Lead Sulfide Nanocrystal Ligand Structure and Its Influence on Superlattice Self-Assembly

by

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Abstract

Colloidal semiconductor nanocrystals (NCs) or "quantum dots" are used in next-generation optoelectronic devices such as photovoltaics, displays, photodetectors, and thermoelectrics. For deployment in these architectures, NCs are cast out into the solid state. Because the NC ensembles are monodisperse, they readily self-assemble into an ordered superlattice (SL). Commonly for PbS NCs, body-centered cubic (BCC), body-centered tetragonal (BCT), and face-centered cubic (FCC) phases are observed with varying degrees of NC orientation relative to adjacent SL sites. Predictive control over the organization of NCs into SLs with long-range order remains a challenge. In this Thesis, oleate-capped PbS NCs are used as a convenient, prototypical system to establish a predictive framework for NC SL formation with respect to newly identified and existing tuning parameters.

I first identify and fully characterize unbound/free ligand as an important, controllable parameter to continuously adjust SL symmetry with theoretically single-molecule resolution. Increasing either the bound or unbound ligand populations shifts the SL uniaxially from the BCC to FCC phase. A high free ligand fraction has implications for the ease of formation of oriented SLs via spin-casting. Next, I measure a universal distortion of SL symmetry when cooling from room to cryogenic temperatures in which the SL contracts along one axis while expanding along the other two, ultimately shifting towards the BCC symmetry. Both hysteresis and non-monotonic, surprising trends in unit cell volume are observed and rationalized. The distortion is delineated by thermal markers of the surface-capping ligands and is generalizable to other material systems.

I establish small-angle neutron scattering (SANS) as a valuable experimental tool for complete characterization of NC surfaces. In order to fit SANS data, I develop a model inspired by the NC structure sampled from molecular dynamics (MD) simulations and introduce a Markov chain Monte Carlo (MCMC) algorithm for efficient parameter inference and uncertainty estimation. I quantify an epitaxial monolayer of $PbCl_x$ on the surface of PbS NCs synthesized from a large excess of $PbCl_2$ instead of from PbO. This elucidation reconciles sizing curves from the literature and explains

the suitability of a specific NC synthesis for different applications.

Finally, I extend the SANS method to measure the structure factor of semi-dilute PbS NC dispersions and liken the interactions to that of a square well fluid. The data-fitting yields a repulsive core size larger than the physical NC core diameter which stems from a densely-packed ligand layer near the NC surface. I also measure a weak attractive strength $\sim 1\, k_{\mathrm{B}}T$. This novel understanding of ligand-mediated NC interactions is extended to parameterize patchy particle simulations which predict a complete PbS NC SL phase diagram consistent with all previous tuning strategies. This Thesis provides a complete description of the predictive framework for self-assembled SLs and develops new computational tools which may be applied to other material systems.

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