Nanomaterials
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 diversity 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$_2$CHSi(OMe)$_3$)$_n$-R_F; R_F =CF(CF$_3$)OC$_3$F$_7$: R_F-(VM)$_n$-R_F] in the presence of magnetite (Fe$_3$O$_4$: ***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, Sugiya 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 (BaTiO3, 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 recuing 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 δ 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. Rubinovich,* 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. Rubinovich, *Surface Science Reports, 38*, 127, **2000**.

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

Author Index

Bold page numbers indicate presenter

— A —
Ahn, K.: NM-WeM2-11, 1
Ali, R.: NM-WeM2-8, 1
— C —
Cheema, G.: NM-WeM2-8, 1
— G —
Gates, B.: NM-WeM2-8, **1**

— J —
Jun, S.: NM-WeM2-11, 1
— K —
Kang, H.: NM-WeM2-8, 1
— O —
Okada, S.: NM-WeM2-10, 1
— P —
Polak, M.: NM-WeM2-12, **1**

— R —
Radford, M.: NM-WeM2-8, 1
Rubinovich, L.: NM-WeM2-12, 1
— S —
Sawada, H.: NM-WeM2-10, **1**
— Y —
Yamashita, K.: NM-WeM2-10, 1
Yu, S.: NM-WeM2-11, **1**