

# A Series of Double Well Semiconductor Quantum Dots

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## ABSTRACT

Five-layered nanocrystals have been prepared that consist of a CdS core covered by a shell of HgS followed by several monolayers of CdS that are covered by again a shell of HgS and an outer cladding layer of CdS. The resulting quantum dots, thus, contain a double well electronic structure. Both HgS wells are either as thick as a monolayer or as two monolayers. The wells are separated by a wall of two to three monolayers of CdS giving rise to a family of double well semiconductor quantum dots. Absorption spectra of eight members of this family are presented together with some first results from TEM measurements.

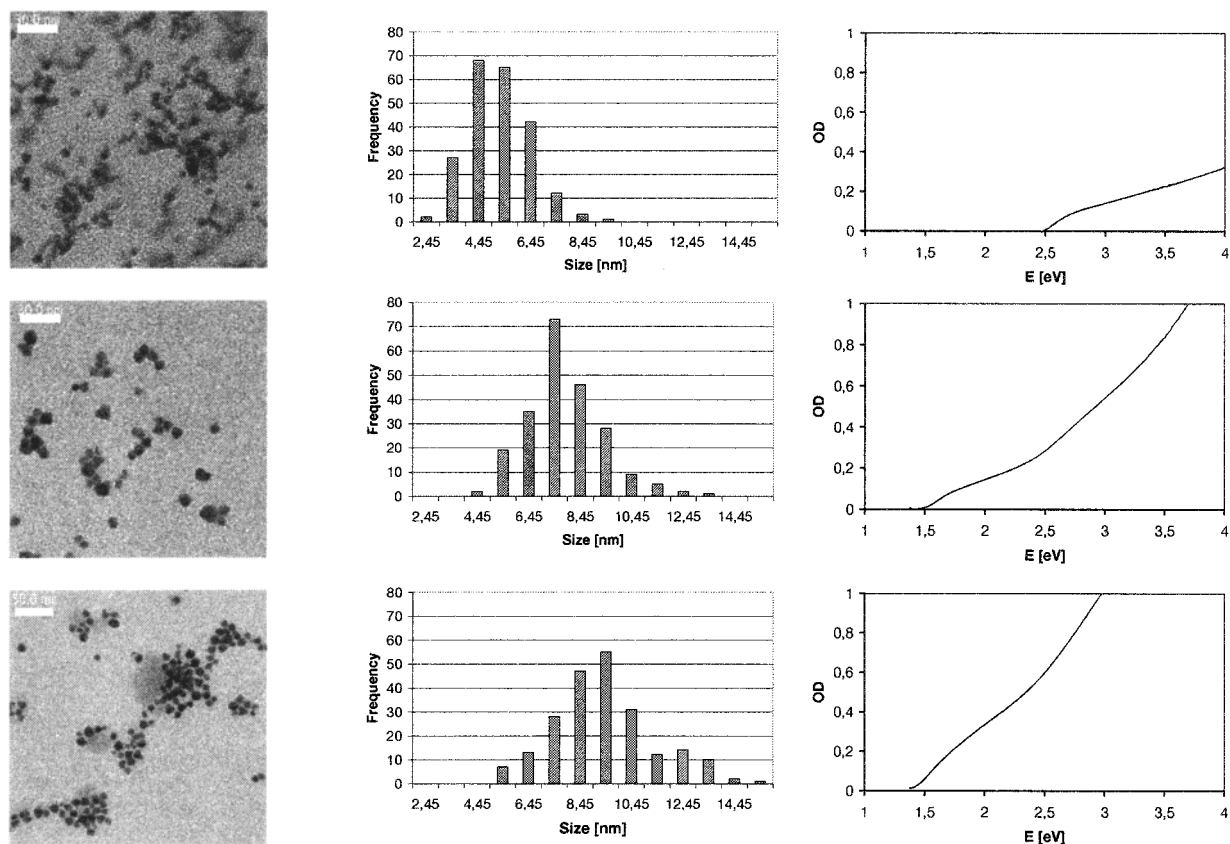
Almost a decade ago the first quantum dot quantum well (QDQW) was prepared.<sup>1</sup> It consisted of a CdS core covered with a shell of HgS and several monolayers of again CdS as the outer cladding layer (CdS/HgS/CdS). These nanoheterostructures were then subject to several studies such as static and time-resolved photoluminescence,<sup>2,3</sup> transient photobleaching,<sup>4–8</sup> high-resolution electron microscopy,<sup>9</sup> hole burning and fluorescence line narrowing,<sup>9</sup> single particle emission spectroscopy,<sup>10</sup> and optically detected magnetic resonance (ODMR).<sup>11</sup> Most of these experimental findings together with theoretical work on these unique structures<sup>12–14</sup> have been summarized in ref 15. A QDQW with a large lattice mismatch, namely ZnS/CdS/ZnS, has been prepared recently by Little et al. The evolving absorption spectra of the particles have been shown together with a theoretical treatment.<sup>16,17</sup> Very recently, the same group published first results on a QDQW system that contains two wells of HgS separated by a wall of CdS.<sup>18</sup> In this letter we outline our efforts pointing in the same direction, namely the preparation and characterization of a series of QDQWs containing two wells.

The preparative route first follows the established procedures outlined in detail in the literature.<sup>2</sup> Briefly, a CdS colloid is prepared in aqueous solution yielding particles of about 5.3 nm mean diameter with a standard deviation of about 22% (cf. Figure 1, top). The absorption spectrum shows a slight blue shift of the first electronic transition compared to the bulk value of 2.4 eV being due to size quantization<sup>19</sup> (Figure 1, top right). The surface layer of the CdS is then replaced by HgS following standard procedures.<sup>2</sup> Addition of a second monolayer of HgS and capping with three monolayers of CdS yields a QDQW with a single well of two monolayers of HgS within the CdS.

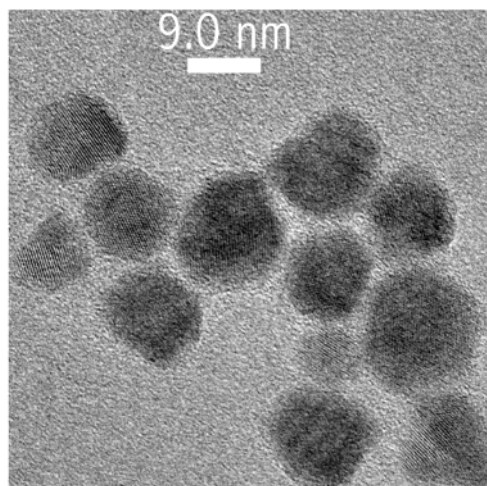
These particles are shown in an overview TEM image in Figure 1, middle left, together with the corresponding size histogram and the sample's absorption spectrum. As expected and described in the literature, the mean particle size merges to about 7.8 nm and the size distribution remains unaltered (19% standard deviation). The red shift of the first electronic transition to about 1.6 eV is understood as a localization of the charge carriers in the HgS well. In the lower part of Figure 1, a TEM overview image together with a histogram and an absorption spectrum of a double well colloidal sample are shown. Those particles have been prepared by following the same concept as for the single well particles, i.e., repetition of the replacement of the surface CdS by HgS, addition of a second monolayer of HgS, and capping of the whole structure by three monolayers of CdS. By this, the particles grow to a mean size of 9.5 nm while maintaining the size distribution at about 20% standard deviation. In part, our preparation follows that of Braun et al.,<sup>18</sup> details of our procedure together with high-resolution TEM and further characterizational work will be published elsewhere.<sup>20</sup>

Figure 2 shows a high-resolution image of the double well structure described above. The picture gives clear evidence of the crystallinity of the nanostructures formed (details also in ref 20) and yields a lattice spacing of 0.334 nm typical for cubic CdS as well as for  $\beta$ -HgS.<sup>2,9</sup> As expected after the observations by Mews et al.,<sup>9</sup> the HRTEM images do not yield clear evidence for the formation of layered nanostructures in a simple manner by, for example, the observation of compartments of different contrasts.

In Figure 3 we summarize the absorption spectra of a total of eight different double well QDQWs prepared according to the above outlined procedures. All eight samples have in common the core size (cf. Figure 1, top) and the outer



**Figure 1.** TEM survey images (left) of CdS (top) and CdS/HgS single well (middle) and double well nanoparticles (bottom) and the corresponding size histograms (220 particles have been analyzed for each fraction). The respective absorption spectra of the colloidal solutions of the three samples are shown on the right-hand side of the figure.



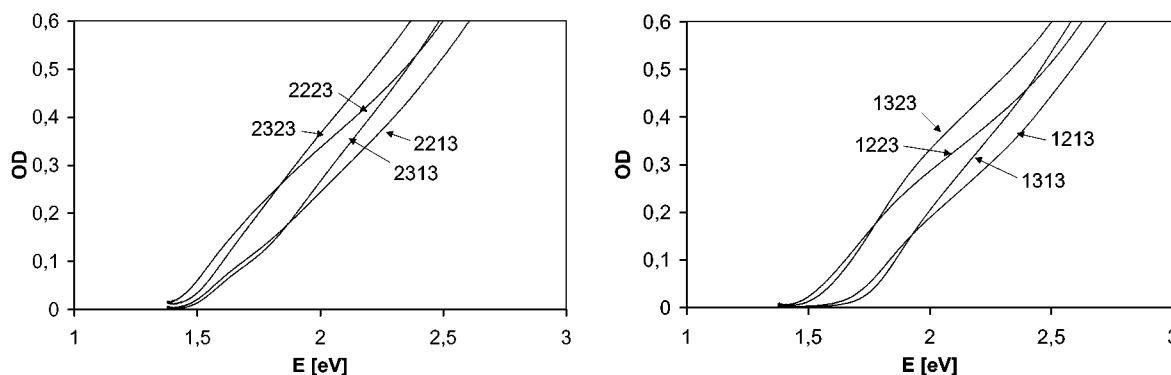
**Figure 2.** High-resolution TEM image of the double well particles from Figure 1 exhibiting a lattice spacing of 0.334 nm and reflecting the crystallinity of the sample.

cladding of three monolayers of CdS. They differ in the three inner compartments: the inner well consists of either one or two monolayers of HgS, the barrier between the wells is either two or three monolayers wide, and the outer well again consists of one or two monolayers of HgS. The nomenclature we suggest for these nanoheterostructures is as follows: CdS/HgS abcd, where starting with a CdS core “a” is the number

of monolayers HgS followed by “b” monolayers of CdS as the barrier between the wells, “c” is the number of monolayers of the second HgS well, and “d” reflects the number of cladding layers. Thus, we prepared the structures: CdS/HgS 1213, 1223, 1313, 1323, 2213, 2223, 2313, and 2323. At this point, it should be mentioned that this picture reflects an idealized situation. The “real” particles might have various kinds of inhomogeneities in all compartments.

The most remarkable findings from the absorption spectra and the TEMs are as follows. (i) There is no indication of separately formed CdS or HgS; homogeneous particle growth is observed exclusively and there is no indication for the formation of alloyed particles (which exhibit completely unstructured absorption spectra reaching into the IR-region<sup>2</sup>). (ii) The position of the first electronic transition is the further in the red spectral region the more HgS is present in the structures. (iii) Comparing the four pairs of samples having the same well composition, the transition is located further in the red when the wells are separated by only two monolayers of CdS instead of three. (iv) The absorption onset of the particles exhibiting an asymmetric inner potential (e.g., CdS/HgS 2313 and 1323) are situated at the same energy. (v) The high energy absorption depends on the total amount of material present in solution.

Comparison of the absorption onsets of these eight samples among each other as well as with those of the single well particles CdS/HgS 13 (1.8 eV) and CdS/HgS 23 (1.5 eV)



**Figure 3.** Absorption spectra of eight different double well QDQWs (for the nomenclature see text).

(“13” refers to particles with a CdS core, one monolayer of HgS and three monolayers of the CdS clad, “23” alike) allows at least the following conclusions. There is clear evidence for the separation of the wells as the CdS/HgS 1213 and 1313 samples are blue shifted compared to the CdS/HgS 23 system (even as the same amount of HgS is present). On the other hand, those samples are red shifted compared to the 13 system. This is interpreted as an electronic interaction in the two well system, even more so because this red shift increases with decreasing distance of the wells. Similar observations are made for all four pairs of particles exhibiting the same well compositions. The CdS/HgS 1323 and 2313 samples show almost similar absorption onsets as the 23 sample indicating no interaction between wells of different thicknesses at a distance of three monolayers. Compared to the single well CdS/HgS 31 (nomenclature as above) system (absorption onset at 1.3 eV),<sup>2</sup> those particles show a blue shifted first electronic transition that again gives evidence for the separation of the wells. The CdS/HgS 2223 and 2323 samples are still blue shifted compared to the CdS/HgS 31 system but red shifted compared to the CdS/HgS 23 sample, again indicating a stronger interaction between wells of the same thickness.

Temperature-dependent absorption and emission studies, HRTEM investigations, ODMR experiments, and a comparison with theoretical considerations<sup>21</sup> are currently planned.

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