

Nanomaterials

Room Naupaka Salon 4 - Session NM-TuE1

NanoCatalysis

Moderator: Ellen Fisher, Colorado State University

5:40pm **NM-TuE1-1 Layered Iron Vanadate Electrocatalyst for Large Current Density Water Splitting**, *Fitri Nur Indah Sari, J. Ting*, National Cheng Kung University (NCKU), Taiwan

Electrocatalysis water splitting is an attractive method to generate hydrogen from water. To date, the state-of-the-art catalysts to split water are based on noble metals, such as platinum for hydrogen evolution reaction (HER) and IrO₂ and RuO₂ for oxygen evolution reaction (OER). However, their scarcity and high cost limit the application. Therefore, great efforts have been devoted to exploring highly active and cost-effective catalyst materials. Recently, noble-metal-free Fe-based catalysts have been demonstrated to be highly efficient for OER. It would be a great advance if such Fe-based catalysts could become bifunctional for overall water splitting. This work investigates a unique layered iron vanadate Fe₅V₁₅O₃₉(OH)₉.9H₂O (FVO) catalyst. The electrocatalytic activity of FVO is controlled by tuning the surface oxidation state and introducing anion and cation vacancies. This work provides a new avenue to design an efficient and stable electrocatalyst Fe-based material with a large current density.

Keywords: layered iron vanadate, surface oxidation state, anion and cation vacancies, water splitting.

6:00pm **NM-TuE1-2 Size Dependence of the N-Doped Graphene Nanocluster on the Oxygen Reduction Reaction Activity**, *H. Matsuyama*, The University of Electro-Communications (UEC Tokyo), Japan; *L. Arellano Sartorius*, The University of Electro-Communications (UEC Tokyo) and Instituto Politécnico Nacional, Mexico; *Jun Nakamura*, The University of Electro-Communications (UEC Tokyo), Japan

N-doped graphene nanocluster (N-GNC) has been proposed as a promising candidate for catalysts of oxygen reduction reaction (ORR) in fuel cells, but its cluster size or concentration dependence has been unknown so far. In this study, the dependence of the ORR activity on the size of N-GNCs was investigated using first-principles calculations. With a radius of about 14 Å, the reaction step which determines the maximum electrode potentials U_{Max} is switched from the H₂O generation step to the OOH adsorption step. Thus, the volcano-shaped trend of U_{Max} was predicted as a function of the cluster size [1,2]. Such a size-dependent ORR activity of the N-GNC is derived from the change in the confinement of a donor electron from the doped N atom. The adsorption energy of the reaction intermediates varies continuously because the spread of the supplied electrons from the doped nitrogen atoms to the surrounding atoms varies with the cluster size. This is due to the development of the so-called edge states as the cluster size increases, causing a decrease in the number of electrons contributing to the chemical bond of the reaction intermediate at the reaction site [3].

[1] H. Matsuyama, A. Akaishi, and J. Nakamura, ACS Omega 4, 3832 (2019).

[2] H. Matsuyama and J. Nakamura, ACS Omega 7, 3093 (2022).

[3] Y. Uchida, S. Gomi, H. Matsuyama, A. Akaishi, and J. Nakamura, J. Appl. Phys. 120, 214301 (2016).

6:20pm **NM-TuE1-3 a New High Entropy Glycerate for High Performance Oxygen Evolution Reaction**, *Thi Xuyen Nguyen, Y. Su, C. Lin, J. Ruan, J. Ting*, National Cheng Kung University, Taiwan

Herein, we report a new high entropy material, i.e., a noble metal-free high entropy glycerate (HEG), synthesized via a simple solvothermal process. The HEG consists of 5 different metals of Fe, Ni, Co, Cr, and Mn. The unique glycerate structure exhibits an excellent OER activity with a low overpotential of 229 and 278 mV at current densities of 10 and 100 mA cm⁻², respectively, in 1M KOH electrolyte, outperforming its subsystems of binary-, ternary- and quaternary-metal glycerates. The HEG also shows outstanding stability and durability in the alkaline electrolyte. The result demonstrates the significance of synergistic effect that gives additional freedoms to modify the electronic structure and coordination environment. Moreover, HEG@HEG electrolyzer shows good overall water splitting performance and durability, requiring a cell voltage of 1.63 V to achieve a current density of 10 mA cm⁻².

6:40pm **NM-TuE1-4 Shape Matters, Nanostructured Materials with Unique Properties in Carbon Capture and Catalysis**, *Ryan Richards*, Colorado School of Mines

The Richards' group is working on new synthetic methods to control the size, shape and composition of nanoscale materials and applying them in systems integral to alternative energy technologies and carbon capture. In particular, the ability to manipulate earth abundant metal oxides presents an important potential technology to develop sustainable materials with novel properties. These materials are of interest due to the coordination environments that can be achieved and to the high degree of control over properties that can result from tailoring the exposed facets and from mixing metal oxides including the formation of high entropy systems. The initial synthesis of MgO and NiO with (111) facets as the primary surface (Angew., Adv. Mater.) has been followed by recent work utilizing a multiscale characterization platform to discover the underlying phenomena associated with the electrolytic properties of NiO(111) for Li ion batteries (Nature Comm., Nano Letters) and electrochromics. In a joint experimental-theoretical work with international collaborators, we unravelled the potential of (111) polar surfaces for carbon capture (JACS). Most recently, in-situ microscopy studies have revealed insights into the NiO active sites for electrolysis (PNAS) and the underlying dynamics of doping with iron (JACS).

7:00pm **NM-TuE1-5 Molecular Single Iron and Cobalt Catalysts Over Carbon Nanotubes for Electrochemical CO₂ Reduction and H₂ Production**, *Paulina R. Martinez-Alanis*, Institut de Recerca en Energia de Catalunya, Spain; *A. Berlanga*, Universidad Nacional Autonoma de Mexico; *G. Montaña, K. Mejía*, Institut de Recerca en Energia de Catalunya, Spain; *F. Güell*, Universitat de Barcelona, Spain; *I. Castillo*, Universidad Nacional Autónoma de México; *A. Cabot*, Institut de Recerca en Energia de Catalunya, Spain; *T. Kallio*, Aalto University, Finland

Molecular single Iron or Cobalt p-terbutyl-calix[8]arene compounds were bonded over carbon nanotubes (CNTs) or multiwall carbon nanotubes (MWCNTs) by π - π stacking. The obtained composites were deposited over a gas diffusion layer and proved in a flow cell in a KHCO₃ solution in a saturated atmosphere of CO₂. High Current densities around 80 mA/cm², with faradaic efficiencies of 100 % for hydrogen production were achieved at pH near 7 in aqueous solutions in the flow cell. The selective production of acetate by the Fe and Co calixarene composites was obtained. The reaction conditions analysis, such as temperature, carbonate concentration, and salt, with the characterization of the samples' pre and post-catalysis by ultraviolet-visible, infrared, raman, x-ray photoelectron, and photoluminescence spectroscopy, scanning, and transmission electron microscopy were used to go further in the analysis of the mechanism around these catalytic systems. The understanding of these catalytic performances provides additional criteria for a new strategy for designing materials based on carbon composites as an option for the rational use of the transition metals, which is an environmentally friendly alternative to energy applications.

Nanomaterials

Room Naupaka Salon 4 - Session NM-WeM1

Nanocharacterization

Moderator: Byron Gates, Simon Fraser University

8:00am NM-WeM1-1 Phase Transition Study of 2D NbSe₂ by in-situ TEM/STEM, *Moon Kim*, The University of Texas at Dallas

Two-dimensional (2D) transition metal dichalcogenides (TMDs) are a family of layered materials with an X-M-X structure, where M and X are transition metal and chalcogen, respectively. TMDs have attracted tremendous interest due to their unique electronic, magnetic, and optical properties with an atomic layer limit depending upon structural elements. The stacking sequence of layers leads to the formation of polytypes such as 1T, 2H, 4H, and 3R, sometimes resulting in significantly different electronic and optical properties.

NbSe₂ is one of the attractive 2D TMDs. It is a superconducting material with a high-superconducting-transition temperature (T_c) of about 7.0 K and shows metallic characteristics at room temperature. The weak van der Waals force between layers allows superconductivity and charge density wave (CDW) with a transition temperature of about 33K. Interestingly, its phase alters its magnetic and electrical properties. However, its thermal stability, which is important for phase engineering and synthesis, has not been intensively examined.

This study investigated the defect dynamics and thermal evolution of NbSe₂ under vacuum by in-situ heating Scanning Transmission Electron Microscopy (STEM). Low thermal stability of the NbSe₂ was confirmed by direct observation of 2H to 1T phase transition and defects induced by inversion domain boundaries. Interlayer gap expansion, Se atom desorption, and intercalation to the atomic layer gap were also observed. Experimental details will be presented and discussed considering its potential applications.

8:20am NM-WeM1-2 Development of Atomic Holography Microscope CoDELMA, *Hiroshi Daimon*, Toyota Physical and Chemical Research Institute, Japan; *H. Momono*, National Institute of Technology, Japan; *H. Matsuda*, Institute for Molecular Science, Japan; *L. Tóth*, University of Debrecen, Hungary; *Y. Masuda*, *K. Moriguchi*, *K. Ogai*, APCO Ltd., Japan; *Y. Hashimoto*, *T. Matsushita*, Nara Institute of Science and Technology, Japan

INVITED

Atomic resolution holography [1] is a powerful technique that can analyze the local stereoscopic atomic arrangement around not only constituent atoms in a crystal but also isolated atoms such as dopants, which has been impossible to be analyzed so far. In photoelectron holography, the photoelectrons emitted from the target atom are used as the reference wave, and the waves scattered by the surrounding atoms are used as the object waves, and the angular distribution (hologram) of their interference patterns can be used to directly derive the three-dimensional atomic arrangement around the emitter atom. Because the atomic-resolution holography required synchrotron radiation facilities so far, its application has been limited. Hence we are developing Atomic Holography Microscope CoDELMA, which can make atomic holography experiment anywhere using a scanning electron microscope (SEM) electron beam.

Atomic-resolution holography microscope is realized by a combination of a SEM and a new two-dimensional electron spectrometer CoDELMA [2]. CoDELMA is the only two-dimensional electron spectrometer that can analyze the angular distribution of high-energy electrons with a high-energy-resolution width of $\Delta E/E = 1/2000$ over a wide two-dimensional angular range of $\pm 50^\circ$ at once. This new microscope enables us to easily measure the atomic resolution holography at each nano region observed with SEM.

References:

- [1] H. Daimon, "Atomic-resolution holography for active-site structure", *Jpn. J. Appl. Phys.* 59, 010504 (2020).
- [2] H. Matsuda, L. Tóth, and H. Daimon, "Variable-deceleration-ratio wide-acceptance-angle electrostatic lens for two-dimensional angular and energy analysis", *Rev. Sci. Instrum.* 89, 123105 (2018).

9:00am NM-WeM1-4 Development of a Nanocomposite Based Films with Antifungal Properties and Containing Encapsulated Nanoemulsion Based on Essential Oils: Effect of Combined Treatment with γ -Irradiation, *Monique Lacroix*, INRS, Canada

Nanocomposite film based on chitosan and nanocrystal cellulose (CNCs) was developed as matrices for incorporation of essential oils as antimicrobial compounds. The addition of CNCs in chitosan based-film has permitted to reinforced the physico-chemical properties of the films. An optimal concentration of 5% (w/w) NNCs improved by 26% the tensile strength (TS) and decreased by 27% the water vapor permeability of the films. A three factor central composite design (CNCs concentration ; microfluidization pressure ; number of cycle of microfluidization) with five levels was designed to optimize the microfluidization process. Microfluidization has permitted to reduce the CNC-chitosan aggregates and improved the mechanical properties of the nanocomposite films by 43%. Two antifungal formulations based on tea tree or on mint in combination with thyme essential oils (Eos) under nano emulsion were developed. When encapsulation under nanoscale, the size of the drop of the antimicrobial formulation was reduced from 219 to 71 nm. The encapsulation efficiency improved from 37 to 83% and the antifungal efficiency was improved from 32 for 3 days to 81% for over one month showing, that the doses required to ensure the biological activity was reduced significantly. The film also showed an effectiveness and slow release of EOs during storage. Combination of active films with γ -irradiation (750 Gy) was synergistic and caused 4 log UFC/gr reduction of fungi for more than 8 weeks of storage. These results showed that the bioactive films and γ -irradiation combination has commercial potentiality to extend shelf life of rice products.

9:20am NM-WeM1-5 Tuning Spin Interactions of Magnetic Molecules on Au(111) by Atomic Adsorbates, *Min Hui Chang*, Korea University, Republic of Korea; *Y. Chang*, Korea Advanced Institute of Science and Technology, Republic of Korea; *N. Kim*, *Y. Kim*, Korea Advanced Institute of Science and Technology, Republic of Korea; *S. Kahng*, Korea University, Republic of Korea

Sensing and tuning spin interactions of magnetic molecules have been actively studied due to possible applications in molecular spintronic and quantum computer. On metallic surfaces, exchange interactions between molecular spins and spins of conduction electrons of substrates have been detected as Kondo resonances at Fermi level. It has been demonstrated that Kondo resonances can be tuned by small molecule bindings, but not by atomic adsorbates. Here, we demonstrate that the Kondo resonances of Co-porphyrin on Au(111) can be tuned by various magnetic atomic adsorbates and be detected using scanning tunneling microscopy and spectroscopy (STM and STS). We observed several adsorbate-induced complexes in STM images, and proposed their atomic structures based on density functional theory calculation results. Our STS results were explained with the redistribution of unpaired spins of Co-porphyrin by atomic adsorbates. Our study shows the spin states and interactions of metallo-porphyrin can be tuned by magnetic atomic adsorbates.

9:40am NM-WeM1-6 Critical Utilization of Scan Probe Microscopy (Spm) Methods for 2d Materials Research, *Jason Tresback*, *J. Deng*, Harvard University

Atomic Force Microscopy (AFM) is a powerful, and critical technology to characterize a diversity of nanomaterials across many interdisciplinary research fields. The use of AFM is rapidly evolving into a myriad of different modes for highly localized (<30nm) property measurement techniques in addition to roughness, and topography with sub-nm spatial resolution. In order to support the momentum of quantum materials research, advanced modes of Scan Probe Microscopy (SPM) techniques are being used to measure electrical, magnetic, and optical properties of new materials as well as Scan Probe Lithography (SP-L) methods for device fabrication. A highly active area of quantum materials research is the characterization and device fabrication of 2d materials (Graphene and TMDs). The goal of this talk is to provide an overview of how SPM is applied for the advancement of 2d materials research, utilizing Kelvin Force (KPFM), Electrostatic Force (EFM), Piezo Force (PFM), and Scattering Near Field Microscopy (s-SNOM) and other advanced modes. The main focus will be on the exquisite, direct imaging of Moire lattice patterns in twisted bi-layer (t-BL) materials by SPM technologies. Each of the imaging modes used to demonstrate direct visualization and angle measurements of t-BL will be discussed. Furthermore, the impact of a closed cell environmental chamber with Ar/N₂ gas flow for each of these modes will be demonstrated. Some

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examples of direct writing and patterning of 2d structures using a lithography mode for device fabrication will also be presented.

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Room Naupaka Salon 4 - Session NM-WeM2

Nanocomposites

Moderator: Ellen Fisher, Colorado State University

10:20am **NM-WeM2-8 Tuning the Surfaces of Nanomaterials: From a Diverse Chemical Functionality to Applications in Assembly and Imaging**, *Byron Gates, R. Ali, M. Radford, H. Kang, G. Cheema*, Simon Fraser University, Canada

INVITED

Controlling the surface chemistry of nanomaterials is equally important to having a fine control over the composition of their core. Nanomaterials, sought for the properties offered by the core material, can be plagued by an inability to control interparticle interactions (e.g., colloidal properties) and/or challenges in precisely controlling the functional groups on their surfaces. Successfully controlling these properties is important for applications of nanomaterials spanning from their use as enhanced contrast agents for use in imaging, to platforms for on-demand drug delivery or triggered hyperthermia, to stabilized catalysts with improved durability and functionality. There are several strategies that can be pursued to tune the chemistry and functionality of nanomaterials. We have specifically been working to broaden the chemistries available for derivatizing the surfaces of metal oxides, whether as a coating (e.g., silica) or as a functional material (e.g., niobates). In this study, we will review the progress made to achieve this surface functionalization of nanomaterials using alcohol condensation reactions. Customized surface chemistries were sought to improve colloidal properties, to diversify the specific chemistries available while simplifying the steps necessary for tuning the surfaces of nanomaterials, and to enable a quantifiable method for adjusting the density of molecular species attached to their surfaces. This presentation will review recent progress towards these goals with examples of custom coatings prepared on a variety of nanomaterials of different core composition.

11:00am **NM-WeM2-10 Preparation of Fluorinated Oligomeric Silica/Magnetite Composites: Application to Selective Removal of Fluorinated Aromatic Compounds from Aqueous Solution under Magnetic Field**, *Hideo Sawada, S. Okada, K. Yamashita*, Hirosaki University, Japan

It is well known that ABA triblock-type two fluoroalkyl end-capped oligomers $[R_f-(M)_n-R_f]$; R_f = fluoroalkyl groups; M = radical polymerizable hydrocarbon monomers] can be synthesized by using fluoroalkanoyl peroxide as a key intermediate to form the nanometer size-controlled self-assembled molecular aggregates through the aggregation of terminal fluoroalkyl segments in aqueous and organic media [1, 2]. The fluorinated oligomeric aggregates can interact with a variety of inorganic guest molecules such as silica nanoparticles to afford the colloidal stable fluorinated oligomeric aggregates/guest molecule nanocomposites [2, 3]. Thus, it is of particular interest to develop the colloidal stable magnetite nanoparticles by using two fluoroalkyl end-capped oligomers. Here we report that fluoroalkyl end-capped vinyltrimethoxysilane oligomeric silica/magnetite composites $[R_f-(VM-SiO_{3/2})_n-R_f/Mag]$ can be prepared by the sol-gel reaction of the corresponding fluorinated oligomer $[R_f-(CH_2CHSi(OMe)_3)_n-R_f]$; $R_f = CF(CF_3)OC_3F_7$; $R_f-(VM)_n-R_f]$ in the presence of magnetite (Fe_3O_4 ; **Mag**) nanoparticles. The $R_f-(VM-SiO_{3/2})_n-R_f/Mag$ composite powders thus obtained were applied to the surface modification of glass to exhibit a superoleophilic/superhydrophobic characteristic on the modified surface. These fluorinated composite powders are also well spread over water interface, not precipitated into water. Especially, it was found that these composite powders can adsorb effectively oil droplets spread on the water interface under a magnetic field (permanent magnet). In addition to the removal of oil over water interface, interestingly, these composite particle powders were applied to the facile removal of aromatic compounds such as bisphenol A and bisphenol AF from aqueous methanol solution under magnetic fields. More interestingly, it was demonstrated that we can observe the more efficient removal ability for the fluorinated aromatic compounds, compared to that of the corresponding non-fluorinated ones.

[1] Sawada H (1996) Chem. Rev. 96:1779-1808.

[2] Sawada H (2012) Polym. Chem. 3: 46-65.

[3] Oikawa Y, Saito T, Yamada S, Sugiyama M, Sawada H (2015) ACS Appl. Mater. Interfaces 7: 13782-13793.

11:20am **NM-WeM2-11 Dielectric Characteristics Comparison between Graphene- and Mxene-Incorporated Composites**, *S. Jun*, Korea Institute of Industrial Technology, Republic of Korea; *K. Ahn, SeGi Yu*, Hankuk University of Foreign Studies, Republic of Korea

Polymer-based dielectric composites were synthesized using fillers of two dimensional (2D) nanomaterial, such as graphene and MXene, and barium titanium ($BaTiO_3$, BTO) in a ferroelectric cyanoethylated pullulan (CEP) polymer matrix, in order to use the interface polarization of interfaces between fillers and a polymer matrix. For graphene, two materials of graphene oxide (GO) and reduced graphene oxide (rGO) and two mixing methods—simple mixing of graphene with BTO and elaborate mixing, i.e., encapsulation of BTO in graphene and subsequent mixing. rGO was synthesized by reducing GO chemically with hydrazine. Among four dielectric composite samples with graphene, the sample with rGO-encapsulated BTO (rGO@BTO) fillers showed better dielectric performance, such as high dielectric constants and low dielectric losses. Mixing conducting nanomaterials in a polymer matrix generally yields to a high dielectric constant due to metal-insulator transition (MIT), when the concentration of nanomaterials approaches to the critical concentration of percolation. However, around this critical concentration, it is difficult to suppress the soaring of the dielectric loss due to percolative connection among nanomaterials. Encapsulation can inhibit an increase in the dielectric loss by removing the main culprit of free graphene platelets during the chemical process of encapsulation. MXene was used as a filler in the simple mix method resulting in positive results comparable to the graphene cases—higher dielectric constant than rGO encapsulation (220 vs. 200) and slightly higher dielectric loss (0.08 vs. 0.04 in $\tan \delta$ at 1 kHz). It is possibly due to its higher conductivity than graphene. AC driven inorganic electroluminescence devices, with a dielectric layer having the above five fillers (four graphene and one MXene), also yield to the similar trend to the dielectric composite. Details will be explained in the presentation.

11:40am **NM-WeM2-12 The Thermal Stability of Separated Configurations in Surface-Segregated Nanoparticles: Atomistic Modeling of Pd-Ir Nanophase Diagrams**, *Micha Polak, L. Rubinchov*, Ben-Gurion University of the Negev, Israel

Compared to alloy bulk phase diagrams, the experimental determination of phase diagrams for alloy nanoparticles (NPs), which are useful in various nanotechnological applications, involves significant technical difficulties, making theoretical modeling a feasible alternative. Yet, being quite challenging, modeling of separation nanophase diagrams is scarce in the literature. The task of predicting comprehensive nanophase-diagrams for Pd-Ir fcc-based three cuboctahedra is facilitated in this study by combining the computationally efficient statistical-mechanical Free-energy Concentration Expansion Method (FCEM) [1], which includes short-range order (SRO), with coordination-dependent bond-energy variations [2] as part of the input, and with rotationally symmetric site grouping for extra efficiency. This nanosystem has been chosen mainly because of the very small atomic mismatch that simplifies the modeling, e.g., in the assessment of vibrational entropy contributions based in this work on fitting to the Pd-Ir experimental bulk critical-temperature.

This entropic effect, together with SRO, leads to significant destabilization of Pd surface segregated Quasi-Janus (QJ) asymmetric configurations of the NP core, which transform to symmetric partially mixed nanophases. First-order and second-order intra-core transitions are predicted for dilute and intermediate-range compositions, respectively. The computed separation diagrams and intra-core solubility diagrams reflect enhanced elemental mixing in smaller QJ nanophases. In addition to these diagrams, the revealed surface and near-surface compositional variations are likely to be pertinent to the utilization of Pd-Ir NPs in heterogeneous catalysis, e.g., of CO oxidation in excess H_2 .

[1] M. Polak and L. Rubinchov, *Surface Science Reports*, 38, 127, 2000.

[2] L. Rubinchov and M. Polak, *Physical Review B* 80, 045404 2009.

Nanomaterials

Room Naupaka Salon 1-3 - Session NM-WeP

Nanomaterials Poster Session

NM-WeP-1 Array of Freestanding Graphene Variable Capacitors on 100 mm Silicon Wafers for Vibration-Based Energy Harvesting Applications, Paul Thibado, F. Harerimana, J. Mangum, University of Arkansas

Highly flexible, electrically conductive freestanding graphene membranes hold great promise for vibration-based applications. This study focuses on their integration into mainstream semiconductor manufacturing methods. We designed a two-mask lithography process that creates an array of freestanding graphene-based variable capacitors on 100 mm silicon wafers. The first mask forms long trenches terminated by square wells featuring cone-shaped tips at their centers. The second mask fabricates metal traces from each tip to its contact pad along the trench and a second contact pad opposite the square well. A graphene membrane is then suspended over the square well to form a variable capacitor. The same capacitor structures were also built on 5 mm by 5 mm bare dies containing an integrated circuit underneath. We used atomic force microscopy, optical microscopy, and capacitance measurements in time to characterize the samples.

NM-WeP-2 On the Theory of the Energetic Spectrum of Lateral Superlattices (LSL) on Vicinal Planes: The Role of Crystal Potential, Victor Petrov, Institute of Radio Engineering and Electronics Russian Academy of Sciences, Russian Federation

As is known, the existence of superlattice effects in quantum wells (QWs) on vicinal planes predicted [1] and discovered independently in 1977 [2] initiated with the appearance in these systems of a new crystallographic translation period in the plane of quantum wells $A \gg a$ (a - lattice constant). The emergence in these LSL of the periodic system of atomic steps allows to explain the appearance of minigaps (MG) in the energetic spectrum of particles in QWs by the scattering of electrons on such steps. At the same time it is evident that the contribution to the MG formation should also be made by all crystallographic planes in the area of localization of the particle wave function.

This paper theoretically shows that the consideration of only crystal potential and of the potential locating the particle in LSL on vicinal planes results in the appearance of MG even without taking into account of the step structure of the QW boundaries. A method has been developed that makes it possible to calculate the energetic spectrum of these systems for the arbitrary localizing potential by leaving the effective mass approximation in single-valley semiconductors of the GaAs type.

For the cases of the rectangular QW and inversion layer analytical expressions have been obtained for MG magnitudes which depend on the parameters of the crystal and localizing potentials as well as on angles that define the orientation of the QW planes in the crystal. It has been shown that for LSL of the GaAs type the magnitudes of MGs approximate several meV.

[1]. V.A.Petrov, a) Sixth All-Union conf. on the Physics of Surface Phenomena in

semicond. Kiev, 1977, Abstracts of Paper, Kiev, part 2, p. 80 (1977);

b) Sov. Phys. Semicond., 12, 212 (1978).

[2]. T. Cole, A. A. Lakhani and P. J. Stiles, Phys. Rev. Lett. 38, 722 (1977).

NM-WeP-3 Fabrication and Physicochemical Analyses of Core-Shell Fe₃O₄-TiO₂ Particles Applicable to Plasmid DNA Purification, Gye Seok An, J. Kim, Kyonggi University, Republic of Korea; J. Shin, Hanyang University, Republic of Korea

Magnetite (Fe₃O₄) and titanium dioxide (TiO₂) composites with core-shell structures have been applied in various applications owing to the advantages afforded by their combined characteristics. In this study, TiO₂ was adsorbed onto Fe₃O₄ by an aqueous process under reflux conditions using titanium(IV) isopropoxide as the TiO₂ precursor. In order to increase the adsorption efficiency of TiO₂ particles, the surface of Fe₃O₄ was treated using a reagent having a hydroxyl group, a carboxyl group, and a citric acid bond. The functional group formed on the Fe₃O₄ surface was expected to act as a site where TiO₂ particles were adsorbed through electrostatic interaction. After the Fe₃O₄-TiO₂ fabrication step, the analyses identified functional groups most suitable for TiO₂ adsorption. In addition, various physicochemical analyses analyzed the characteristics of Fe₃O₄-TiO₂ particles prepared using the particles with the optimal functional group.

The surface functional groups and TiO₂ particles on Fe₃O₄ were observed by Fourier transform infrared spectroscopy and adsorbed TiO₂ particles were observed by electron microscopy and elemental composition analysis. Additionally, agarose gel electrophoresis tests confirmed the suitability of the Fe₃O₄-TiO₂ particles for plasmid DNA purification.

NM-WeP-4 Synergistic Effects of Carbon Nanotube and Modified Reduced Graphene Oxide Covalently Bonded Hybrid and 3D-Foam on Electromagnetic Interference Shielding Properties of Polymer Composites, Keun-Byoung Yoon, S. Lee, J. Kang, D. Lee, Kyungpook National University, Republic of Korea

Exploring light-weight electromagnetic interference (EMI) shielding material with high EMI shielding effectiveness (SE) is of great significance to alleviate the growing EMI pollution problem, prevent electronic instruments from the EMI, and protect human health. Hence, several methods are being explored to efficiently restrain EM pollution. Among these studies, carbon nanotubes (CNT) and graphene nanoplates are of particular favor on account of their unique structures and remarkable conductivities.

In the frame of this work, hybrid reduced graphene oxide (rGO) and multi-walled carbon nanotube (MWCNT) nanofiller were designed and covalently bonded through an amide bond. A hybrid nanofiller was prepared through the reaction of modified GO with ethylenediamine and oxidized MWCNT and reduced to hydrogen iodide. Another design is 3D-foam of modified GO and oxidized MWCNT, which is mixed, and 3D-foam is manufactured using various surfactants and used as a nanofiller of the epoxy and polydimethylsiloxane (PDMS) matrix.

The chemical and electrical properties of the hybrid and 3D-foam nanofillers are characterized to establish the correlation between the material characteristics and the EMI shielding performance of the nanocomposites. The mechanical and electrical properties and EMI shielding effectiveness of nanocomposites as functions of hybrid and 3D-foam nanofillers types and contents were investigated in detail.

The addition of rGO significantly increases the electrical conductivity, because CNTs can fill the gaps between rGO sheets [<https://www.sciencedirect.com/topics/engineering/graphene-sheet>], and bridge the neighbor graphene sheets to form a preferable conductive network. In a low areal density 3D-foamed MWCNT/rGO aerogel, vein-structured MWCNT expands the conductive network of mesophyll-structured rGO, which promotes reflection and absorption of electromagnetic waves inside the materials, resulting in excellent EMI shielding effectiveness of 65dB in C-band and absorption-dominant shielding mechanism.

This study not only put forward a facile and effective approach to fabricating epoxy nanocomposites with excellent electrical conductivity and EMI shielding effectiveness but also provided a framework to study the interfacial interaction in rGO/MWCNT hybrid and 3D-foam nanofillers.

NM-WeP-5 Synthesis of Vertically Aligned Carbon Nanotubes Using Carbon Monoxide as a Carbon Source, Kosuke Homma, S. Mori, M. Endo, Tokyo Institute of Technology, Japan; H. Nakamura, Tokyo Institute of Technology / Yaskawa Electric Corporation, Japan; S. Tanaka, Yaskawa Electric Corporation, Japan

Recently, vertically aligned carbon nanotubes (VACNT) grown vertically from substrates have been attracting attention in fields such as Through Silicon Via (TSV). Although hydrocarbons such as ethylene and acetylene have been mainly used as carbon sources for the synthesis of VACNT, there have been few reports of VACNT growth using carbon monoxide as a carbon source. This study is aimed at searching for and modeling the optimum conditions for aligned growth of CNTs from carbon monoxide. As the catalyst preparation method, we use the dip-coating method, which has been reported for the aligned growth of CNTs from carbon monoxide. The sputtering method, which has been used in many reports on the aligned growth of CNTs from hydrocarbons, was also investigated.

In the dip coating method, cobalt and molybdenum were used as catalysts. Cobalt acetate was used as the source of cobalt and molybdenum acetate as the source of molybdenum, and ethanol was used as the solvent. The optimum conditions for dip coating were investigated using the lifting speed of the dip-coating and the concentration of the solution as parameters. Experiments were conducted in the range of 0.03~0.9 cm/s as the lifting speed of the dip-coating. The concentrations of cobalt and molybdenum in the solution were 0.01~1.2 wt%. Quartz substrates were dipped in a mixed solution of cobalt and molybdenum and pulled up to coat the surface with cobalt and molybdenum. Subsequently, calcination

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was performed at 400°C for 5 minutes in an atmosphere. The substrate after calcination was inserted into a quartz tube reactor, and after being evacuated with a vacuum pump, a mixture of Ar and H₂ flowed into the reactor for reduction treatment at 700°C for 10 minutes under atmospheric pressure. After that, the feed gas was switched to CO and synthesis was performed at 700°C for 60 minutes under atmospheric pressure. The surface and cross-section of the substrate after synthesis was observed by SEM. The crystallinity of the CNTs was evaluated using Raman spectroscopy. The results showed that CNTs grew randomly on the surface of the substrate in most conditions; the Raman spectroscopy analysis indicated that single-walled CNTs were synthesized since the strong RBM peak was observed. VACNT was observed when the lifting speed was 0.9 cm/s and the concentrations of cobalt and molybdenum were 0.2 wt%. Based on the results, the conditions necessary for aligned growth and the model were discussed. We also tried to specify the conditions for aligned growth of CNTs using the sputtering method and its optimum condition and growth model are discussed.

NM-WeP-6 Electrical Characteristics of Multi-Layer Germanium Telluride Switching Device, Chae Ho Lim, J. Park, S. Park, H. Kim, Sungkyunkwan University (SKKU), Republic of Korea

Abstract

Various ovonic threshold switching (OTS) materials with unique insulator-metal transition (IMT) characteristics are being actively studied for applications in phase-change memories [1]. Germanium telluride is one of the most actively studied materials and some variants, including germanium-antimony-telluride, are already in commercial use [2]. To improve the switching characteristics of germanium telluride, many approaches, such as stoichiometric control, doping, and process optimization, have been proposed [3,4].

In this presentation, we propose a multi-layer GeTe₆/GeTe structure to increase the on/off current ratio of OTS devices with a single GeTe₆ layer. The GeTe₆ layers with distinctive IMT characteristics were deposited by adjusting the power ratio during co-sputtering of GeTe and Te targets, and the GeTe layers were deposited in situ by sputtering the GeTe target. For fabrication of the switching device with a metal-insulator-metal structure, tungsten was used for both top and bottom electrodes having a crossbar shape. The on/off ratio of the multi-layer structure was increased compared to that of the single-layer structure (GeTe₆). Additionally, the threshold voltage was increased, and cycle stability was improved. The detailed origins for the improved characteristics will be discussed based on the experiments with various GeTe₆/GeTe stack numbers.

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NM-WeP-7 Vertically Enhanced Ferroelectric α -In₂Se₃/GaN Heterostructure for Steep Switching High Electron Mobility Transistors, M. Yeom, J. Yang, Geonwook Yoo, Soongsil University, Republic of Korea

A highly crystalline two-dimensional (2D) ferroelectric material, α -In₂Se₃ has been extensively studied for neuromorphic, ferroelectric tunnel junction devices, and phototransistors [1-3] because of its unique material characteristic, a ferroelectric semiconductor. Here, we demonstrate, for the first time, a ferroelectric α -In₂Se₃/GaN HEMT van der Waals heterostructure, in which the switchable ferroelectric polarization of α -In₂Se₃ can induce steep subthreshold switching (SS) and large memory window. In-plane polarization within the α -In₂Se₃ layer was successfully suppressed via self-aligned-gate etching process as analyzed by micro-Raman spectroscopy. On the other hand, out-of-plane polarization is strongly coupled to two-dimensional electron gas. Therefore, a record low SS of ~ 12 mV/dec with high on/off ratio of $\sim 10^{10}$ was obtained. The transfer curve exhibits a counter-clockwise hysteretic behavior with a memory window of ~ 0.9 V, induced by the ferroelectric switching above the coercive field of α -In₂Se₃. The results show that ferroelectric polarization and semiconductor characteristic of α -In₂Se₃ is a promising for ferroelectric/III-V heterostructures, enabling emerging III-V based reconfigurable and neuromorphic applications.

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NM-WeP-8 Electrochemical Powered Nano-Actuator from Carbon Nanoscroll, Chae-Lin Park, HYU-KITECH Joint Department, Republic of Korea; K. Kim, S. Kim, KITECH, Republic of Korea

Recently, nanobots are receiving great attention due to their high potential for use in various fields such as intelligent robots, biomedical devices, and drug delivery. Nanobots are realized through the use of nanomaterials and assembly of nanomaterials, and research on driving nanobots using electromagnetic fields, electrochemistry, and specificity of enzymes is in progress. Among them, studies on actuators of carbon nanotubes and graphene based structures driven by electrochemical power have been reported. Electrochemical-based actuators have the advantage of being operated with a low voltage and can be used in places made of electrolyte, such as the human body. However, a useful electrochemical power-based nanoactuator is driven by ion entry and exit, so it is difficult to drive it with a single nanomaterial rather than structures. The development of electrochemical-powered single nanomaterial-based nanoactuators remains a challenge. In this work, we implemented an electrochemical-powered actuator by using graphene as a carbon nanoscroll (CNS) structure with a diameter of 50 nm. Unlike carbon nanotubes and graphene, CNS has a scroll structure and is a material that can be driven independently based on electrochemical power through the input and output of ions between layers. We measured the actuation performance of CNS. When the voltage was applied to CNS on electrolytes, CNS charged and it let the apparent diameter of the scroll increase significantly. Changes of the CNS diameter were measured in real-time using atomic force microscope equipment. It was confirmed that the type of electrolyte and the magnitude of the applied voltage play an important role in controlling the performance of the CNS. Additionally, we have structured the CNS and confirmed that it operates electrochemically. It is expected to see the possibility of using it as a nanobot.

NM-WeP-9 Nanopattern Transferred Oxide and UV Curable Polymer Hybrid Films for Liquid Crystal Systems, Da-Bin Yang, D. Seo, Yonsei University, Korea

In the present study, nanopatterns were transferred using the UV-NIL method; in this method, the patterns are cured with UV radiation to produce the LC alignment layers. For high-quality LC alignment layers, transparent conducting oxides (TCOs) with excellent transmittances are mixed with a UV-cured polymer to prepare a hybrid solution.[1] In this study, we assessed whether high-quality nanopattern transitions can be obtained while reducing the steps of the NIL process by mixing these inorganic materials and polymers. The hybrid solution was coated on a glass substrate and cured by UV irradiation to prepare the nanopattern, and the nanopattern and LC alignment characteristics were analyzed by varying the UV curing time. The film surface was analyzed through X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) analyses. The LC alignment characteristics were confirmed via polarized optical microscopy (POM) and pretilt angle measurements.

ACKNOWLEDGE

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NM-WeP-10 Advanced Nanostructured Architectures via Nanoimprint Lithography on Hybrid Sol-Gel of SnGaO Thin Films, Jin Young Oh, D. Seo, Yonsei University, Korea

Line pattern replication process through nanoimprint lithography (NIL) method has been used in numerous of research fields. NIL technology is not yet utilized for displays industry, and we propose an alignment layer of

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the sol-gel process using NIL. One-dimensionally nanopatterned by polydimethylsiloxane sheets cause surface changes in hybrid SnGaO thin films mixed in a 3:7 ratio, which aligns the liquid crystals (LCs) uniformly in the line pattern direction. These surface changes are confirmed through atomic force microscopy data analysis, and changes in surface shapes for different the curing temperatures in the furnace are analyzed. X-ray photoelectron spectroscopy (XPS) shows that the chemical composition of the thin films changes according to curing temperatures, and the intensities of SnO and GaO increase exponentially at 200°C compared to those at 50 °C. Through this, the van der Waals force increases between surface molecules, in the anisotropic direction to help align the LCs. Furthermore, we performed polarized optical microscopy and pre-tilt angle analysis confirm that the LCs are energized uniformly. Finally, the performance of an actual display device transmittance and electro-optical properties; the transmittance of SnGaO is 4.51p% higher than that of the currently commercialized PI-rubbing thin films, and the voltage-transmittance curve is a perfect graph. Thus, nanopatterned SnGaO thin films using NIL are expected to become the basis for next-generation displays.

Keywords: Nanoimprint lithography, Sol-gel method, Tin-gallium oxide, Atomic force microscopy, X-ray photoelectron spectroscopy

ACKNOWLEDGE

This research was supported by the Brain Korea 21 FOUR Project for Medical Science, Yonsei University

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NM-WeP-11 First Demonstration of the Fully Euv Patterned Dram Capacitor, *Seung Jin Kim, J. Hong, B. Choi*, Sungkyunkwan University (SKKU), Republic of Korea

DRAM is continuously scaled down to improve productivity and low power operation. A DRAM cell consists of one transistor and one capacitor, and the pattern of the capacitor consists of storage poly (s-poly) and supporters. The s-poly is main body of capacitor, which is ultra-high aspect ratio structure with metal (Storage TiN)/dielectric/metal (Plate TiN) composition. The supporter prevents leaning or bending of the capacitor. To fabricate both s-poly and supporter, previous immersion-argon-fluorine (I-ArF) technology had been used up to 3rd generation 10 nm devices. In this process, a line-and-space simple double patterning technique (sDPT) was used to create a honeycomb array of highly integrated s-poly contacts. However, the sDPT method has significant problems such as multiple process steps and unit block s-poly not opening due to complex mask stacks and line-space asymmetry. The EUV technology simplifies mask stack and expose all s-poly cell by 1-set, which allow uniformity of contact. We believe that this work opening a feasibility of an inevitable EUV era to guarantee the extremely scaled sub-10nm patterning with high performance, high yield, and cost-effective process.

Nanomaterials

Room Naupaka Salon 4 - Session NM-ThM2

Nanofabrication and Nanodevices

Moderator: Moon Kim, The University of Texas at Dallas

10:20am NM-ThM2-8 Harnessing Quantum Effects to Control Nanoscale Properties and Carrier Dynamics in Heterojunction Nanowires, *Bryan Wong*, University of California, Riverside

The unique electronic properties of quantum-confined semiconducting nanowires hold great promise for their incorporation in next-generation transistors, circuits, and electronic devices. This reduction in dimensionality results in a dramatic change in their carrier dynamics and electronic structure, leading to novel properties such as ballistic transport and conductance quantization. One area of particular interest is the formation and understanding of electron gases in heterostructured nanowires which provides new avenues for exploring enhanced carrier dynamics in these materials.

To tailor these nanostructures with the desired physical properties, we must first understand their electronic properties as a function of size and material composition. To this end, we have developed a series of self-consistent predictive computational methods to calculate the properties of heterojunction electron gases in quantum-confined core-shell nanowires. Under certain conditions (depending on doping density and spatial geometry), we find that quasi-one-dimensional electron gases can localize at the corners of the nanowire, leading to carrier dynamics that are dramatically different than analogous bulk heterojunctions. In addition, we highlight several areas where many-body quantum effects play a significant role in these low-dimensional structures. In particular, we surprisingly find that simple theoretical approaches can (1) considerably overestimate the number of occupied electron levels, (2) overdelocalize electrons, and (3) significantly underestimate the relative energy separation between electronic subbands. Our results allow a guided understanding of electron carrier dynamics in heterostructure nanowires and further indicate that electron gases in free-standing nanoscale systems are qualitatively different from their bulk counterparts.

10:40am NM-ThM2-9 A New Tool for Quantum and Nanoscale Materials Engineering, *Kate McHardy, A. Bellew, G. Aresta, P. Blenkinsopp*, Ionoptika, UK

Quantum computing is the next great frontier of science. It has the potential to revolutionise many aspects of modern technology, including digital communications, "quantum-safe" cryptography, as well as incredibly accurate time measurements.

Single impurity atoms in semiconductors are receiving attention as potential quantum technologies, and proof-of-concept devices have shown promise. However, such devices are incredibly challenging to manufacture, as single atoms must be placed within ~ 20 nm of each other within a pure ^{28}Si matrix.

All working devices thus far have been fabricated using hydrogen lithography with an STM followed by atomic layer deposition. It is labour-intensive and requires several days of meticulous preparation to create just a single quantum bit (qubit). Real-world devices will require arrays of hundreds or thousands of impurity atoms, highlighting the requirement for a scalable method of positioning single atoms with nanometre precision.

We report on a new commercial instrument for the fabrication of quantum materials and devices via ion implantation. A well-established technique in the semiconductor industry, ion implantation is both flexible and highly scalable. The instrument features a high-resolution mass-filtered focused ion beam (FIB), a high-sensitivity deterministic implantation system, 6-inch wafer handling, and a high-precision stage.

The ion dose delivered to the sample can be adjusted across a wide range, providing several materials engineering capabilities in a single tool. The deterministic implantation system allows single ion implantation with confidence levels as high as 98%. Operating in a high beam current mode provides direct-write capabilities such as isotopic enrichment and targeted ion-implantation of nanomaterials such as nanowires and graphene.

The liquid metal ion source and mass filtered column can implant many different elements with isotopic resolution. Available sources include

silicon, erbium, gold, and bismuth, while many others of technological interest are in development.

11:00am **NM-ThM2-10 On-Surface Synthesis of Higher Acenes and Their Derivatives**, *R. Zuzak*, Jagiellonian University, Poland; *R. Dorel*, Institut Català d'Investigació Química, Spain; *I. Izydorczyk*, Jagiellonian University, Poland; *O. Stoica, R. Blicek*, Institut Català d'Investigació Química, Spain; *M. Krawiec*, Maria Curie-Skłodowska University, Poland; *A. Echavarren*, Institut Català d'Investigació Química, Spain; *Szymon Godlewski*, Jagiellonian University, Poland

In recent years we observe renewed interest in the development of electronics based on electron transport through single molecules. Among different families of organic species, acenes and nanographenes hold the special position. In particular a lot of effort is undertaken to achieve efficient synthetic strategies to generate such well-defined sections of graphene or graphene-like modules with diverse topological modifications. However, the reactivity/instability of numerous molecules as well as the insolubility of large polycyclic aromatic hydrocarbons limits the applications of conventional chemistry methods. An attractive alternative to the solution chemistry is based on its combination with the on-surface synthesis approach.

Acenes are attracting considerable interest due to the intriguing electronic properties originating from only one Clar π -sextet regardless of the molecule length. However, the unique π -electron system causes the molecules to be more reactive and less stable with increased number of annulated rings. Consequently this makes their synthesis, detailed characterization and functionalization a very challenging task. In recent years some successful strategies toward fabrication of higher acenes and their derivatives have been reported, e.g. some long acenes were stabilized and detected within noble gas matrices or in polymers. However, only recently the on-surface chemistry approach allowed for synthesis and characterization of higher acenes.

Herein we present the on-surface generation of higher acenes [1-2] and their derivatives [3], as well as the detailed study of their electronic structure on the Au(111) surface. Our method is based on the two-step dehydrogenation and thermally induced cyclization of a stable and easily handled molecular precursors.

High-resolution non-contact atomic force microscopy (NC-AFM) imaging was applied for the detailed visualization of the internal structure of the intermediates, as well as the target molecules with diverse topologies. Details on the electronic structure were revealed using high resolution dI/dV mapping.

The research was supported by the National Science Center, Poland (2017/26/E/ST3/00855; 2019/35/B/ST5/02666).

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11:20am NM-ThM2-11 Nanotechnology in Plant Protection Applications, *Ahmet Ozan Gezerman*, Toros Agri- Industry, Turkey

To date, plant protection research has mainly focused on the suppression of pests, diseases and weeds. Research has been primarily single-disciplinary and cause-effect-oriented, and innovation has often been equated with the development of new product lines or single-component technologies such as agrochemicals. Today, the aim of contemporary "plant protection" approaches is not to completely eliminate the harmful factors in plant production, but to keep and manage them at a certain population level by using the natural mechanisms found in nature. The most important factor in realizing this aim is to know the harmful factors and the factors limiting their populations and to have basic knowledge about the biology of the pests. In this direction, the "Whole War method", which we can name as keeping the populations of harmful agents below the Economic Damage Threshold, is emphasized today, by supporting each other with the methods of combat. Taking this concept one step further, considering the ecosystem as a whole and taking into account the basic demands of agricultural products and their relationship with the environment, using all appropriate plant growing methods and techniques in harmony, "taking into account the population dynamics of harmful species and their relationship with the environment, Integrated Product Management (ICM), which can be defined as a product and pest management system that keeps their populations below the level of economic damage, by using all appropriate control methods and techniques in harmony, has come to the

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fore. In this context, future plant protection strategies; It is possible to collect them under four headings as preventive practices, monitoring, effective struggle and smart agriculture. These developments, which have emerged in this way, will contribute to the development and realization of much more effective and environmentally friendly plant protection practices in the future, starting from today, and these topics are discussed in this paper.

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