Validation: Semiconducting Nanomaterials

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Introduction

Semiconducting nanoparticles are building blocks of numerous materials with tunable electronic properties. Predicting the properties of these systems is challenging as the atomistic structure of nanoparticle-ligand interfaces is often unknown. We aim at validating structural models of nanoparticles interfaced with organic and inorganic ligands.

Ligand Engineering

Inorganic ligands

• We investigated InAs NPs with SnS ligands using first principles molecular dynamics (FPMD) and the Qbox code.
• We validated interfacial structural models using a feedback loop between theory and experiment.
• FPMD pointed at ligand decomposition for all initial configurations.
• XPS and Raman experiments validated predictions.

Organic ligands

Cd3Se2X6L4/10, Cd4Se6X12L4/22, Cd4Se6X56L56 (X=PhCO2-, L=NH2-C6H4)

We chose NPs of known structure and stoichiometry and we investigated the atomistic and electronic structure of the interface with ligands. FPMD simulations (Qbox code) indicated the crucial role of hydrogen bonded amine in the stabilization of the cluster; GW calculations (WEST code) of electronic states for comparison with experiments are ongoing.

Interacting Nanoparticles at Finite Temperature

We used FPMD (Qbox code) to generate realistic models of interacting PbSe NPs, with the goal of comparing computed and measured dipole moments.

• We found that at finite temperature, interacting NPs act as dynamical dipolar systems – average dipole moments/polarizabilities are increased compared to the isolated NPs, with large dipolar fluctuations.
• We also found that interacting NPs have smaller fundamental gaps than isolated ones, which decrease as a function of T, and radiative lifetimes that are greatly reduced at finite T.

Our results were used to interpret a variety of experimental results on dipole moments of chalcogenide NPs.

Atomically-Precise II-VI Semiconducting Nanoplatelets

The synthesis of atomically-precise nanoplatelets eliminates heterogeneities often present in nanoparticles, and hence offers the opportunity of validating theory and simulations for nanomaterials of known atomistic structure.

We used DFT calculations to compute the properties of nanoplatelet heterostructures of CdSe and CdS. Compared to CdSe NPLs, in agreement with experiment for CdS/4CdSe/CdS we found:
• A decrease in band gap
• An expanded lattice (axial) with layer-dependent lattice constant.

Dipoles and Polarizabilities of Nanoparticle Superlattices

We developed a modelling framework that links the collective behavior of nanoparticle superlattices to the properties of the underlying building blocks. The model is based on DFT calculations for CdSe NPs and simulations for CdS NPs, and validated our theoretical model using the properties of CdSe/CdS superlattices.

Embedded Nanoparticles

We initially sought to validate interfacial states observed experimentally. The end results was the identification of interfacial defects and trap states detrimental to charge carriers in PbSe/CdSe embedded NP systems.

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