Revealing the Chemistry, Structure, and Self-Assembly of the Lead Sulfide Nanocrystal Ligand Shell through Small-Angle Neutron Scattering

by

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Abstract

Colloidal, semiconducting nanocrystals (NCs), or quantum dots, are composed of an inorganic core coated in an organic ligand shell and are of interest for next-generation sensing, photovoltaic, and computing devices. Successful integration of NCs into devices requires rigorous synthetic control and materials characterization. In pursuit of this goal, the impact of the inorganic core of NCs on devices has been thoroughly studied, where the size, composition, and monodispersity of the core determine the bandgap of NCs through quantum confinement effects. The organic ligand shell is also critical to the processibility, self-assembly, and functional properties of NCs, but the structure-property relationships of ligands are not well understood due to the insensitivity of common structural characterization methods to the ligand shell.

This thesis advances understanding of the structure and impact of the organic ligand shell coating the surface of semiconducting nanocrystals by studying the chemistry, structure, and self-assembly behavior of the ligand shell for the model system of lead sulfide (PbS) NCs. We apply a combination of experimental techniques and thermodynamic modeling, and in particular, leverage small-angle neutron scattering (SANS) to directly characterize the structure of the ligand shell, resolving details of NC surface termination, ligand shell thickness, and ligand shell solvation that cannot be seen with other methods.

This thesis highlights best practices for ligand shell characterization and new insights for the synthesis of NCs and design of NC SLs in our studies of PbS NCs. First, we show that the surface termination and ligand passivation of PbS NCs are sensitive to the post-synthetic purification method. Using a combination of SANS, ^{1}H-NMR, and optical characterization, we distinguish the core size, optical emission, and ligand exchange properties of PbS[$RNH_3^+Cl^-$] and PbS@$PbCl_x$ NCs. Then, we apply a suite of scattering techniques, including SANS and small-angle X-ray scattering (SAXS), to quantify how the colloidal structure of the ligand shell coating PbS NCs impacts interparticle interactions and self-assembly. We observe unexpected trends in the colloidal structure of the NC ligand shell, arising from curvature and solvent-dependent interactions, and find that the colloidal ligand shell structure correlates with the structure of self-assembled NC superlattices. Finally, we show that ligand entropy impacts the coherent orientation of NCs within close-packed NC superlattices.

Since SANS methods are nascent within the field of colloidal nanocrystals, this thesis documents the theory of scattering methods and presents an optimal experimental design framework for SANS studies. Using statistical information theory, we quantify how the uncertainty of the structural parameters describing the NC ligand shell varies with SANS experimental design. Ultimately, the experimental design framework provides a rational framework through which to navigate tradeoffs of cost, measurement time, and parameter certainty in SANS experiments.

This thesis advances understanding of the structure-property relationships of the organic ligand shell coating semiconducting NCs, pioneering SANS as a uniquely sensitive method to understand organic ligands. These studies lay the groundwork for future efforts of ligand shell design with unprecedented structural understanding through SANS.

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