Monday Morning, October 15, 2007

Nanometer-scale Science and Technology

Room: 616 - Session NS-MoM

Nanoscale Assembly and Manipulation I

Moderator: L.E. Ocola, Argonne National Laboratory

8:00am **NS-MoM1 On-Surface Synthesis of Metallo-Porphyrin Nanotubes by Vacuum Sublimation onto Noble Metals Substrates**, *M. Trelka, C. Urban, D. Ecija,* Universidad Autonoma de Madrid, Spain, *P. de Mendoza,* Insituto Catalan de Investigaciones Quimicas (ICIQ), Spain, *J.M. Gallego,* Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Spain, *R. Otero,* Universidad Autonoma de Madrid, Spain, *A. Echavarren,* ICIQ, Spain, **R. Miranda**, Universidad Autonoma de Madrid, Spain

Molecular electronics is a promising alternative for the continuing miniaturization of electronic devices. The capability of synthesizing and depositing molecular wires on solid surfaces is a key step within this context. The majority of the most promising current candidates to molecular wires, such as carbon nanotubes, DNA strands or individual polymer molecules, are too large and fragile for depositing them on solid surfaces by in-vacuum sublimation. Other kinds of wet deposition methods, such as drop-casting, are not so well controlled, which, in turn, hinders the understanding and design of their conductivity. Since the molecular mass of the chemical species well-suited for deposition on solid surfaces by in-vacuum sublimation is limited, one could envisage a mechanism to grow the polymeric molecular wires by depositing smaller subunits that would subsequently assemble into the polymer on the surface. This approach has successfully been used to steer the assembly of organic molecules into 1D structures. The 1D molecular wires so created are mostly like 'ribbons', due to the fact the molecules tend to lie flat on the surface to maximize substrate-adsorbate interaction. The on-surface synthesis of molecular wires with more complex geometrical shapes, such as tubular or cylindrical, has only been described for the case of carbon nanotubes, and only on surfaces covered with catalytic nanoparticles or on silicon carbide surfaces, where the constituent carbon for the nanotube growth arises from bulk segregation. The aforementioned ideal situation in which molecular subunits assemble into 1D structures with cylindrical symmetry has not been described so far in the literature. In this work we describe the growth of 1D tube or cylinder-looking structures obtained after deposition of a metallo-porphyrin (Zn-Tmp) on the noble-metal surfaces Au(111) and Cu(100) by vacuum sublimation with the substrate held at room temperature (RT). Our experiments indicate that the 'nanotubes' are only a meta-stable structure, since they disassemble into flat-lying Zn-Tmp monomers upon annealing to 500 K. The disassembled Zn-Tmp adsorbates are tightly bound to the surface, as evidenced by the fact that they can be easily imaged by Scanning Tunnelling Microscopy even at room temperature, and the difficulty to manipulate them even under the harsher tunnelling conditions. Two mechanisms for such a phenomenon will be discussed.

8:20am **NS-MoM2 Interactions of Nanoparticles with a Dewetting Solid Film**, *J.S. Palmer, P. Swaminathan, J.H. Weaver,* University of Illinois at Urbana-Champaign

Capillary forces at the interfaces between particles, fluids, and solid substrates lead to the self assembly of structures during liquid film evaporation. We introduce a related process that involves nanoparticle assembly during dewetting and sublimation of a solid thin film. Metal atoms evaporated onto condensed inert gas films form clusters that can be delivered to a substrate of choice by subliming the film. Warming leads to hole formation at defects or grain boundary triple points and surface tension causes hole spreading and film breakup. For Au on Xe we show that, as for liquids, the physics underlying aggregation involves capillary forces as films dewet amorphous carbon substrates. The cluster mobility reflects the dynamics of the boundary of the retreating solid film and results in the formation of nanostructures, whose sizes and densities are controlled by adjusting the film thickness. Kinetic Monte Carlo simulations reproduce the experimentally-observed shapes and distributions and provide insight into the particle assembly process. In contrast to liquid films, particle motion is limited to the dewetting front where capillary forces drive cluster aggregation. This nanoparticle assembly process is not limited to noble metals on rare gas films but occurs in a variety of systems where particles are deposited onto thin volatile films, e.g. II-VI semiconductor particles and condensed CO_2 layers.

8:40am **NS-MoM3 Solidification and Melting of Mercury in Nanotube Cavities**, *A. Kutana, K.P. Giapis,* California Institute of Technology

We present molecular dynamics simulations of solidification and melting of mercury nanoparticles inside carbon nanotubes as a function of nanotube diameter. The mercury liquid is described by an ab initio potential for mercury dimer, rescaled to match the experimental density at 300K and melting point of mercury. The liquid-wall interactions are optimized based on the wetting angle of a mercury drop on graphite. The liquid-solid phase transition is marked by a discontinuity of the energy when monitored as a function of temperature. A significant depression of the melting point of mercury nanoparticles is predicted as the nanotube diameter decreases from 5.4 nm to 1.4 nm. The transition is less pronounced in smaller tubes, as the limit of one-dimensional system is approached. Below the freezing point, the crystal structure of solid nanoparticles is represented by a set of concentric shells in small nanotubes, while larger nanotubes show multiple domains with bulk crystal structure. Above the melting point, the central part of the nanoparticle is amorphous, while the liquid within a few atomic layers of the wall remains partially ordered. Near-wall liquid density profiles exhibit oscillation with the amplitude that increases as the tube diameter becomes smaller. In overall, the ordering inside nanotube cavities is stronger in comparison with the liquid near a flat wall. The contact angles are predicted to be larger inside nanotubes than on flat graphene sheets, indicating less favorable conditions for wetting on concave surfaces.

9:00am **NS-MoM4 Template Guided Self-Assembly of Metal Oxide Quantum Dots**, *Y. Du, I. Lyubinetsky, D.R. Baer,* Pacific Northwest National Laboratory, *J.F. Groves,* University of Virginia

This talk reports the use of focused ion-beams (FIB) to direct the self-assembly of Cu_2O quantum dots (QDs) on $SrTiO_3$ (100) substrates via point implants of Ga^+. Oxygen plasma-assisted molecular beam-epitaxy (OPA-MBE) is used to grow Cu_2O QDs. It is found that, for high FIB implant dose ($>10^{18}$ ions/cm^2) and large interdot spacing (~1000 nm), multiple QDs can be formed preferentially on the edges of FIB modified pits. For lower doses ($<10^{15}$ ions/cm^2) and/or smaller interdot spacings (~100 nm), individual QDs nucleate first within the pits. Under carefully controlled conditions, the separation and arrangement of the Cu_2O QDs follows the FIB patterned template. This study finds that the FIB directed self-assembly technique works for different FIB doses, interdot spacings and deposition thicknesses, suggesting that this method is robust and flexible. Examination of QD growth on low-dose implant surfaces revealed a multi-step growth process. To further interpret the low dose implant results, calculations of total free-energy changes have been performed to study the differences between nucleation on a flat substrate surface and nucleation within a surface pit. This analysis shows that nucleation within a pit is almost always energetically favorable. In some special cases, assuming the pits have an inverted pyramidal shape, calculations show that island formation within the pits lowers the system total free-energy from the beginning of growth, i.e. there is no critical radius or energy barrier before a stable nucleus can be formed. Continued study of directed self-assembly of metal oxide quantum dots should lead to better understanding of the creation of well ordered, precisely controlled, high density QD arrays, ultimately contributing to the development of next generation nanoelectronic, magnetic, and optical devices.

9:20am **NS-MoM5 A Generic Method for Coupling Quantum Dots to Biomolecules**, *A.S. Blum, C.M. Soto,* Naval Research Laboratory, *C.D. Wilson,* SAIC, *K.E. Sapsford,* George Mason University, *J.L. Whitley,* SAIC, *A. Chatterji, J.E. Johnson,* Scripps Research Institute, *B.R. Ratna*, Naval Research Laboratory

We present a new technique that allows the generic coupling of quantum dots to any biomolecule without the use of specially engineered domains. Using well-developed chemistry short histidine-containing peptides can be conjugated to lysine-containing protein scaffolds to controllably attach quantum dots (QDs) to the scaffold. This technique was used to bind quantum dots from aqueous solution to both chicken IgG and Cowpea mosaic virus (CPMV), a 30 nm viral particle. These quantum dot-protein assemblies were studied in detail. The IgG-QD complexes were shown to retain binding specificity to their antigen after modification. The CPMV-QD complexes have a local concentration quantum dot greater than 3000 nmol/mL, and show a 15% increase in fluorescence quantum yield over free quantum dots in solution.

9:40am **NS-MoM6 Luminescent Nanocrystals Labelled Beads for Directed Patterned Assembly**, *E. Fanizza,* Università di Bari, Italy*, L. Malaquin,* LPN CNRS, France*, T. Kraus, H. Wolf,* IBM Research GmbH, Zurich Research Laboratory, Switzerland*, M. Striccoli, A. Agostiano,* **M.L. Curri**, CNR Italian National Research Council IPCF, Italy

Polystyrene (PS) beads have been functionalized with luminescent (CdSe)ZnS core shell type nanocrystal (NC), generating a versatile core-shell type of material, able to combine the size dependent optical property of (CdSe)ZnS NCs with the versatility and prompt processability for assembly of micrometer sized PS beads. The novel colloidal nanocomposite system has been fabricated by using a layer-by-layer (LbL) approach.[1] Polystyrene beads have been firstly coated with polyelectrolyte (PE) layers and subsequently functionalized with fluorescent (CdSe)ZnS nanocrystals, synthesized following established procedure with minor adjustment. The obtained luminescent NC functionalized beads have been subsequently assembled onto patterned polydimethylsiloxane (PDMS) substrate by means of a capillary force induced process,[2] thus providing an original example of physical directed assembly. Here the patterned stamp, fabricated with a top-down approach, act as template for the construction of well-defined discrete nanoscale structures at two- and three dimensions. The ordered fluorescent nanoparticle arrangement has been successful preformed by using two different patterns. A precise positioning of the PS functionalized beads has been achieved. Such original structures based on colloidal particles, which now carry the unique spectroscopic signatures of the luminescent NCs, are of considerable interest either in optoelectronic systems, and the ability to assembly and precisely positioning the functionalized nano-object into ordered assembly the venue to their prompt integration in bio-engineering due to their potential application in multiplexed bioassays, medical diagnostic, drug screening.[3]

[1]V. Salgueriño-Maceira, F. Caruso, L. Liz-Marzan, J. Phys. Chem. B, 2003, 107, 10990; M. Correa-Duarte, A. Kosiorek, W. Kanduloski, M. Giersig, L. Liz-Marzan, Chem. Mater., 2005, 17, 3268, F. Caruso, M. Spasova, A. Susha, M. Giersig, R.A. Caruso, Chem. Mater. 2001, 13, 109; H. Singh, O.E. Laibinis, T.A. Hatton, Langmuir 2005, 21, 11500; D. Wang, A. L. Rogach, F. Caruso, Nano lett. 2002, 2, 857

[2]T. Kraus, L. Malaquin, E Delamarche, H Schmid, N.D. Spencer, and H.Wolf. Adv. Mater., 2006, 17, 2438. L. Malaquin, T. Kraus, H. Schmid, E. Delamarche, H. Wolf, manuscript submitted.

[3]The partial support of the EC-funded project NaPa (Contract no. NMP4-CT-2003-500120) MIUR SINERGY programme (FIRB RBNE03S7XZ) is gratefully acknowledged.

10:20am **NS-MoM8 Selecting and Driving Nanoscale Assembly in Monolayer Films through Tailored Intermolecular Interactions**, *T.J. Mullen, C. Srinivasan, M.J. Shuster, J.N. Hohman, M.W. Horn, A.M. Andrews, P.S. Weiss*, Penn State University

Active chemical surfaces that selectively capture and separate specific analytes from competitive environments are useful for detecting and isolating complex biological molecules as well as small molecules found in chemical weapons and toxic industrial waste. The development of self- and directed assembly strategies is key to the fabrication of molecularly precise structures for such applications. As the dimensions of patterned surface structures have decreased to the sub-100 nm scale, traditional lithographic techniques have not demonstrated the ability to fabricate reproducible structures over larger areas with molecular-scale organization. We have developed, utilized, and evaluated self- and directed nanoscale assembly strategies to fabricate, to register, and to functionalize chemical surface structures at the supramolecular 1-100 nm scale. We will highlight two hybrid soft-lithography strategies - microdisplacement printing and microcontact insertion printing - where monolayers with specifically tuned intermolecular interactions were engineered and the chemical and physical properties of the resulting patterned structures were characterized on both the ensemble and the molecular scales. Additionally, we will demonstrate that these chemical films can be functionalized with small-molecule probes that selectively capture large biomolecules while resisting nonspecific binding.

11:00am **NS-MoM10 Assembly and Transfer of Functional Nanoparticle Arrays**, *H. Wolf, T. Kraus, L. Malaquin, A. Decker, H. Schmid,* IBM Research GmbH, Zurich Research Laboratory, Switzerland*, N.D. Spencer*, Swiss Federal Institute of Technology, Switzerland**INVITED**

Nanoparticles provide multiple properties that make them potential building blocks of novel optical and electronic devices. Significant progress has been made in the bulk synthesis of nanoparticles with controllable composition, shape, structure, and size. However, in general the products are disordered colloidal suspensions or powders, whereas devices usually require ordered arrangements of particles on a substrate. Self-assembly processes can order large numbers of particles in parallel on surfaces, but they usually provide only dense regular arrays without the long-range order required for large-scale integration. In addition to particle order, also the particle-substrate junction is often crucial for device performance, and the reliable creation of well-defined particle-surface interfaces remains a challenge. We will show in this talk how directed self-assembly can be combined with a transfer step to produce arbitrary patterns of nanoparticles on a substrate. The combined process, called "SATI" for "Self-Assembly, Transfer and Integration", maintains the advantages of self-assembly but relaxes the requirements on the substrates, and is more flexible than single-step self-assembly. Directed self-assembly uses a topographically or chemically patterned template to assemble nanoscale objects. Compared to template-free self-assembly it has less requirements and restrictions with regard to the assembled object. It is not limited to regular patterns but still a highly parallel process. Directed self-assembly comes at the cost of producing a template. However, the template can be re-used or fabricated as a low-cost replica of a topographical master made by standard top-down patterning techniques. After assembly, the nanoscale objects are printed in the transfer and integration steps onto the target substrate, retaining the parallel nature of the process. The transfer requires to tailor adhesion in a way that makes the nanoparticles leave the template or intermediate carrier and stay on the target substrate. Further processing of the arrays allows to exploit the specific particle functionality, e.g. as a catalyst, optical activity, or simply as a resist.

11:40am **NS-MoM12 Cyanuric Acid and Melamine on Au(111): Structure and Energetics of Hydrogen Bonded Networks**, *W. Xu, M. Dong, H. Gersen, E. Rauls, T. Linderoth, F. Besenbacher*, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark

Supramolecular chemistry based on non-covalent interactions is a powerful synthetic tool for the preparation of complex molecular architectures. In particular hydrogen bonds are considered to be useful for controlling molecular self-assembly due to the reversibility, specificity, directionality, and co-operative strength of this class of interactions. The highly specific interaction between the molecules Cyanuric Acid (CA) and Melamine (M), based on three complementary hydrogen bonds, is a key structural motif in supramolecular chemistry. Here we investigate the adsorption and co-adsorption M and CA on a Au(111) surface under Ultra High Vacuum conditions using Scanning Tunneling Microscopy with submolecular resolution. In addition to the expected structure with a 1:1 CA:M ratio, we identify a novel phase with 1:3 CA:M ratio formed upon sequential deposition. The hierarchy of binding energies for homo and heteromolecular dimers as well as for the observed network structures has been evaluated through theoretical modeling by the SCC-DFTB method, rationalizing the experimental observations.

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