The use of Langmuir-Blodgett films of PbSe/CdSe quantum dots for the determination of the PbSe/CdSe band alignment

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The alignment of the energy bands between the core and the shell of core/shell quantum dots (QDs), determines to a large extent the localization regime for electrons and holes. As such, it is one of the key properties of these materials. Nevertheless, only few studies exist that report on the experimental determination of the band alignment in these structures, and very often, the bulk band alignment is used to understand the optical properties of core/shell QDs. Here, we make use of densely packed double and triple layers of PbSe/CdSe QDs, made by Langmuir-Blodgett (LB) [1] and Langmuir Schaeffer (LS) [2] deposition to determine the band alignment between the PbSe core and the CdSe shell by ultraviolet photoelectron spectroscopy (UPS).

First, we demonstrate that LB deposition leads to dense, hexagonally ordered monolayers of PbSe/CdSe QDs with a high degree of surface coverage (>99%) over large surface areas as can be seen in figure 1. Importantly, this result is obtained on different substrates, with varying degrees of surface roughness. To our surprise, the resulting films show a strong quenching of the photoluminescence in comparison with the original PbSe/CdSe colloid, as it is shown in figure 2a. Further analysis of the PbSe/CdSe luminescence in suspension shows that this can also be quenched by the addition of methylviologen, a known electron scavenger for CdSe [3], as can be seen in figure 2b. On the other hand, addition of dodecanthiol, a hole scavenger for CdSe [4], has no effect on the luminescence quantum yield. This observation suggests a delocalization of the electron over the entire PbSe/CdSe nanocrystal (or a localization in the CdSe shell), while the hole remains localized in the PbSe core.

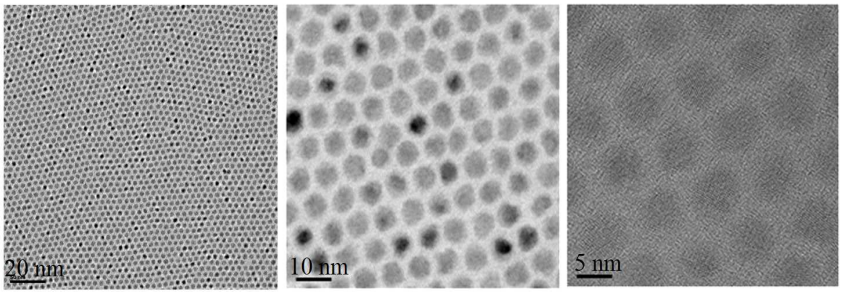

Figure 1: TEM images of a PbSe/CdSe LB layer at different magnifications

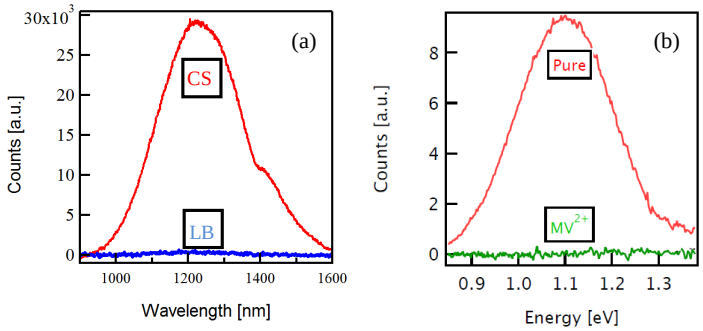

Figure 2: (a) Photoluminescence of the colloidal solution (CS) and Langmuir Blodgett monolayer (LB). (b) Photoluminescence spectra before and after adding methyl viologen (electron scavenger).

Thanks to the possibility of forming high quality monolayers and multilayers of QDs over large areas, PbSe/CdSe QD LB films proved to be excellent substrates for the analysis of the PbSe/CdSe band alignment by UPS. These measurements are summarized in table 1 and demonstrate that with shell thicknesses above 1 nm, the valence bands of PbSe and CdSe show an offset of about 1.2 eV, while an offset of only 0.24 eV is measured for the conduction bands. Importantly, these numbers significantly deviate from the reported bulk values of about 0.7 eV offset for both bands. In addition, we observe a clear trend with decreasing shell thickness, with thinner shells yielding larger conduction band offsets. Based on XPS measurements, we attribute this to the intermixing between Pb and Cd in the shell.

Materials system	ΔE_V	ΔE_C
PbSe/CdSe 6.3 nm/0.8nm	0.97	0.49
PbSe/CdSe 3.6 nm/1.1nm	1.22	0.24
PbSe/CdSe 5.6 nm/1.1 nm	1.22	0.24
PbSe/CdSe 5.2 nm/2 nm	1.28	0.18

Table 1: Comparison of the offset of the valence band (ΔE_V) and the offset of the conduction band (ΔE_C) among different core sizes and shell thicknesses.

Using an effective mass model, we find that the band alignment determined with UPS results in a core-shell QD with a quasi-type II delocalization, where the electron is fully delocalized over the entire nanoparticle while the hole remains confined in the PbSe core. This confirms the luminescence quenching experiments on PbSe/CdSe colloids and shows that a loss of luminescence upon LB processing is not unexpected since the electron wavefunction extends to the CdSe surface. These results point out that the PbSe/CdSe QDs is a rare example of QD heterostructure showing a quasi type II delocalization in the near IR. Clearly, this opens up new possibilities for engineering opto-electronic properties in this technologically interesting wavelength range.

References

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