

Role of ligand exchange at CdSe quantum dot layers for charge separation

Elisabeth Zillner, Steffen Fengler, Thomas Dittrich

Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin

Semiconductors quantum dots (QD) are interesting for application in photovoltaics due to the tunability of their electronic properties which opens a wide range of additional materials. Working solar cells of PbSe and PbS QDs with efficiencies of up to 5 % were realized by Sargent et al.^[1,2] Even though the control of charge separation and charge transfer remains a major challenge in the application of QD in devices. A systematic study of the influence of the surface and interparticle distance of quantum dots on charge separation and transport processes is presented. Charge separation is measured by time and spectral dependent surface photovoltage on thin layers of CdSe QD.

The surface and interparticle distance of CdSe QD is varied by surfactant exchange. Quantum dots stabilized by a multilayer of oleic acid (OA) and trioctyl phosphine (TOP), a monolayer of OA and TOP and pyridine as ligand are studied. An additional exchange of ligands in thin layers by 1-4-benzenedithiol and OH groups was performed. Thin layers (1 to 15 monolayers) were prepared by dip coating of ITO substrates.^[3]

Transmission electron micrographs of (sub-) monolayers of QD show a decreasing interparticle distance with proceeding ligand exchange from a multilayer of OA and TOP to a monolayer for OA and TOP and pyridine (Figure 1a). For the ligand exchange with dithiol no decrease in the average distance but a higher distribution was found. The dithiol molecule binds to two neighboring QD, what reduces the interparticle distance of these bridged QDs but also increases the distances between non-bridged QD, as this exchange was done in a layer.

Stroboscopic Photoluminescence measurements show a radiative recombination of charge carriers from the first excitonic peak and some quasi white background from radiative recombination from defects (figure 2). Both radiative recombination from the first excitonic peak and defects decrease with proceeding

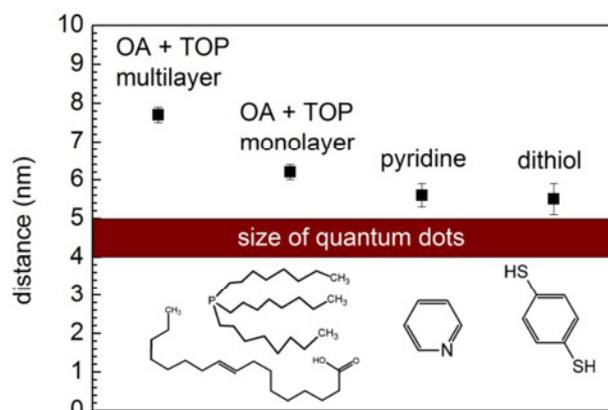


Figure 1: Determination of interparticle distances from transmission electron micrographs.

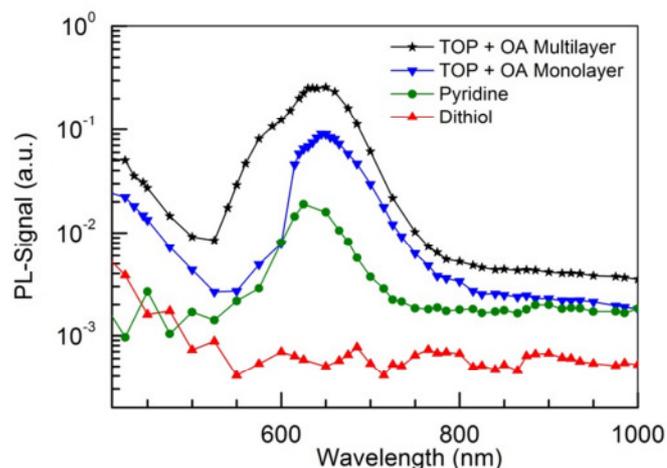


Figure 2: Stroboscopic Photoluminescence measurements at CdSe QD thin layers.

ligand exchange. Charge carriers recombine non radiative over defects at the surface of QD created during ligand exchange.

The formation of defects during ligand exchange is also confirmed by modulated spectral SPV measurements (figure 3). The spectra reveal an increase of PV amplitude below the bandgap (1.9 eV). Thus a higher number of charge carriers from defect states is excited and separated. Furthermore an overall increase in PV amplitude is observed with proceeding ligand exchange. Transient SPV measurements (figure 4) show the same trend. Both the amplitude and the half life increase with proceeding ligand exchange.

Previous experiments showed that the initial charge separation in those layers take place in the first monolayer.^[3] We claim that the asymmetry introduced by the substrate induces the charge separation. Electrons are trapped on the surface of the substrate; holes are trapped in defect states on the QD surface. If the distance between substrate and QD is too high trapping of electrons on the substrate is not possible (CdSe QD with OA + TOP multilayer). A decrease in QD substrate distance and an increase in defect concentration increases the initial charge separation and thus leads to a higher SPV signal. With proceeding ligand exchange the SPV transients decrease slower. The transients can be fitted by a single stretched exponential, what points towards one dominating recombination process from a distribution of energy states.

The measurements of this study proof the importance of ligand exchange for charge separation, while two steps are involved into the initial charge separation, first, disruption of excitons due to trapping and second, following asymmetric trapping, leading to an SPV signal.

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Literature

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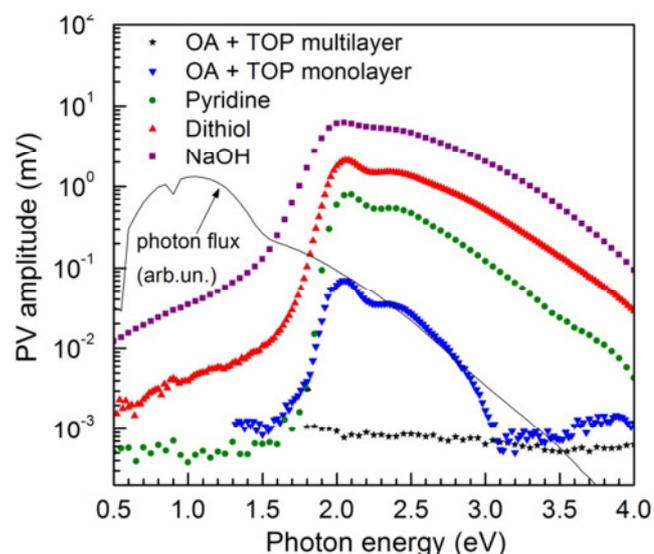


Figure 3: PV amplitude of spectral dependent SPV measurements at CdSe OD thin layers

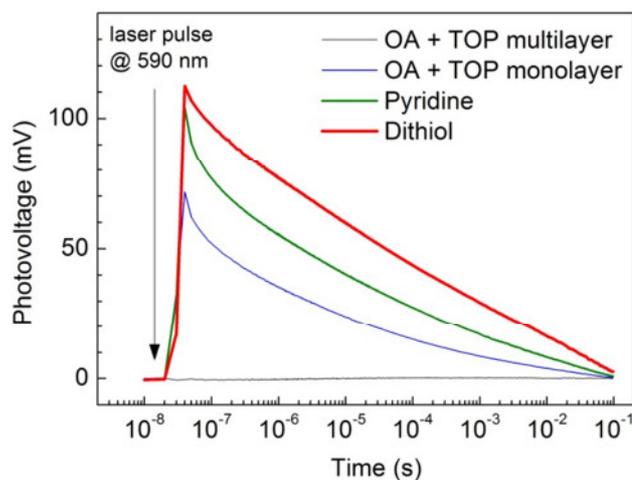


Figure 4: Transient SPV measurements (excitation at 590 nm) at CdSe OD thin layers