Oriented Attachment of Lead Sulfide Colloidal Quantum Dots Superlattice Assembly

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The solution-processable colloidal quantum dots (CQDs) with tunable size and properties are among the most attractive class of materials for applications in optoelectronic and energy-harvesting technology. Several efforts have been made to optimize the performance of CQDs-based devices, such as controlling the stoichiometry of the QDs as well as the ligand-related surface doping. Recently, it was shown that the performance of charge carrier transport on the CQDs solid assembly is strongly affected by the degrees of dot-to-dot connection and the corresponding structural factors.[1] In fact, obtaining disorder-free of CQDs assembly still remains a challenge. Conventionally, ligand-exchange process (long- to short-surface-ligand) must be introduced in order to achieve electronically coupled assembly. Another possible approach is by pursuing the formation of superstructure of CQDs assembly through the manipulation of the self-assembly process. This process shows an intriguing ability to organize CQD into quasi-2D superstructure with oriented attachments of its facets, leading to a promising way to obtain a structure that is able to support the demonstration of remarkable performance of CQDs-based technology.[2]

In this study, we demonstrate facile control of lead sulfide (PbS) CQD assemblies to form large-scale superlattice with oriented attachment. By modifying the so-called liquid/air interfacial assembly method, we can control the process and the orientation of the CQD upon self-assembling. The orientational attachment of the CQDs can be driven by the attached short ligands. The conventional ligand exchange by 1,2-ethanedithiol can also induce the orientation to some extent. However, oriented attachment in combination with atomic connection of the respective facets can be induced by performing chemical stripping of the native ligand using ethylenediamine. The formation of the CQD superlattices was investigated comprehensively using combinations of transmission electron microscopy (TEM/HR-TEM), grazing-incidence small-angle x-ray scattering (GISAXS), and grazing-incidence wide-angle x-ray scattering (GIWAXS) measurements. The GISAXS/GIWAXS measurements were performed using Synchrotron radiation source SPring8 BL38B1. Using these measurement combinations, we can observe the orderings in the length scale of the superlattice and to determine the orderings in the atomic details to judge the specific orientation and the specific atomic connections on the QD facets. The strong correlations of both the electron microscopy and the x-ray scattering data suggest that the formed PbS CQDs solids are connected-superlattice structures with a high-degree of oriented attachment in a reproducible manner with variations of the constituent QD size. This achievement will therefore open a new capability to significantly enhance the electronic transport performance in the CQDs solids that will be more practical for many electronic device applications.

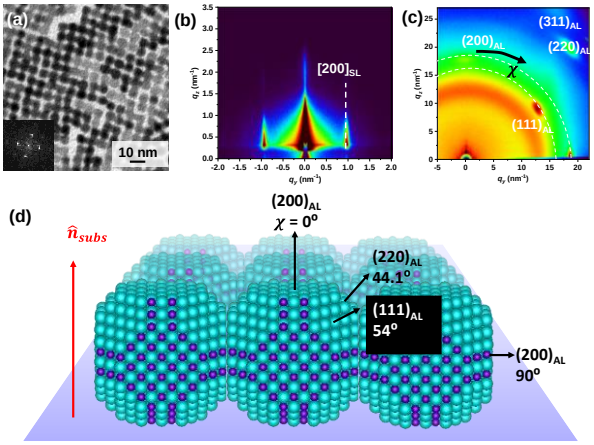

Figure 1| (a) TEM images of PbS CQDs superlattice with the average size of 6.2 nm, (b) GISAXS and (c) GIWAXS of the related CQDs, and (d) the illustration of oriented attachment.

Refs.:[1] Septianto, R. D., et al. *NPG Asia Materials* 12.1: 1-14 (2020), [2] Liu, Liming, et al., *Nanoscale* 11.43: 20467-20474 (2019)