

Theoretical framework for charge transport in QD solids

Colloidal quantum dots (QDs) are nanometer-sized crystalline semiconductors solution-synthesized using low-cost chemical reactions. Chiefly due to their tunable optical and electronic properties, they are attractive for next-generation thin-film optoelectronics. Appropriate modification of their size, shape, surface chemistry, and chemical composition can help tailor QD properties. Typically, a thin film assembled from QDs via industrially compatible coating methods such as slot-die coating, spray coating, and inkjet printing, several tens to hundreds of nanometers in thickness, is used as the “active” layer to demonstrate semiconductor device applications. Perovskite QDs and lead chalcogenides (such as lead sulfide) are the two most promising families of this material.

The nature of charge transport in QD films has allured researchers. Precise understanding and control over the flow of charge carriers promises improvements in the resulting semiconductor device performance, and is an area of active research. Because of their large surface-to-volume ratio, significant improvements in charge transport have been realized over the years by smart manipulation of the QD surface. The as-synthesized QDs are capped with long-chain organic molecules, such as oleic acid, that aid in their synthesis and help disperse them in organic, green solvents. However, due to their long alkyl chains, the organic surfactants render the QDs electrically insulating when deposited into a thin film. A facile process to improve charge transport has been to perform an exchange of these surfactants, by dipping the initial QD film into a solution of smaller-chain ligands. This enables the QDs to pack closer and improves the flow of charge carriers. However, further understanding on the nature of charge transport is urgently needed to push this promising field forward.

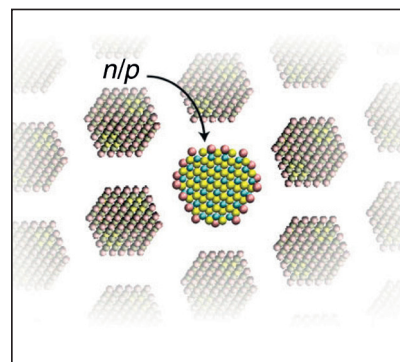
A research group from ETH Zürich led by Vanessa Wood has now presented a theoretical platform, backed with experimental evidence, that furthers the fundamental

understanding of charge transport in QDs. The insights were recently published in *Nature Communications* (doi:10.1038/s41467-020-16560-7).

The research team started by theoretically simulating the transport of charge carriers in a solid made from QDs. The researchers realized that hopping of charges between neighboring QDs involves deformation of the QD surface. More specifically, the chemical bond between the surface metal atom (lead, Pb) and the surfactant on the PbS QDs deformed when the QD accepted or donated a charge during the transport process. This insight suggests a link between vibrations of the QD surface and charge transport, directly implying that the choice of surfactants and the resulting vibrations can be manipulated to tune charge transport.

Introducing doped QDs into the QD film is a commonly used strategy to improve charge transport. However, the simulations suggest that an unintentional oxidation or reduction of these doped QDs can convert them into carrier trap sites. Unintentional oxidation of *n*-type QDs can occur simply via interaction with the environmental oxygen. These doped QDs were found to behave as energetically favorable “pockets” for the charge carriers, which would get “stuck” and trapped, hurting charge transport. In other words, care must be observed when introducing doped QDs into the film, as unwanted redox chemistry can compromise charge-carrier mobilities, a metric used to quantify charge transport. It was seen that this effect is prominent for smaller-sized QDs, while larger QDs are more forgiving. The researchers experimentally validated their predictions by carrying out photocurrent transient measurements. This technique relies on exciting the charge carriers in the QD films with a laser source. The excited carriers were then made to transverse the film thickness under an electric potential, and the carrier mobility was determined from the resulting current.

Thus charge transport in QDs is seen as a property strongly coupled to the QD surface chemistry. A keen look into the interactions of carriers with QDs reveals transient phenomena occurring as the carriers hop during transport. The nature of



Simulation results demonstrating that trap states impact charge transport in smaller-sized quantum dots (QDs) more than larger ones. Credit: Nature Publishing Group.

these interactions then defines whether carrier traps can emerge and inhibit transport. In the context of doped QD systems, the researchers suggest that choosing doped QDs that have smaller sizes and wider bandgaps compared to intrinsic, larger-sized QDs in the matrix will offer the charge carriers a smoother path for transport and avoid formation of carrier traps. Overall, such a strategy should boost charge-carrier mobilities in QD solids.

Maria A. Loi, a professor at the University of Groningen, The Netherlands, and an expert in the photophysics of optoelectronic materials, feels this wonderful demonstration by the research team opens avenues to more complex and efficient optoelectronic device structures. “This is a new contribution to the discussion about transport in ordered QD arrays. So far, this discussion was dominated by experimental research groups and mostly dealt with the question of band-like transport. It is nice to see researchers trying to explain charge transport using modeling approaches. In this study, the Wood group advocates the importance of the surface ligand bonds, doping, and the consequent hopping transport.”

Loi says that, as the next step, experimentalists should work to obtain better QD superlattices—arranged and ordered arrays of size-monodisperse QDs with minimal bandgap disorder—and measure their transport properties, to verify and benefit from the insights developed in the current work.

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