Soft Nanostructured Interfaces

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In this project, students will first synthesize inorganic nanomaterials, like semiconductive quantum dots or metallic nanoparticles in the chemistry department using standard air-free or aqueous colloidal synthesis procedures. The surface of each nanoparticle will then be modified with an assortment of biomaterials, such as; oligonucleotides (ssDNA), polypeptides, or engineered proteins, using a number of surface chemistry approaches. Then, students will utilize the molecular recognition capabilities of the biological interface to induce 'self-assembly' of the nanoparticles into larger multi-particle assemblies. Some of the main goals in this project include; controlling the interparticle spatial properties (distances), tailoring assembly morphology, phase, or symmetry, and to monitor assembly in-situ. The role of the underlying nanoparticle shape will also be explored. This research thus encompasses the design, fabrication, and implementation of these 'biomimetic' nanoparticles. Due to its broad scope, this project calls for graduate student who wishes to explore both empirical and theoretical experiments in materials chemistry, soft condensed matter physics, and chemical/biological engineering.

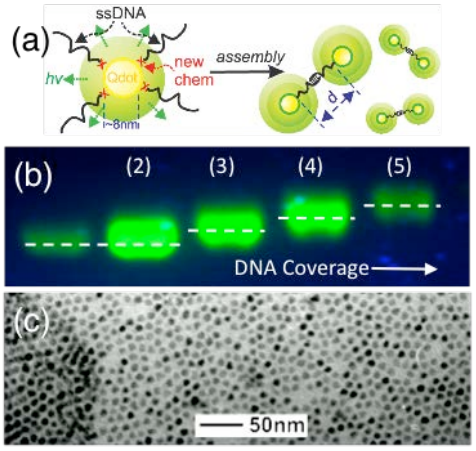

Fig.1: (a) A schematic of the DNA-modified qdots fabricated. (b) Gel result showing tailored DNA-coverage. (c) TEM micrograph of the large qdots. Maye Group. Modified from Reference 1-4.

While the inorganic synthesis of the nanoparticles uses established "hard" chemistry and physics, the functionalization of the nano-interface with biomaterials is less understood by comparison, and involves understanding and modeling "soft" interactions that occur when many biomaterials are bound to a nano-interface in close proximity. Interaction forces, molecular crowding, and cooperative phenomena are often observed. These soft interactions must be both overcome, and harnessed, if successful control of the self-assembly behavior is to occur.

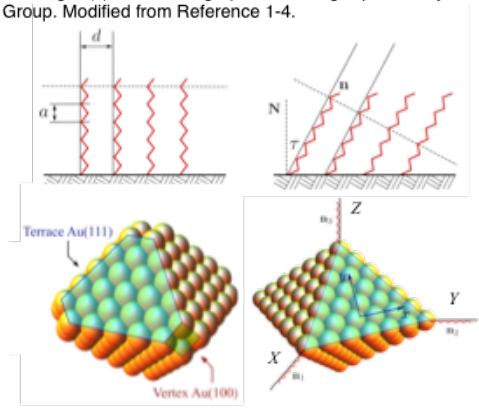

Fig.2: (Top Panel) A schematic of thiol-terminated Alkyl chains at a surface (Top Panel), and illustration of gold nanoparticles with octahedral symmetry. Modified from Reference-5.

In addition to synthesizing the nanomaterials studied, students will also perform modeling of the orientation of the organic or biological monolayer at the nano-interface using models such as the Ginzburg-Landau model (5). The dependence on monolayer phase behavior will be related to the underlying nano-interface faceting, symmetry, and binding chemistry.

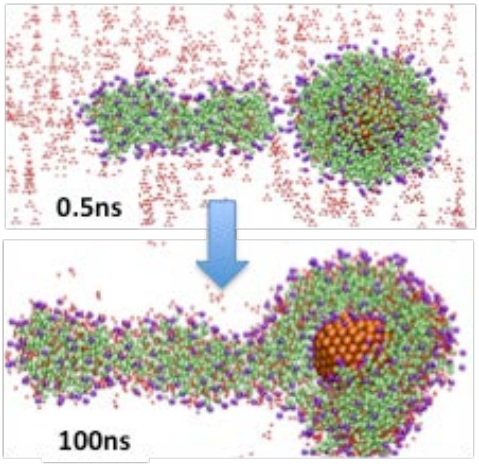

Fig.3: Recent molecular dynamic simulations Modeling surfactant/nanoparticle interactions. See Reference-6 (Sureshkumar Group).

The functionalization and assembly process will also be studied using molecular dynamics simulations. These studies give a time resolved picture that allow for better understanding of how materials are organized at the interface, as well as interactions between the molecules, as well as solvent interactions (6).

Working on this project will allow the student to gain valuable experience in the following fields:

- **Nanomaterial Synthesis & Functionalization**: Synthesis of nanomaterials via traditional colloidal routes as well as modern inorganic and organometallic routes. These particles will be functionalized with; Self-Assembled Monolayers (SAMS), macromolecules/polymers, oligonucleotides, polypeptides, and engineered proteins (Maye Group, Fig.1, Ref 1-4).
- **Morphological & Interfacial Characterization**: Nanoparticle morphology will be studied using: Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Powder X-ray Diffraction (XRD), Atomic Force Microscopy (AFM), UV-visible Spectroscopy (UV-vis), and Fluorescence Spectroscopy. The organic or biological interface will be studied using Infrared Spectroscopy (FTIR), 1D & 2D Nuclear Magnetic Resonance (NMR), dynamic light scattering (DLS), and gel electrophoresis.
- **Self-Assembly*:*** The self-assembly will be monitored and characterized in-situ using dynamic light scattering (DLS), small angle X-ray Scattering (SAXS), TEM, confocal microscopy, and Forster Resonance Energy Transfer (FRET).
- **Modeling the Effect of Nanoparticle Shape on Assembly**: It is expected that the faceted nature of the nanoparticle surface influence the ordering of nanoparticle coatings. In this project we will model and examine the role of edges and vertices as preferential locations for binding and the effect on self-assembly routes (Figure 2, Bowick Group, Ref 5.).
- **Molecular Dynamic Simulations**: The organization of surfactants, monolayers,and biomaterials at the nanoparticle interface will also be modeled using molecular dynamic (MD) simulations. Using coarse-grained (CG) potentials the potential mean force (PMF) values will be calculated, which allow or insights into the time-resolved organization of the coatings at the nanoparticle interface. These new simulations will be used to evaluate long-ranged electrostatic interactions, and solvent polarizability. (Fig. 3, Sureshkumar Group, Ref 6.)

References: (1) *Chem. Mater.* **2011**, 23, 4975–4981; (2) *Langmuir,* **2011**, *27,* 4371–4379; (3) *Nature Nanotech.***, 2010,** *5,* 116-120; (4) *Nature Mater.*, **2009**, *8*, 388-391; (5) arXiv:1111.2244 [cond-mat.soft] (to appear in EPL Letters); (6) *Langmuir* **2012**, (In-Press, dx.doi.org/10.1021/la203745d)