CNM Workshop 7: NanoBio Interfaces: From Materials Design to Complex Systems

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Nature possesses the ability to design highly functioning, regenerative materials that cover every imaginable process and physical characteristic desired in modern materials. Energy production and storage, mechanics, and catalysis are but a few of these processes that nature handles well. This workshop identified many overlapping themes at the NanoBio interface that continue to produce a wide spectrum of materials attributing their functional inspiration from nature. The eight invited speakers highlighted their current research regarding the biological systems they use or have been inspired by in producing new materials for energy. Younger faculty and scientists offered a fresh perspective in their respective fields together with more established speakers who offered very detailed insights into their areas of expertise. This led to very engaging scientific discussions as well as conversations regarding the establishment of new user collaborations.

The first two speakers gave their perspective on fuel cell development derived from natural photosynthetic processes. Ana Moore (University of Arizona), deeply inspired by photosystem II (PSII), utilized the well-established knowledge of the tyrosine Z-histidine pair (TyrZ/His190) mediated charge transfer between the photo-oxidized donor ($P680^{+\cdot}$) and the oxygen evolving complex (OEC) to develop a synthetic analog consisting of a porphyrin covalently attached to a benzimidazole-phenol pair mimicking the TryZ-His190 pair. When this synthetic analog is attached to titanium dioxide (TiO_2) nanoparticles and is excited with visible light, the PSII inspired system undergoes charge separation with the electrons being injected into the semiconducting metal oxide and the hole residing on the phenol. EPR and transient absorption were used to highlight one of the key components found in PSII, proton coupled electron transfer (PCET). Prof. Moore illustrated this event with her elegant system highlighting the importance of PCET to mediate and tune the photoinduced properties of fuel cell materials. Shankar Balasubramamanian (CNM) followed this presentation with a different approach for solar hydrogen generation. A majority of research regarding bio-related fuel cell materials focuses on the catalytic active site. Dr. Balasubramanian utilizes a TiO_2 nanoparticle decorated with platinum (Pt) nanoparticles as the photo-catalytic active site for H_2 production. Bacteriorhodopsin (bR) is a transmembrane protein found in photosynthetic bacteria that pumps protons across the cell membrane when illuminated with visible light. By coupling bR to Pt/TiO_2 hydrogen production is dramatically increased upon illumination. The bR simply serves as a pump to bring protons to the catalytic surface of the inorganic material where it is catalyzed to H_2. Dr. Balasubramanian clearly indicated that the production was due to the presence of bR on the surface.

The focus then shifted to soft matter and exploring the biomolecular phenomenon of self-assembly and its utility in the production of novel materials. J. D. Tovar (Johns Hopkins University) discussed research that implements the covalent linking of pi-conjugated molecules to peptides designed to self-assemble

via beta-sheet formation. The peptide was shown to self-assemble into a highly organized one dimensional electronically delocalized structure. By processing these materials via a sheer flow process, highly stable noodle-like structures were generated and were comprised of aligned nanofibers. The alignment was shown to have a significant enhancement on the conductivity of the material in the direction of the fiber alignment. Electrostatic interactions play an important role in designing self-assembled peptide materials. Matthew Tirrell (Director of the Institute for Molecular Engineering at the University of Chicago) presented his work on multivalent interactions with highly charged polymers. He exhibited how the attraction between a polyelectrolyte and multivalent ions results in the collapse of the material leading sometimes to precipitation but also the formation of fluid complex coacervate phases. This observation was used to create new self-assembled materials such as physically cross-linked hydrogels.

Coupling peptide self-assembly to peptide interactions with inorganic materials has lead to the development of many bottom-up materials. The work of Rajesh Naik (Wright Patterson Air Force) was presented by his colleague Milana Vasudev. Phage display is a technique that utilizes viruses to identify peptides that are overexpressed in the presence of foreign materials. Specific sequences with high binding affinities for specific materials have been identified. Dr. Vasudev illustrated the utility of these peptide sequences combined with self-assembly properties to generate bottom-up biomolecule-inorganic hybrid nanostructures. One fascinating phenomenon observed was the generation of an optically active chiral gold molecule simply by immobilizing an alpha helical peptide on the surface of a gold nanoparticle. The plasmon resonance was shown to adopt a chiral signature in the circular dichroism spectrum of the Au-peptide material. These unprecedented chiroptical properties have tremendous implications in the design of metamaterials.

The final three talks focused on the engineering of existing biological systems to afford novel or enhanced properties. Jared Lewis (University of Chicago) presented the redesign of metalloenzymes by incorporating unnatural amino acids into an existing active site to tune or generate new catalytic properties. These artificial enzymes were designed with the intention of enhancing reaction selectivity and generating tandem reaction sequences. An active site that could catalyze and control polymer formation and growth was also discussed. From The Molecular Foundry, Caroline Ajo-Franklin presented her work on engineered bi-directional electronic communication between living cells and non-living systems. By incorporating a series of MTR proteins (multi-heme containing electron transfer proteins) into E. coli, a transmembrane electron transfer pathway was generated giving the cell the ability to reduce metal ions, solid metal oxides, and electrodes. This biological-to-electronic adapter has implications in the development of programmable, self-replicating cellular electronics. Milan Mrksich (Northwestern University) presented some fascinating work where patterned substrates were used to control cell-shape which in turn controls cell function. Cells like to find surfaces to stick to; by patterning different shapes for the cells to adsorb to, the cells adopted those shapes. The different shapes were shown to have a significant influence over the mechanical properties of the cytoskeleton. Using mesenchymal stem cells, a star shaped cell had a tense cytoskeleton and differentiated into bone cells whereas a flower-shaped cell, which produces a less tense cytoskeleton, differentiated into fat cells. This reveals that shape and possibly some external forces dictate cell function.