Computational Study of the Self-Assembly, Structure, and Optics of Bio-Inspired Nanoparticles

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Nanoparticle self-assembly is relevant to engineering materials for a wide array of applications including optics, catalysis, biomedicine, sensing, and electronics. Directed self-assembly of nanoparticles near surfaces/interfaces (e.g., in thin films, droplets in emulsion assembly) enables formation of 3-dimensional "supraparticle" assemblies that are used in optics and photonics applications. Such supraparticle assemblies produce structural colors by constructive interference of specific wavelengths of light as it moves through the assembled structure. The direct relationship between the assembled supraparticle structure and resulting optical properties requires structural characterization as a necessary step during the design of materials with tailored optical or photonic properties. Structural characterization of assembled nanoparticles is performed primarily using microscopy and small angle scattering techniques. While microscopy is beneficial for visualizing the nanoparticle assemblies, both transmission electron microscope, TEM, and scanning electron microscope, SEM, probe limited length scales. In contrast, small angle scattering techniques characterize structures over a broader range of length scales and present ensemble averaged information from the sample. Interpreting the small angle scattering output data, I(q) vs. q, typically requires fitting the scattering data with an appropriate analytical model that is relevant for the material under consideration; however, for supraparticle assemblies (e.g., high packing fraction, amorphous structure), the existing analytical models may be too approximate.

In the first part of this dissertation, I describe the development and application of molecular modeling and simulations to investigate nanoparticle self-assembly and optical properties as well as polymer solution behavior when confined within a nanoparticle assembly. Our work identified design rules governing nanoparticle self-assembly under shrinking spherical confinement mimicking a reverse-emulsion assembly process. I then describe a molecular simulation study probing the structure and dynamics of polymer chains in a solution confined within pores of a nanoparticle assembly. After that, I present our work combining coarse-grained molecular dynamics simulations of nanoparticle assembly with optical modeling to link the assembled nanoparticle structure to the resulting optical properties.

In the second part of this dissertation, I present my development of the computational method, 'Computational Reverse Engineering Analysis of Scattering Experiments' (CREASE) to analyze, interpret, and reconstruct structure from small angle scattering measurements of nanoparticle solutions, mixtures of nanoparticles, and concentrated solutions of core-corona shaped particles (e.g., micelles). I describe the development and validation of the CREASE method first and follow that with applications of CREASE to analyze small-angle X-ray scattering and small-angle neutron scattering results from nanoparticle mixtures and solutions. By incorporating

machine learning into CREASE, I demonstrate a significant reduction in analysis time for running CREASE, enabling high throughput analysis of scattering profiles using modest computational resources (e.g., an average laptop). Going beyond the determination of structure in solutions/mixtures of nanoparticles with known shape (i.e., form factor), I then describe my extension of CREASE to simultaneously determine both the assembled particle form (e.g., micelle core/corona dimensions) and the structure (e.g., spatial arrangement of micelles) in concentrated solutions of core-corona shaped particles (e.g., micelles).

In the third part of this dissertation, I combine CREASE with optical modeling (i.e., finite difference time domain, FDTD method) to quantitatively predict the color of nanoparticle-based materials. The combined CREASE-FDTD approach predicts quantitative color and optical response resulting from the structural arrangement of nanoparticles. I conclude this part of this dissertation by providing a proof-of-concept study that uses CREASE-FDTD in a high throughput manner to identify new materials with a desired coloration.

Overall, my dissertation presents application of coarse-grained models, molecular simulation, genetic algorithm, and machine learning to predict structure in materials comprised of nanoparticles and/or polymers and to connect that nanostructure to optical properties.