

Band-Edge Modification of Quantum Dots by Solvation

Y. B. Vogel¹, A. J. Houtepen^{1*}

¹Department of Chemical Engineering, Delft University of Technology

We show that band edge positions of colloidal quantum dots (QDs) shift over 0.6 eV depending on the solvent they are immersed in. We find that the direction of this energy shift is not purely a dielectric effect, and instead scales with the solvent Lewis basicity. This trend is independent on the QD material, and passivating ligand and matches well density functional theory calculations. This finding has immediate implications for the design of many emerging optoelectronic devices such as light emitting electrochemical cells, photocatalysts, and chemical sensors, where QDs are solvated, and the band edge positions determine device functionality. It also provides a means for stable electrochemical doping, as in-gap states related to material degradation are less sensitive to solvation than band edges.

Measurement of the band edge position is usually performed under ultrahigh vacuum, preventing inclusion of solvents. We overcome this challenge by developing a spectroelectrochemical approach that allows to measure the number of electrons/holes in solvated QD as the Fermi level is electrochemically shifted. This yields good agreement with expected shifts on the conduction band edge position with the QD size and the presence of different passivating ligands. Using this method, we demonstrate that the conduction band edge shifts up in energy as the solvent Lewis basicity increases.

Finally, we explore the implication of solvation for electrochemical doping. Electrochemical doping is arguably the most controllable way to regulate charge density in QDs, but the injected charges often end up localizing to in-gap states leading to material degradation. We find that the energetic position of these in-gap states can be brought outside the bandgap by leveraging solvation effects, providing a means to stabilize electrochemical doping.

