledge of nanoscale surface chemistry, allowing the alteration of physical properties in a defined and predictable manner to obtain unique bio-electronic interfaces. Here, we aim to both quantify and control interface chemistry and molecular confinement to allow researchers the ability to alter surface chemical composition on a given polymer substrate in a methodical and predictable manner.

We fabricated nanostructures using nanoimprint lithography on the synthetic polymer poly(methyl methacrylate) (PMMA), which is often used for biomedical devices. A consequence of such a process is confinement induced reordering of polymer chains which is strongly affected by the mold geometry, mold surface properties, and imprinting process variables. Using thermal imprinting, and the combined topographical and nanoscale chemical mapping of photoinduced force microscopy (PiFM) (Nowak et al. Sci. Adv. 2016), we found that nanopillars (100-700 nm range) confine functional groups differently depending on the pattern geometry used. These findings are very surprising, and suggest that surface chemistry, as well as nanoscale phenomena, can be controlled for use in adhesion and bio-electronic interfaces.

NM-WeP18 Non-volatile Memory Based on Negative Capacitance and Photovoltaic Effect, *Kai-Wen Chen, S.-Y. Chen, Y.-C. Tseng, S.-J. Chang*, National Chiao Tung University, Republic of China

The investigation for solid-state non-volatile memory has triggered great research into new materials combination. Here we demonstrate that the significant photovoltaic effect of the multiferroic heterostructure. This work GdFe_{0.8}Ni_{0.2}O₃/SrTiO₃ (GFNO/STO) ferroelectric capacitors have been successfully fabricated on an Nb-doped SrTiO₃ substrate, in which the GFNO and STO film were prepared by magnetron sputtering. When GFNO layer was combined with an STO layer, the total capacitance appeared increased, which suggested the negative value of the ferroelectric capacitance. In addition, the amplified photocurrent was induced by positive poling which led to polarization pointing down and vice versa. The direction of photocurrent could be reproducibly switched along with the polarization flips. Using x-ray absorption spectroscopy (XAS) with in-situ electrical characterization, we investigated the poling dependence of transport properties at an interface of a GFNO/STO devices. We found that electrons were pushed upward or downward by dipole moment inside GFNO thin film with the occurrence of polarization flipping which decreased the rate of recombination of electron-hole pairs. In addition, photoelectron spectroscopy (PES) indicated that oxygen vacancies accumulated mainly at one side of GFNO with poling dependence and motivated the change of Schottky barrier height at the interface. With the combination of modern x-ray technique and photocurrent measurement, our results pave a way for ferroelectric electro-optic memory by manipulation of multiferroic interfaces. This work was financially supported by the "Center for the Semiconductor Technology Research" from The Featured Areas Research Center Program within the framework of the

Wednesday Afternoon Poster Sessions, December 5, 2018

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Bold page numbers indicate presenter

— A —

Al Mamun, M.: NM-TuM9, 6
 Aloni, S.: NM-MoM2, 1; NM-MoM8, 2
 Aoyama, Y.: NM-TuM11, **6**
 Asaoka, H.: NM-TuM12, 6
— B —
 Baddour, F.: NM-MoE7, 3
 Bae, C.: NM-WeP11, **12**
 Barja, S.: NM-MoM1, 1; NM-MoM2, 1
 Baumann, T.F.: NM-MoM9, 2
 Biener, M.M.: NM-MoM9, 2
 Boczkowska, A.: NM-TuE10, 10; NM-WeP15, 13
 Boldin, A.: NM-WeP8, 12
 Borrás, A.B.: NM-TuE10, 10
 Borys, N.: NM-MoM2, 1
 Braun, J.: NM-TuE9, 10
 Brutchey, R.L.: NM-MoE7, **3**; NM-MoM4, 1; NM-TuM1, 5
— C —
 Cao, Z.Q.: NM-TuM4, **5**
 Chang, S.-J.: NM-WeP18, 13
 Chen, C.T.: NM-MoM2, 1; NM-MoM8, 2
 Chen, K.-W.: NM-WeP18, **13**
 Chen, S.-Y.: NM-WeP18, 13
 Choi, H.: NM-WeP6, **11**
 Chu, J.P.: NM-MoE4, 3; NM-MoE5, 3
 Chun, H.: NM-TuP11, 8
 Cochrane, K.: NM-MoM2, 1
 Cole, N.A.: NM-TuM9, 6
 Cristobal, A.P.: NM-MoE4, **3**; NM-MoE5, 3
 Cumpson, P.: NM-WeP7, **12**
— D —
 Dydek, K.: NM-WeP15, 13
— F —
 Fletcher, I.: NM-WeP7, 12
 Fujii, S.: NM-TuE7, **9**
 Furuya, K.: NM-TuP12, **8**
— G —
 Gammon, S.A.: NM-MoM9, 2
 Gaskins, J.: NM-TuE9, 10
 Gingras, M.J.P.: NM-TuE3, **9**
 Giri, A.: NM-TuE9, **10**
 Gonzalez-Eliphe, A.G.: NM-TuE10, 10
— H —
 Haam, S.: NM-TuP10, 7; NM-TuP11, 8
 Habas, S.: NM-MoE7, 3
 Heedy, S.: NM-WeP17, **13**
 Henry, A.: NM-TuE9, 10
 Hitchcock, A.: NM-MoM9, **2**
 Ho, T.A.: NM-WeP11, 12
 Hong, J.: NM-TuE1, **9**
 Hong, J.E.: NM-MoE8, **4**
 Hopkins, P.: NM-TuE9, 10
— I —
 Ikeda, N.: NM-WeP2, **11**
 Ishfaq, H.A.: NM-MoE8, 4
 Ishikawa, F.: NM-TuE4, **9**
 Ito, M.: NM-TuM3, 5
— J —
 Jang, H.: NM-WeP16, 13
 Jeon, J.B.: NM-WeP16, 13
 Jerigova, M.: NM-TuP8, **7**
 Jiang, N.: NM-MoM3, **1**
 Juodkakis, S.: NM-TuM9, 6

— K —

Kang, A.: NM-TuP11, 8
 Kang, H.: NM-WeP16, 13
 Kastl, C.: NM-MoM2, 1; NM-MoM8, 2
 Kim, E.: NM-WeP16, 13
 Kim, H.O.: NM-TuP10, 7
 Kim, H.-O.: NM-TuP11, 8
 Kim, J.: NM-TuP11, 8
 King, S.: NM-TuE9, 10
 Ko, J.: NM-TuE1, 9
 Koch, R.: NM-MoM2, 1
 Kotorova, S.: NM-TuP8, 7
 Kozera, R.K.: NM-TuE10, 10
 Kubo, M.: NM-TuM11, 6
 Kuga, T.: NM-TuP9, **7**
— L —
 Lacroix, M.: NM-TuP1, **7**
 Lai, B.Z.: NM-MoE5, 3
 Lamb, H.H.: NM-MoE3, **3**
 Lanford, W.: NM-TuE9, 10
 Latko-Duralek, P.: NM-WeP15, 13
 Lee, G.: NM-WeP16, 13
 Lee, J.R.I.: NM-MoM9, 2
 Lee, K.T.: NM-MoE8, 4
 Lee, N.-E.: NM-WeP12, 13
 Lee, S.-B.: NM-MoE8, 4
 Li, F.: NM-MoE3, 3
 Li, T.T.: NM-MoM9, 2
 Lim, J.-W.: NM-TuP10, 7; NM-TuP11, 8
 Lim, T.H.: NM-MoE8, 4
 Lorenc, D.: NM-TuP8, 7
 Louie, S.: NM-MoM2, 1
 Lu, J.: NM-TuM4, 5
— M —
 Maboudian, R.: NM-TuM5, **5**
 Machida, S.: NM-TuM12, 6
 Mahapatra, S.: NM-MoM3, 1
 Malmstadt, N.: NM-MoE7, 3
 Minami, K.: NM-TuM3, 5
 Miyazaki, N.: NM-TuM11, 6
 Montallana, A.D.: NM-MoE4, 3; NM-MoE5, **3**
— N —
 Na, W.: NM-TuP11, 8
 Neaton, J.: NM-MoM1, 1; NM-MoM2, 1
 Nishino, T.: NM-WeP1, **11**
 Novotný, P.: NM-MoE3, 3
— O —
 Ogletree, F.: NM-MoM1, 1; NM-MoM2, 1
 Ootani, Y.: NM-TuM11, 6
 Ozawa, N.: NM-TuM11, 6
— P —
 Park, C.: NM-TuP10, 7; NM-TuP11, **8**
 Park, G.: NM-TuP10, **7**; NM-TuP11, 8
 Park, J.: NM-WeP16, 13
 Prochazka, M.: NM-TuP8, 7
 Przybyszewski, B.: NM-TuE10, **10**; NM-WeP15, **13**
— Q —
 Qiu, D.: NM-MoM1, 1; NM-MoM2, 1
— R —
 Rafaely-Abramson, S.: NM-MoM2, 1
 Ramos, M.G.K.: NM-MoE4, 3
 Refaely-Abramson, S.: NM-MoM1, 1
 Roberts, E.J.: NM-MoE7, 3; NM-TuM1, **5**
 Ruddy, D.: NM-MoE7, 3

— S —

Saito, K.: NM-WeP4, **11**
 Sakai, K.: NM-TuM3, **5**
 Sano, N.: NM-WeP7, 12
 Sato, K.: NM-TuP12, 8; NM-TuP9, 7; NM-WeP10, 12; NM-WeP2, 11; NM-WeP3, 11; NM-WeP4, 11
 Sato, T.: NM-TuM3, 5
 Schuler, B.: NM-MoM1, 1; NM-MoM2, **1**
 Schulmeyer, T.S.: NM-TuP2, **7**
 Schultz, J.: NM-MoM3, 1
 Schwartzberg, A.M.: NM-MoM2, 1; NM-MoM8, **2**
 Seiberg, L.: NM-WeP8, 12
 Sekiguchi, A.: NM-WeP1, 11
 Shapiro, D.A.: NM-MoM9, 2
 Shin, H.: NM-WeP11, 12
 Shin, S.: NM-WeP16, **13**
 Shirakashi, J.: NM-TuM3, 5
 Smock, S.R.: NM-MoM4, **1**
 Soleymani, L.: NM-MoM5, **2**
 Song, D.: NM-TuP11, 8
 Song, R.H.: NM-MoE8, 4
 Stoddart, P.: NM-TuM9, **6**
— T —
 Takase, M.: NM-WeP3, **11**
 Tani, S.: NM-TuM3, 5
 Tanigawa, H.: NM-WeP1, 11
 Terasawa, T.: NM-TuM12, 6
 Tian, Q.Y.: NM-TuM4, 5
 Ting, J.-M.: NM-WeP14, **13**
 Trung, T.Q.: NM-WeP12, **13**
 Tseng, Y.-C.: NM-WeP18, 13
— V —
 Vasquez, M.R.: NM-MoE4, 3; NM-MoE5, 3
 Velic, D.: NM-TuP8, 7
 Volokhova, M.: NM-WeP8, **12**
— W —
 Wang, G.: NM-TuM2, **5**
 Wang, L.: NM-MoE7, 3
 Wang, Y.: NM-TuM4, 5
 Weber-Bargioni, A.: NM-MoM1, 1; NM-MoM2, 1; NM-MoM8, 2
 Whiteman, P.: NM-MoM3, 1
 Wickenberg, S.: NM-MoM1, 1
 Wu, J.: NM-MoM9, 2
— Y —
 Yagi, M.: NM-TuM3, 5
 Yang, W.: NM-WeP6, 11
 Yano, M.: NM-TuM12, **6**
 Yasuda, S.: NM-TuM12, 6
 Yasuzawa, T.: NM-WeP10, **12**
 Yee, A.F.: NM-WeP17, 13
 Yeo, J.-S.: NM-TuM8, **5**
 Yeom, M.: NM-TuP11, 8
 Yin, X.T.: NM-TuM4, 5
 Youn, P.: NM-WeP16, 13
 Yun, D.: NM-TuP11, 8
 Yusuf, S.: NM-MoE3, 3
— Z —
 Zhang, K.: NM-TuM4, 5
 Zhang, L.B.: NM-MoE4, 3
 Zhu, X.: NM-MoM9, 2