## Topic: Quantum dot solar cell

Colloidal PbS quantum dots (QDs) exhibit a tunable band-gap with a corresponding broad absorption range covering the entire visible range and reaching mid-wave infrared (MWIR), which enables QDs being promising for various optoelectronic applications such as light-emitting diodes, photodetectors as well as solar cells.[1-2] As a direct semiconductor material, PbS QDs can be used as a thin-film function layer in 3rd generation solar cell applications due to their strong absorption coefficient. Moreover, as the most distinguished feature of the QDs which is different from conventional Si, polymer as well as perovskite, the long-wavelength absorption behavior endows QDs being able to collect the solar energy at wavelengths beyond 1100 nm. Also, PbS QDs are attractive for the design of a multi-exciton-generation (MEG) device which may enable a breakthrough of the Shockley-Queisser limitation for conventional solar cells. In our group, we are focusing on fundamental studies, such as QD particle self-organization behavior during large scalable depositions, the inner structure determination of QD solids after different functionalization treatments, and also highly efficient QD optoelectronic devices, especially for QD based solar cells. The QD solid/device optimization, as well as degradation studies, are also part of our investigations with the state-of-the-art grazing incidence X-ray scattering (GIXS).

Conventional size-monodisperse QDs are synthesized in solution phase condition, in which QDs are normally wrapped by the organic ligands, such as oleic acid. The ligands help the QDs maintain a good solubility in the desired solvent, which makes the QDs compatible with most large scale deposition methods, such as printing and spray deposition, in which QDs can form excellent superlattice structures automatically via self-organization processes. Grazing incidence small-angle X-ray scattering (GISAXS) is an ideal tool to observe the superlattice structure and obtain the particle kinetics during the different deposition methods.[3]

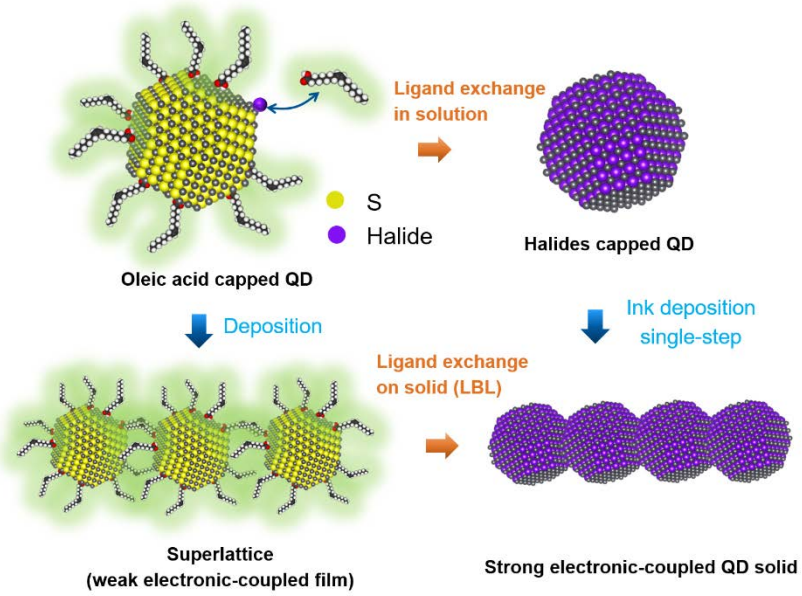


**Figure 1**. Schematic of the ligand exchange of QDs in solution and in a solid-state QD film, in which the ligand exchange converted the QD film from a weakly electronically-coupled superlattice into a strongly electronically-coupled mode.

The energy transport rate of the QD films strongly depends on the inter-dot distance of neighboring QDs. Specifically, longer edge-to-edge distances (over 2 nm) make QDs transporting energy mainly via a dipole-dipole resonance known as Förster resonance energy transfer (FRET), in which the charge carriers are mostly excitons rather than electrons or holes. When the edge-to-edge distances are less than 2 nm, the electrons can transfer from one QD site to another one via the tunneling effect (known as the Dexter transfer) due to the short distance induced electronic coupling as a result of the overlapped electron wavefunctions. Notably, a tandem effect with a higher energy transport rate is even predicted when QDs are in a facet-to-facet touching configuration. In practical applications, the long-chain ligands form a distance barrier between neighboring QDs after deposition, which results in a lower electronically-coupled configuration of the QD film and thus hinders the charge carrier transport. Therefore, the ligand exchange process is necessarily implemented to improve the electronic coupling of the QD film in photovoltaic as a functionalization process. As indicated in **Figure 1**, there are mainly two main strategies for the ligand exchange namely the QD solid-state exchange and the QD ink. The ligand exchange normally happens automatically due to the different binding energies of the ligands.

In case of the solid-state exchange, the superlattice structure of QDs collapses immediately after long-chain ligands are removed. The phase transitions, as well as the thermal annealing induced structural disorder, can be tracked non-destructively via GIXS. The corresponding charge carrier dynamics associated with energetic disorders are investigated via ultrafast spectroscopies, such as transient absorption measurements.[4] The ligand exchange processes are normally integrated with a layer-by-layer (LBL) process to increase the overall thickness and decrease the collapse induced cracks simultaneously. **Figure 2** demonstrates the classic QD solar cell device architecture and a cross-sectional particle stacking sketch, in which the active layer, as well as the blocking layer, can be fabricated via the LBL process.

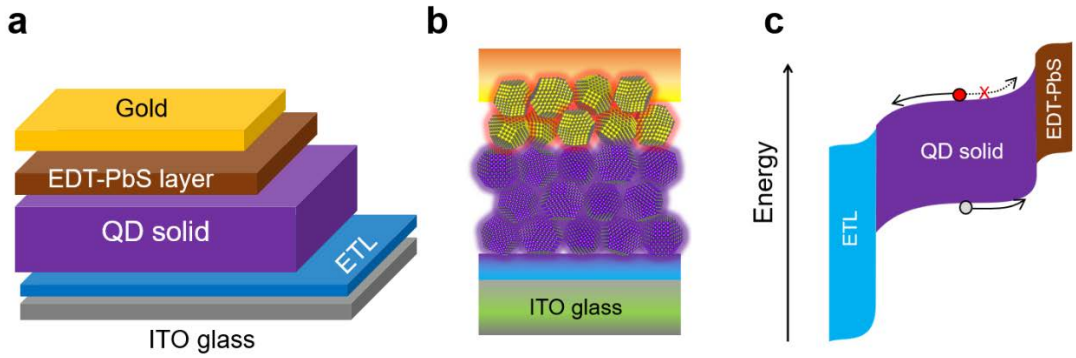


**Figure 2**. a) Classic planner structured QD photovoltaics device architecture and b) the cross-sectional QD stacked sketch, in which a QD solid acts as the active layer in a sandwich structure between the hole transport layer (which is normally a thiol treated QD layer) and electron transport layer. c) Energy diagram indicates the working principle of the PV device.

In case of the QD ink, the strategy is developed to address some drawbacks in the LBL process, such as the redundant processing flow. The ligand exchange process makes QDs transferring from oleic acid capped state to a ions capped state with apparent phase separation. The QD solid with a desired thickness can be obtained by one-step deposition from a highly concentrated QD

ink, in which the QDs can directly form a strong-electronic coupled QD solid. The structural configurations and the disorders are influenced by the deposition methods, which is observed and studied by the GISAXS analysis, and the results provide evidence about the structural influenced energy state information of the QD solid.

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