Developing Quantum Dot Solids for Next-Generation Photovoltaics

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Quantum dot building blocks for optoelectronics

Nanometer-sized crystals with size-dependent properties

self-assembly from solution

quantum confinement - particle in a box

\[ E_n \propto \frac{n^2}{d^2} \]

smaller diameter

C. Murray, C. Kagan
Motivating context: QD photovoltaics

Carrier multiplication promises high efficiency


Towards Breaking the Shockley-Queisser Limit using QD Photovoltaics

Ligand exchange to make conductive QD films

\[ \text{PbSe QD} \]

\[ \text{Substrate} \]

\[ \text{EDT} = \text{HS} - \text{SH} \]

\[ \psi (r) \]

\[ i = 2-4 \text{ nm} \]

\[ \text{insulator} \]

\[ i = 0.1-1.0 \text{ nm} \]

\[ \text{conductor} \]

Charge transport in QD solids

Factors affecting transport:

1. Coupling energy
   - barrier size
   - quantum confinement
   - site energies
   - charging energies

2. Disorder
   - spatial
   - energetic

3. Surface defects
   - traps
   - recombination centers

QD solids: granular conductors with tunable electronic coupling

\[ G \propto e^{-2d \sqrt{2mE_B/\hbar^2}} \]
Key role of disorder in charge transport

Multiple sources of disorder localize carriers and frustrate transport:

- Lack of periodicity
- Distribution of QD spacing
- Distribution of QD size/shape
- Defect states in the band gap

Spatial disorder:

- Ideal
- Real

Energy disorder:

- Energy levels in a disordered landscape
Electronic phase diagram for QD lattices

Charge transport studies
QD spacing

in the weak coupling limit:

\[ \mu = \mu_0 \exp(-0.865 \kappa l) \exp\left(-\frac{\Delta E}{kT}\right) \]

- Mobility decreases exponentially with increasing QD separation
- Kappa as expected for tunneling through alkane barriers
- Transport occurs by sequential phonon-assisted tunneling
QD size and size distribution

QD Size

- Trend opposite that expected from pairwise coupling
- Probably results from fewer hops thru bigger dots, possibly shallower traps too

QD polydispersity

- Surprising lack of dependence, contrary to basic theory
- Suggests “true” $\Delta \alpha$ is set by factors other than polydispersity, such as gap states and percolation networks

Need #1: better transport models of mesoscale systems

Mesoscale heterogeneity and percolation

Carriers may percolate through continuous networks of the larger QDs in the film to avoid hops with large activation energies.

path A: full QD polydispersity is sampled
path B: low-disorder percolation pathway
Electronic defects in QD films

QDs are rich in surface area and defects. Electronic states in the band gap greatly increase the energy disorder, lowering lifetime and mobility.

Need #2: exp/theory tools to characterize defect states, especially surface states

- traps
- recombination centers
Abundant evidence of gap states in QD solids

Deep gap states

Band tail states

PC of PbS
Klimov, V. 2012.

PL of PbS
Johnson, J. C. 2012.

DFT of PbS
Sargent, E. 2012.

IMPS of PbS
Luther, J. PRB 2012.

IR spectroscopy of PbS
Sargent, E. 2012.

IR spectroscopy of PbS
Sargent, E. 2012.

PDS of CdSe
Guyot-Sionnest, P. 2012.
Gap states limit diffusion length in QD solar cells

![Graph showing EQE vs. photon energy for different materials.]

- 20% CIGS
- 12.8% CdTe
- 24.4% Textured Si
- 18.2% untextured Si
- PbSe QDSC

short diffusion length $\rightarrow$ poor red EQE

$$L_d = \sqrt{D\tau} = \sqrt{\mu\tau V_{th}}$$

now: $L_d \approx 50 \text{ nm}$
(e.g., 10 ns, $\mu = 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)

need: $L_d \approx 1000 \text{ nm}$
for unity EQE
(10 ns, $\mu = 40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
Improving QD solids: surface engineering by ALD

Low-temperature atomic layer deposition can be used to infill QD films, creating robust, functional QD nanocomposites.

The ALD matrix:
- can passivate surface states
- can decrease the barrier height and $E_C$
- prevents QD oxidation/degradation

Improved spatial order for better transport?

**QD glass**
- poor order
- slow electron transport

**QD crystal**
- significant order
- fast electron transport (?)

Given inevitable energy disorder, will spatial order matter? Can superlattice order help achieve >1 um diffusion length?
Why QD superlattices?

Periodic potential favors emergence of Bloch states (mini-bands)

- band conduction
- higher mobility
- longer diffusion length

Summary & research needs

- Synthesis of better building blocks and improved assemblies
- Atomic-level 3D structural and elemental characterization
- Tools for characterizing defects, especially surface states
- Atomistic electronic structure models of “big” systems
- Realistic multiscale transport models
End