



Designing Conductive Quantum Dot Superlattices for Perfect Charge Collection from Next-Generation Quantum Dot Solar Cells

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Background and Introduction

Solar cells based on thin films of colloidal PbSe or PbS quantum dots (QDs) are emerging as a promising next-generation photovoltaic (PV) technology with the potential to achieve 45% conversion efficiency at one sun by using multiple exciton generation (MEG) to reduce thermalization losses.

Recent Progress in QD PVs :

- Efficiencies of QD solar cells are now 5-6%
- 1000-hour stability has been demonstrated
- QD PV devices have been added to NREL's official chart of PV technologies (with a 4.4% certified PbS QD cell)
- Clear evidence of MEG- enhanced photocurrents has recently been found in working QD cells

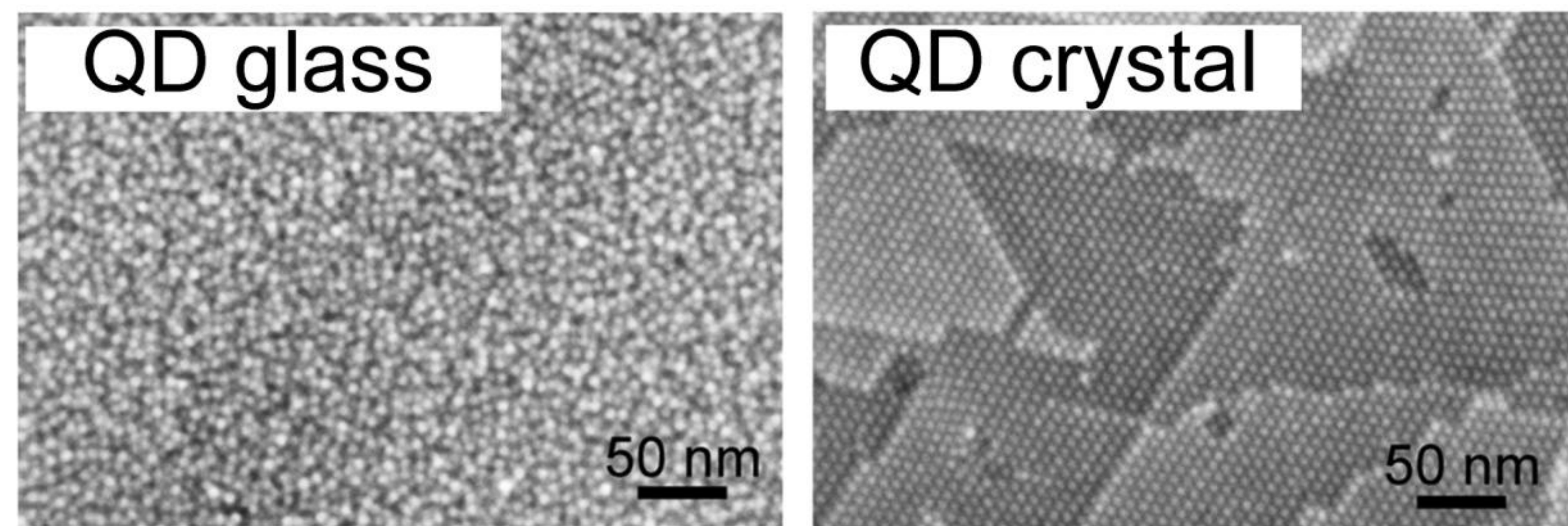
The Issues to Address:

- All QD cells made to date employ highly-disordered (glassy) QD films (see Figure 1).
- QD active layers are usually made thin (< 250 nm) to minimize the quasi-neutral region and guard against poor charge collection, but this technique limits the photocurrent and cell efficiency.

One Possible Solution:

I propose to design conductive PbSe QD superlattice films in which charge transport occurs by band-like (miniband) conduction through extended states (QD superlattices; see Figure 1). These QD superlattices will be made by a novel ion exchange, ligand exchange, and self-assembly approach, then thoroughly characterized and employed in QD PV. Recently, ligand exchanges with inorganic metal chalcogenide complexes have been shown

to produce charge-stabilized colloidal CdSe QDs, but the harsh conditions of the process destroy PbSe and PbS QDs. This project will significantly advance the state-of-the-art by developing the first strongly-coupled, conductive PbSe QD superlattices. These superlattices will simultaneously feature (i) strong electronic coupling (via very small inter-QD spacing), (ii) a high degree of spatial order, and (iii) a low concentration of surface states that act as charge traps or recombination centers.

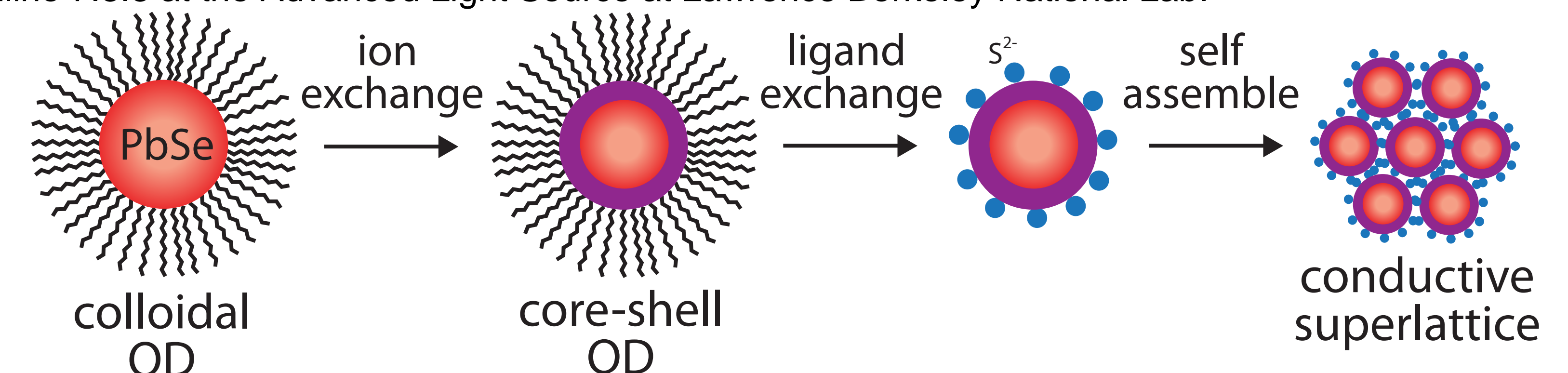


- poor order
- incoherent hopping transport
- superlattice order
- band-like transport

Figure 1. Comparison of glassy and crystalline PbSe QD thin films. Each dot in the SEM images is a 6-nm diameter PbSe QD. Note that the superlattice is an insulating, oleate-capped film. The goal of this project is to make conductive QD superlattices with excellent spatial and energetic order.

Approach

I am developing a simple, four-step procedure to make conductive PbSe QD superlattices that have unprecedented spatial and energetic order and low surface state densities, resulting in miniband transport with diffusion lengths > 800 nm (Scheme 1). First, I will circumvent the chemical instability of PbSe surfaces by forming ~1 nm-thick protective CdSe shells on the PbSe QDs via solution-phase cation exchange. I will then subject these core-shell QDs to a solution-phase ligand exchange to quantitatively replace the long-chain, insulating oleate ligands with small inorganic ligands (S^{2-} , Se^{2-} , CN^- , OH^- , F^- , or Cl^-) to yield charge-stabilized PbSe/CdSe QDs in polar solvents. In the third step, spin coating of the QD suspension onto device substrates will form conductive QD superlattice films. These self-assembled films will show both excellent superlattice order and strong inter-QD electronic coupling (as a result of the very small inorganic ligands). Currently, we have the ability to fabricate thin films by spin casting or dip coating in an air free wet box. We can enhance the stability of our thin films via an ALD apparatus housed in an adjacent dry box. We characterize our thin films with FEI Magellan 400 XHR SEM, FEI/Philips CM-20 TEM, and Rigaku Ultima III XRD. We will also obtain GISAXS measurements from beamline 7.3.3 at the Advanced Light Source at Lawrence Berkeley National Lab.



Scheme 1. Proposed process for forming conductive PbSe QD superlattice films. The TEM image shows a PbSe/CdSe core-shell QD made by ion exchange

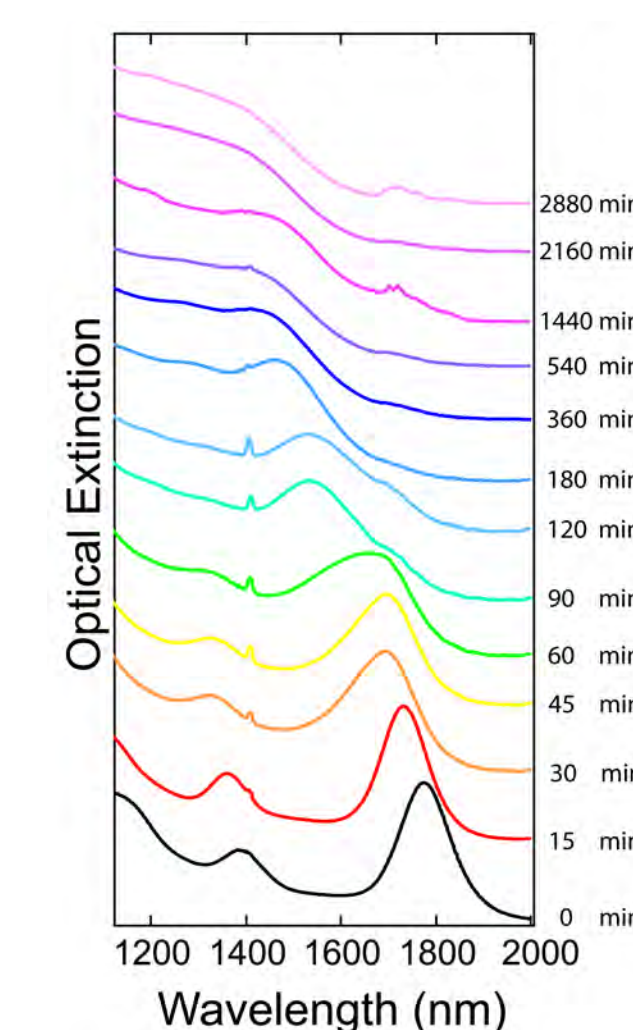


Figure 2. UV-Visible spectrum of the as-made PbSe QDs (black) and subsequent spectra of QDs after exposure to Cd-oleate from 15 minutes to 48 hours.

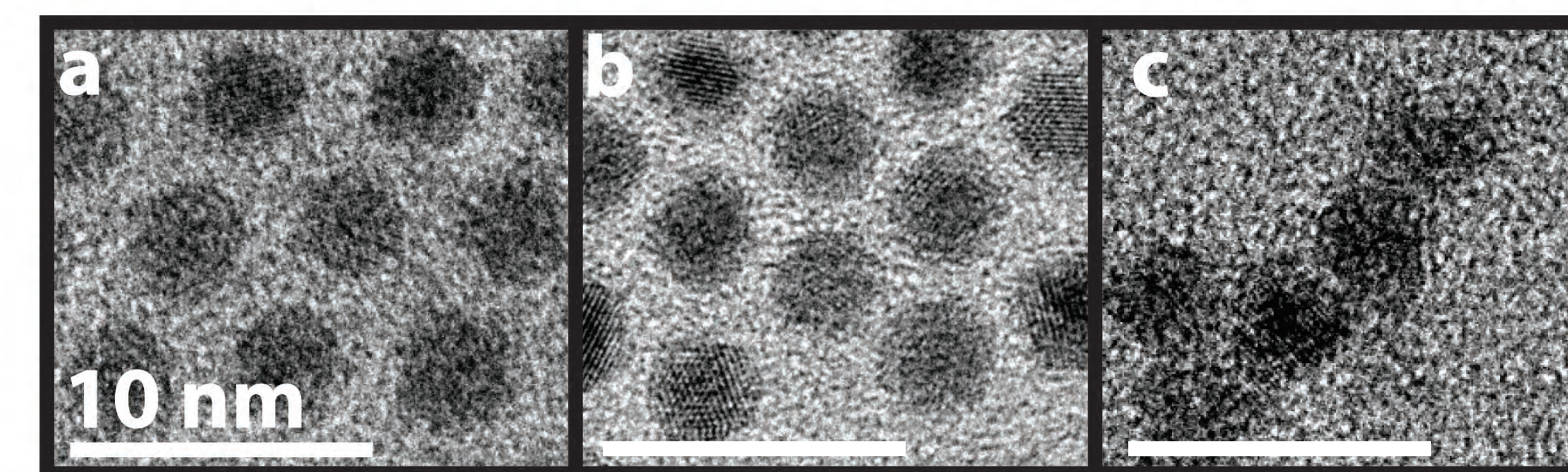


Figure 3. transmission electron microscopy images of (a) as-made, oleate capped PbSe quantum dots (QDs) with a first exciton of 1775 nm and a diameter of 6.3 nm, (b) the same dots after treatment with Cd-oleate for 12 hours, yielding PbSe/CdSe core/shell QDs, and (c) the PbSe/CdSe core/shell dots after treatment with a 5mg/mL solution of Na_2S . The white scale bar corresponds to 10 nm.

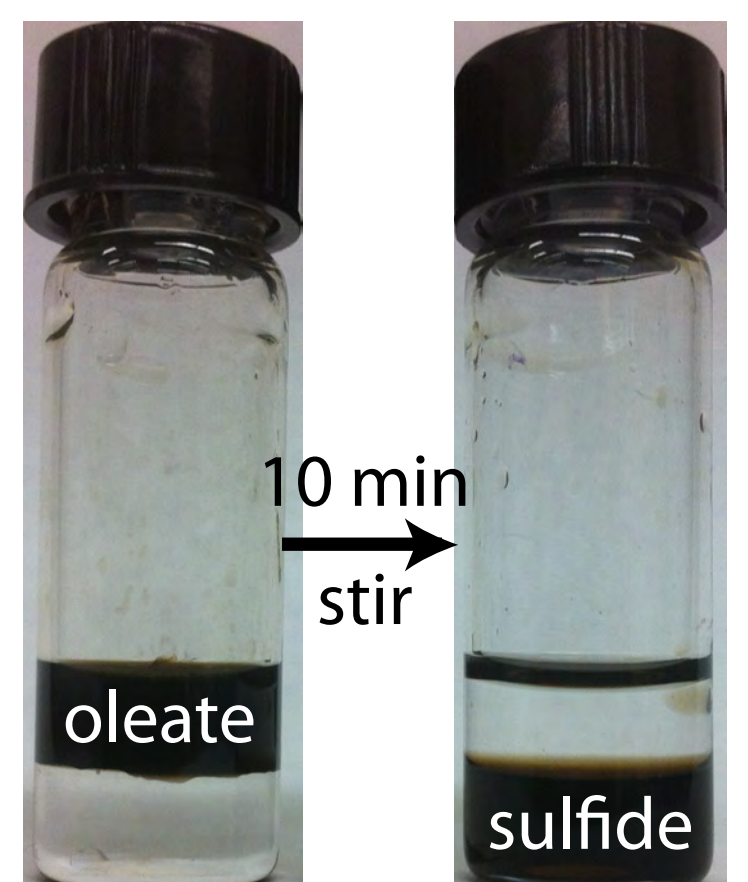


Figure 4. solution exchange of oleate to sulfide ligands on the surface of core/shell QDs.

Impact

QD PVs are a promising 3rd generation PV technology, but the relatively short diffusion lengths of QD films limit the photocurrent and efficiency of these devices. This project will dramatically increase the diffusion length of QD films by making conductive QD superlattices that possess a high degree of spatial and energetic order and transport charge by band-like conduction rather than sequential hopping. These breakthroughs will remove existing limitations on EQE, increase cell efficiencies, and speed the commercialization of QD PV by the U.S. PV industry.

Acknowledgments

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Colloidally stable lead chalcogenide nanoparticles with short, inorganic ligands can be fabricated into 2D and 3D super crystals for perfect charge collection.