

Synthesis and Self-assembly of Nanomaterials

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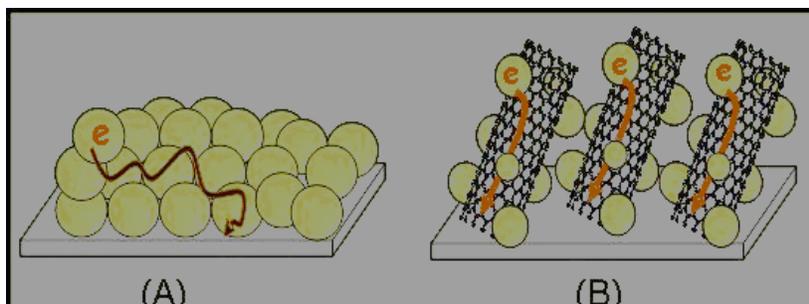
A combination of advanced synthesis and assembly of molecular and nanoscale building blocks is one of the most promising routes to new macroscopic hybrid materials with unique and complex functionalities. During the past decade, many molecular and nanoscale building blocks have been synthesized with different morphologies and compositions, including conjugated polymers, inorganic nanocrystals, nanowires and nanotubes. Despite the continued advances in various aspects, many challenges remain to be addressed at different stages en route to applications. This full day workshop, organized by Xiao-Min Lin (CNM) and Moonsub Shim (UIUC), focused on how to create functional nanoscale building blocks in a more systematic and controllable fashion, as well as how to engineer the interaction between the building blocks which would lead to unique assembly pathways. This symposium aimed to stimulate interactions and build momentum among a diverse group of experts working on synthesis and assembly of molecular and nanoscale systems, with the ultimate goal of initiating new research directions in this field.

Xiaogang Peng, from University of Arkansas, kicked off the workshop by highlighting some of the latest development in colloidal semiconductor quantum dots. Using chemical reactions at high temperatures (>200 degrees C) in non-polar solvents, he forms different types of high quality colloidal nanocrystals. He emphasized that although water is not usually added into the reaction systems, it has been identified as a major reagent in several of these reactions. Water was found to affect the size, shape, and size/shape distribution of the resulting nanocrystals. The absence of water substantially changes the reaction pattern for some reaction systems. He also described a specific example of Mn-doped ZnSe quantum dot (Mn:ZnSe d-dots) formation using a nucleation-doping strategy. The resulting d-dots displayed high (near 50%) photoluminescence (PL) quantum yield (QY), which was achieved by the controlled formation of small-sized MnSe nanoclusters as the core and a diffused interface between the nanocluster core and the ZnSe overcoating layers.

Bartosz Grzybowski (Northwestern) discussed how the peculiar nature of electrostatic and photoinduced dipole-dipole forces acting between nanoscale components can mediate their self-assembly into various superstructures and materials. He showed how the interactions underlying self-assembly can be controlled and understood in quantitative detail, and how they can be tailored to synthesize unusual higher-order architectures: ionic-like crystals of nanoparticles, crystalline aggregates that can be assembled and disassembled by light, as well as extremely durable and yet very flexible metallic structures. One specific example detailed the functionalization of gold nanocrystal surfaces with linkers that incorporate a photoswitchable azobenzene unit. This allowed for precise control of the assembly process and of the dimensions of the forming spheres by ultraviolet (UV) light. These materials display a range of novel optical, electrical and mechanical properties.

Ken Suslick from the University of Illinois, Urbana-Champaign, unable to attend due to illness, was ably represented by his student Richard Helmich. He described the group's latest efforts in re-examining the use of ultrasonic spray pyrolysis (USP) for materials synthesis. Although USP, and spray pyrolysis more generally, are well-established techniques that remain in heavy industrial use, the chemical reactions that take place are generally within solid particles formed after solvent evaporation. By the introduction of high boiling liquids or relatively low melting salts, they have found new and interesting approaches to the USP synthesis of semiconductor quantum dots, unusual morphologies of metal oxides and sulfides, and micro- and macro-porous carbon networks.

Using nanoscale materials for photovoltaic applications is currently a very active research field. Prashant V. Kamat, University of Notre Dame, detailed research efforts in his lab using photoactive hybrid nanostructures with tailored light harvesting properties. The unique approach he adopted is using semiconductor nanoparticles and carbon nanotubes as active media. The ability of these materials to convert light energy into electrical energy or chemical energy makes them useful for designing solar cells. Single wall carbon nanotubes (SWCNT) can be successfully assembled on conducting carbon paper and conducting glass electrodes using electrophoretic deposition. The photoactive semiconductor nanoparticles (TiO_2 , ZnO) are then dispersed on conducting scaffold of SWCNT. An increase of photoconversion efficiency (IPCE) observed with the composite architecture represents the beneficial role the carbon network plays in facilitating charge collection and charge transport in semiconductor nanostructures. He showed that the photoresponse of TiO_2 nanoarray can be extended into the visible by attaching CdSe quantum dots. These composite semiconductor nanostructures have been successfully employed in photoelectrochemical cells for generating photocurrent under visible light excitation. He also discussed the salient features of nanowire/nanotube architecture in improving the efficiency of light harvesting assemblies.



Scheme 1. Electron transport across nanostructured semiconductor films: (A) In the absence and (B) in the presence of a nanotube support architecture.

As a condensed matter theorist who focuses on computer simulation of molecular and nanoscale systems, Amit Chakrabarti from Kansas State University has a unique prospective on how to tackle the problem on self-assembly phenomena. His current work focuses on understanding the driving force for small particles to form larger clusters when the small particle system becomes, by some manner, unstable. From a broad

perspective, the “particles” can be atoms, ions, or molecules, as well as colloidal particles, aerosols, and nanoparticles. The transition from a dispersed phase to clusters can include the formation of precipitated crystalline solids from solutions as well as the formation of fractal aggregates in colloids and aerosols. Formation of condensed, crystalline solids or open, random aggregates represent the equilibrium and non-equilibrium limits of this transition. In the context of this grand problem, he presented some recent results from simulations carried out by his group on aggregation and superlattice formation in surface ligated nanoparticles.

After the coffee break in the morning, the workshop continued with two talks focus on self-assembled molecule systems. However, their approaches and potential applications are vastly different. In the talk presented by Luping Yu from University of Chicago, the focus was on the synthetic approach to engineering molecular species for molecular electronic applications. He pointed out there are serious challenges for the assembly of molecules into electric circuits, and reliable measurements on electron transport of single molecules in a true circuit configuration are still rare. His lab has



Figure 1. Luping Yu of the University of Chicago.

synthesized simple conjugated diblock co-oligomers that exhibit pronounced rectification effects. These p-n junction types of molecules incorporate an electron-rich dithiophene segment and an electron-deficient dithiazole segment. By controlling the assembly in two dimensional films, the rectifying direction of diode molecules can be controlled in a two-terminal circuit configuration. Prof. Yu concluded his talk by pointing out the opportunities that CNM presents in advancing organic nanoelectronic research.

Michael R. Wasielewski (Northwestern University) introduced several different experimental techniques to explore the fundamental structural and electronic requirements for efficient energy and charge transfer in extended, ordered assemblies of donor-acceptor molecules. He described several new molecules and materials produced by a combination of chemical synthesis and self-assembly that use energy and charge transport strategies inspired by natural photosynthesis. One example was photoexcitation of a series of donor-bridge-acceptor (D-B-A) systems. The time-resolved EPR (TREPR) studies of the photogenerated radical pairs (RPs) show that, above a critical temperature, the radical pair-intersystem crossing mechanism produces spin-correlated radical ion pairs having electron spin polarization patterns indicating that the spin-spin exchange interaction in the radical ion pair is positive, $2J > 0$, and is temperature dependent. This temperature dependence is most likely due to structural changes of the bridging molecule. Charge recombination in this system exhibits a spin-polarized signal similar to that observed in photosynthetic reaction-center proteins and some biomimetic systems.

The afternoon session concentrated on self-assembly of one-dimensional nanoscale building blocks. Bret N. Flanders (Oklahoma State University) introduced a directed electrochemical nanowire assembly (DNA) technique to fabricating metallic nanowires and interconnecting them with external circuitry. He showed that he can direct single crystalline metallic nanowire growth between electrodes and interconnect between on-chip electrodes. He identified that the dendritic solidification as an important component of the DNA process, and exploited this mechanism to realize diameter-tunable nanowire growth. He pointed out that the experimental parameter that provides this control is the frequency ω of the alternating voltage that induces the DNA process. Increasing ω increases the metal cation concentration gradient at the wire-solution interface, thereby increasing the growth velocity of the wire. In turn, the anti-correlation between growth velocity and tip-radius, a fundamental characteristic of dendritic solidification, gives rise to a wire of reduced diameter. For indium wires, increasing ω from 0.5 to 3.5 MHz increases the growth velocity of the wires from 11 to 78 $\mu\text{m/s}$ and reduces their diameter from 770 to 114 nm. Gold wires exhibit diameter-tunability that ranges from $\sim 1 \mu\text{m}$ down to 45 nm. Thus, it is possible to tune the wire diameter from the microscale down to the nanoscale. This combination of capabilities will enable the future interrogation of the intrinsic transport properties of nanomaterials.

Robert J. Hamers from University of Wisconsin-Madison described the synthesis, functionalization, and electrocatalytic properties of vertically aligned carbon nanofibers (VACNF) and VACNF-nanoparticle hybrid materials. He pointed out that VACNFs consist of nested cones of graphene sheets, such that the sidewalls of the nanofibers have large amounts of edge-plane exposed. This gives them unique properties that are quite distinct from concentric multiwalled nanotubes. His group has been investigating the chemical functionalization and electrical properties of VACNFs, with the goal of combining the high stability and high surface area of carbon with novel types of catalytic materials that can be linked to the VACNF surface. They modified the surface using a chemical functionalization reaction with organic alkenes in the presence of ultraviolet light. This provides a way to covalently functionalize and photopattern the chemical groups on the nanofibers. They used this approach to link redox-active proteins such as cytochrome c to the nanofiber surfaces, demonstrating that molecular redox agents linked to VACNFs retain good electrocatalytic properties. The photochemical functionalization of VACNFs with molecules that expose carboxylic acid groups greatly enhanced the electroless deposition of Au and Pt onto nanofibers. By controlling the conditions it is possible to create structures in which very large numbers of Pt nanocrystals of $\sim 8 \text{ nm}$ diameter are bonded to the nanofibers. Even though there is an organic linkage present, measurements of the electrocatalytic oxidation of methanol show very good redox properties. Comparison with a conventional Pt/C catalyst support show similar catalytic currents, but the Pt/VACNF arrays achieve this using 40 times less platinum.

Masaru Kuno from the University of Notre Dame described recent investigations into the ensemble and single-wire properties of solution based semiconductor nanowires (NWs). They have investigated the absorption cross section of the wires in order to determine how well they absorb light. By using ensemble transient differential absorption measurements, they have explored the relaxation mechanisms in this system.

This is followed by investigations of their emissive properties through single NW optical measurements. Such studies reveal strong polarization anisotropies in the absorption and emission. Furthermore, the group's recent work has focused on the size and frequency dependence of the polarization anisotropy to probe and ultimately deconvolute contributions from dielectric contrast as well as confinement effects. Additional single wire studies reveal unexpected optical heterogeneity both in the emission intensity and spectrum of individual wires. In effect, the wires appear to exhibit fluorescence intermittency as well as spectral diffusion. Applying an external electric field induces unexpected spatial and intensity modulation of the NW emission. He proposed a model based on mobile surface charges to explain these observations as well as the aforementioned emission intermittency and spectral diffusion. The hypothesis is also interesting in that it may also have implications for fluorescence intermittency in other systems such as colloidal quantum dots.

The feedback from the both attendee and speakers after this workshop were unanimously positive. The central theme of self-assembly and self-organization permeated in many molecular and nanoscale systems. Therefore, it is crucial to bring researchers from many disciplines together to discuss the variety of different systems they are working on. Understanding these phenomena can help to create new generations of materials using bottom-up approaches.