

An upconversion layer with a quantum-dot-in-a-matrix nanostructure: a fully colloidal synthesis

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A nanostructured layer with upconversion capabilities, consisting of cadmium selenide quantum dots (QDs) embedded in a cadmium sulfide matrix, has been synthesized by using a low-cost, bench-top approach based on colloidal chemistry. As the conduction bands of CdS and CdSe are nearly aligned, such a structure is expected to lead to a peculiar energy band structure [1], where an intermediate electronic band (IB) forms – granted that the size and spacing of the embedded QDs matches specific criteria (figure 1).

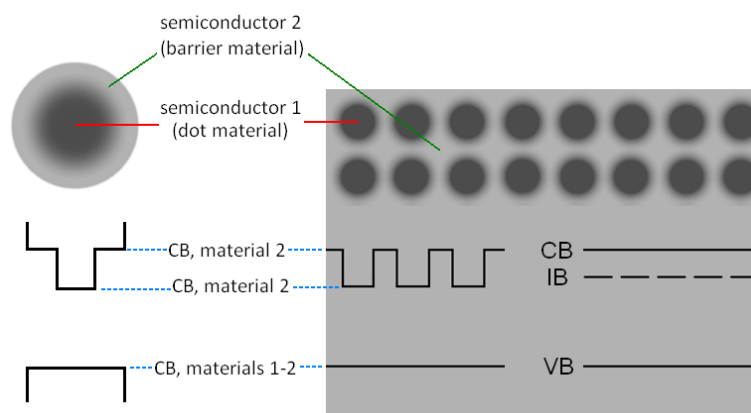


Figure 1. Two-phase core-shell semiconductor nanocrystal (left) and nanostructured two-phase material consisting of semiconductor nanocrystals embedded into a wider bandgap semiconductor (right). The approximated electron energy structure is sketched in the bottom part of the figure, showing how appropriate spacing and size of the embedded QDs may lead to the formation of an intermediate band (IB) within the bandgap. CB and VB indicate the limits of the conduction and valence bands, respectively.

All previous work on realizing QD-based nanostructures with an intermediate band has focused on molecular beam epitaxy [2, 3], a highly sophisticated and hardly scalable technique. Colloidal films, on the other hand, can be produced by cheap and scalable approaches, and a number of parameters such as the size, composition, shape, and mismatch strain of the nanostructures – all very important for the performance of IB-based devices – can be finely controlled and tuned [4].

In this work, CdSe-CdS core-shell nanocrystals were first synthesized as colloidal suspensions and then self-assembled on glass substrates to form 2 to 5 μm thick layers. A subsequent heat treatment in controlled atmosphere at temperatures ranging from 300 to 500 $^{\circ}\text{C}$ for up to 2 hours lead to partial sintering of the CdS shells and to the formation of a continuous film with the desired nanostructure (top right portion of the sketch in figure 1). As shown in figure 2, left, the photoluminescence (PL) of the assembly initially closely matches that of isolated quantum dots in suspension (A). Upon treating the sample at higher temperature, PL drops to reach a value of about 1.85 eV (B), regardless of the temperature, at a rate that depends exponentially on the temperature and varies from about 0.002 eV/min for treatments at 300 $^{\circ}\text{C}$ to 0.065 eV/min for treatments at 500 $^{\circ}\text{C}$. This behavior is compatible with the intimate interconnection of the CdS shells to form a continuous CdS matrix (figure 2, right). The PL peak energy never reaches values below 1.85eV, thus excluding the hypothesis that the shell material is lost upon heat treating the sample, leaving only aggregated CdSe (figure 2, E). By continuing the heat treatment, the PL changes; the time- and temperature-dependent kinetics of such

transformation are analyzed and found to be compatible with an interdiffusion mechanism between the embedded QDs and the CdS matrix (C). Over time, the PL approaches the expected value for a fully homogeneous $\text{CdSe}_x\text{S}_{1-x}$ alloy (D), where x is determined by the initial molar ratios between the core and the shell material.

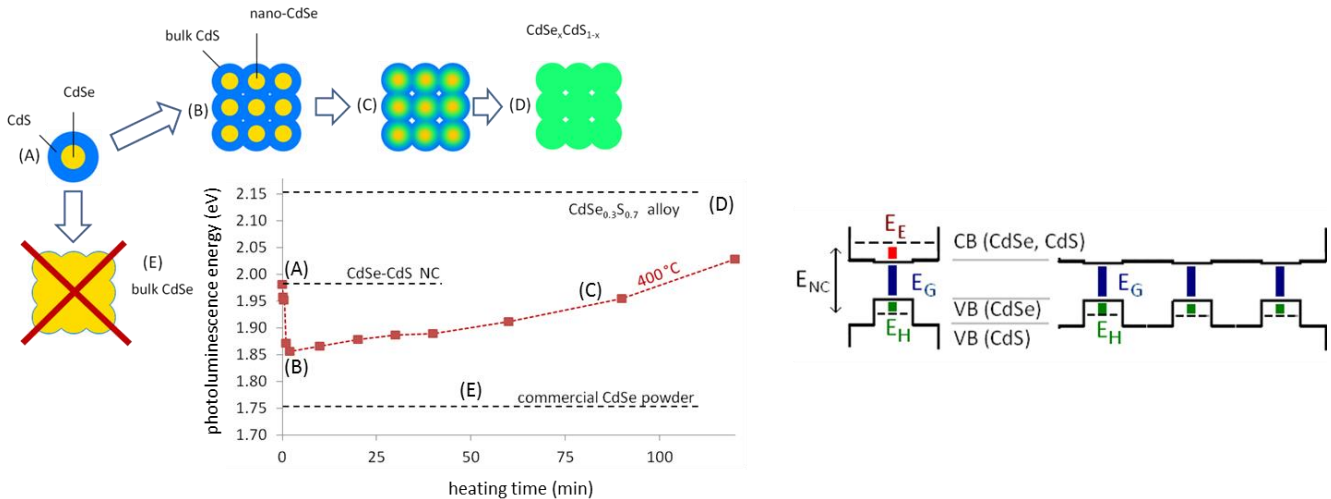


Figure 2. (Top left) sketch of the nanostructural evolution of the system upon heat treatment. (Inset) energy of the observed photoluminescence upon heat treatment at 400°C. (Right) evolution of the energy band structure upon merging of the CdS shells into a continuous matrix, leading to a reduction of the difference between the E_H and E_E energy levels and consequently to a decrease of the photoluminescence energy.

Upon the heat treatment, approximately in correspondence of the formation of the desired structure as in figure 2 (B), an additional PL peak appears at about 2.4 eV, which we associate to the CdS matrix. The simultaneous presence of such PL peaks is interpreted as the formation of the desired energy structure depicted in figure 1, where within the main bandgap associated to the matrix an intermediate band is formed, the position of which can be tuned by the heat treatment parameters, as these affect the degree of interdiffusion between the CdSe quantum dots and the CdS matrix, and therefore the electronic structure and the optical properties of the composite.

This work demonstrates the possibility of synthesizing intermediate-band materials via a colloidal approach compatible with integration in solar cell fabrication. This approach also leads to a largely improved possibility of engineering the optical properties of such materials, with respect to current approaches.

References

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