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Photoluminescent Properties of CdSe Quantum Dots at Different Synthetic Conditions – Relationship with Structure and Surface Ligands

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This study is directed to the synthesis of size-homogenous, highly luminescent CdSe quantum dots (QDs) in large-scale, using different synthetic conditions. Two main types of CdSe QDs are described: (1) QDs synthesized at room temperature that are characterized with small size (approximately 2 nm in diameter), well-defined size-homogeneity (~95% monodispersed), broad-band fluorescent spectrum, long fluorescence life-time (40-120 ns), and comparatively high quantum yield (~40% in organic solvents, and ~50% in aqueous solutions); (2) QDs synthesized at high temperature that are characterized with sharp-fluorescent PL spectrum, size-homogeneity (6-8 different colors are synthesized, corresponding to 2-5.5 nm in diameter), high quantum yield (~75% in organic solvents). The photoluminescent properties of the obtained CdSe QDs were investigated at different synthetic conditions and under the treatment with different surface-modifying agents. Strong dependence of luminescence on chemical environments was observed for CdSe QDs rather than their crystallinity in the quantum confinement regime. First-principle density functional methods were employed to determine geometries and corresponding electronic properties of CdSe QDs. Absorption singularities as a function of sizes and stoichiometries of CdSe QDs were tabulated.

Key words: CdSe quantum dots, photoluminescence, surface ligands, chemical structure

1. INTRODUCTION

In last several years, the interest in synthesis of CdSe quantum dots (QDs) revived and the studies increase enormously due to their great potential for application in many industrial and life science technologies. All synthetic strategies are directed to development of photochemically stable CdSe QDs with high quality (quantum yield more 50% in organic solvents and more 20% in aqueous solutions). It has been observed that small changes in the synthetic conditions lead to a significant change of QD properties. The present study describes a synthesis of several different types CdSe QDs and analyzes the relationship between their photoluminescent (PL) characteristics, chemical structure, and surface ligands.

2. METHODS

Details of the synthetic protocols can be found in refs. 1-7.

3. RESULTS AND DISCUSSION

Figure 1 represents a synthesis of six-eight size-defined colors CdSe QDs using conventional synthetic protocol (with slight modifications). The synthesis was carried out at high temperature (120-280 °C) and Cd:Se ratio 1:1 [1-6]. The obtained QDs possessed: a good crystallinity, a high quantum yield (50-75% in organic solvents), size-defined sharp emission spectra (fwhm ~30 nm), and a size-distribution ~2.5-5%. Small changes in the synthetic conditions (e.g., an excess of Se-precursor, Cd:Se ratio 1:4) influenced markedly the PL properties of the obtained CdSe QDs in the time of synthesis at relatively low temperature (Figure 2). The small nanocrystals (~1.6-1.8 nm in diameter), obtained 30 sec after initiation of the nucleation, possessed a broad PL-spectrum consisted of a red-shifted trap PL which dominates over the band edge PL (a blue-shifted shoulder). Obviously, the deep trap PL dominates over the band edge PL for the small CdSe QDs synthesized at relatively low temperature in the excess of Se. With the increase of the time of synthesis (2-10 min) and the growth of CdSe QDs, the deep trap PL almost disappeared and the PL spectra become sharp.

It is necessary to note that the direct water-solubilization of CdSe QDs, represented in Figures 1 and 2, resulted in almost complete lose of their PL properties.

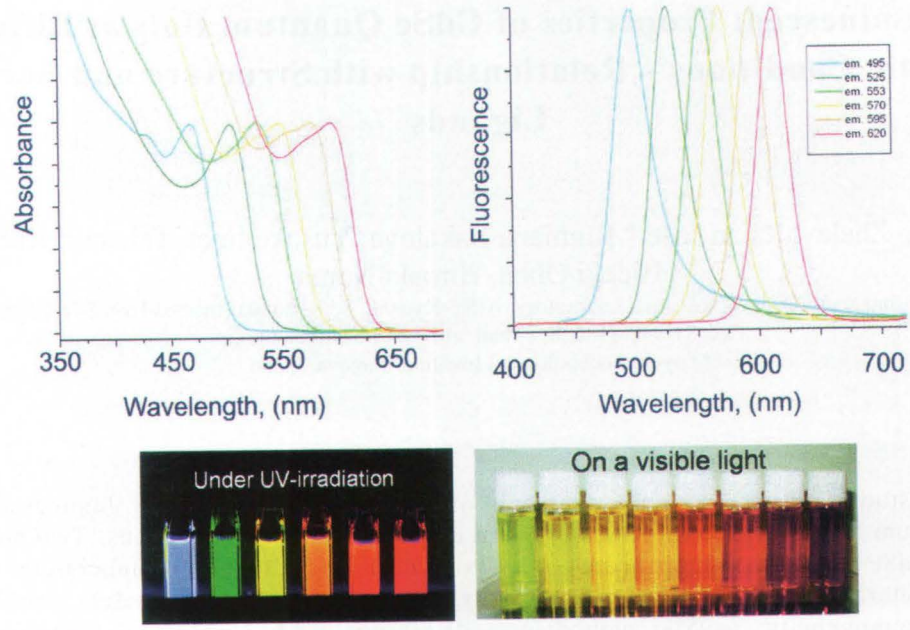


Fig. 1. Spectral characteristics of CdSe quantum dots synthesized at high temperature (120-280 °C, from blue to red color) at Cd:Se ratio 1:1.

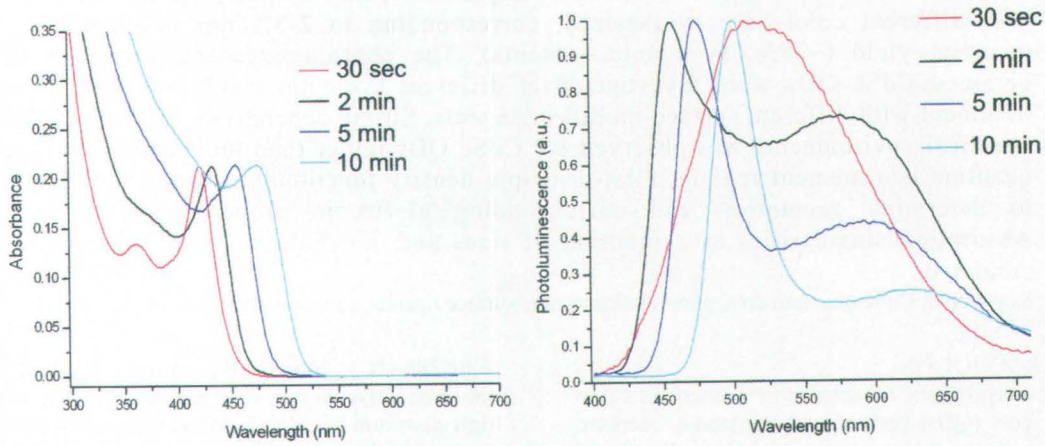


Fig. 2. Spectral characteristics of CdSe QDs synthesized at high temperature (150 °C) in excess of selenium (Cd:Se = 1:4).

Similar phenomenon – size-homogenous broad fluorescent CdSe QDs, was discovered recently changing the temperature of synthesis. Figure 3 demonstrates the spectral characteristics and HRTEM images of CdSe QDs synthesized at room temperature (RT) and Cd:Se ratio 1:1 [7]. These QDs are characterized with unusual properties: a small size (~2 nm in diameter), a very high size-homogeneity (in 97% homodispersed), a broad white/yellow fluorescent spectrum (fwhm ~150 nm), a high quantum yield (~40-80% in different organic solvents), and an impressive photochemical stability – no bleaching, no blinking, no aggregation. The large distance between absorbance and emission spectra (more 100 nm) gives a possibility to minimize self-quenching at high concentration.

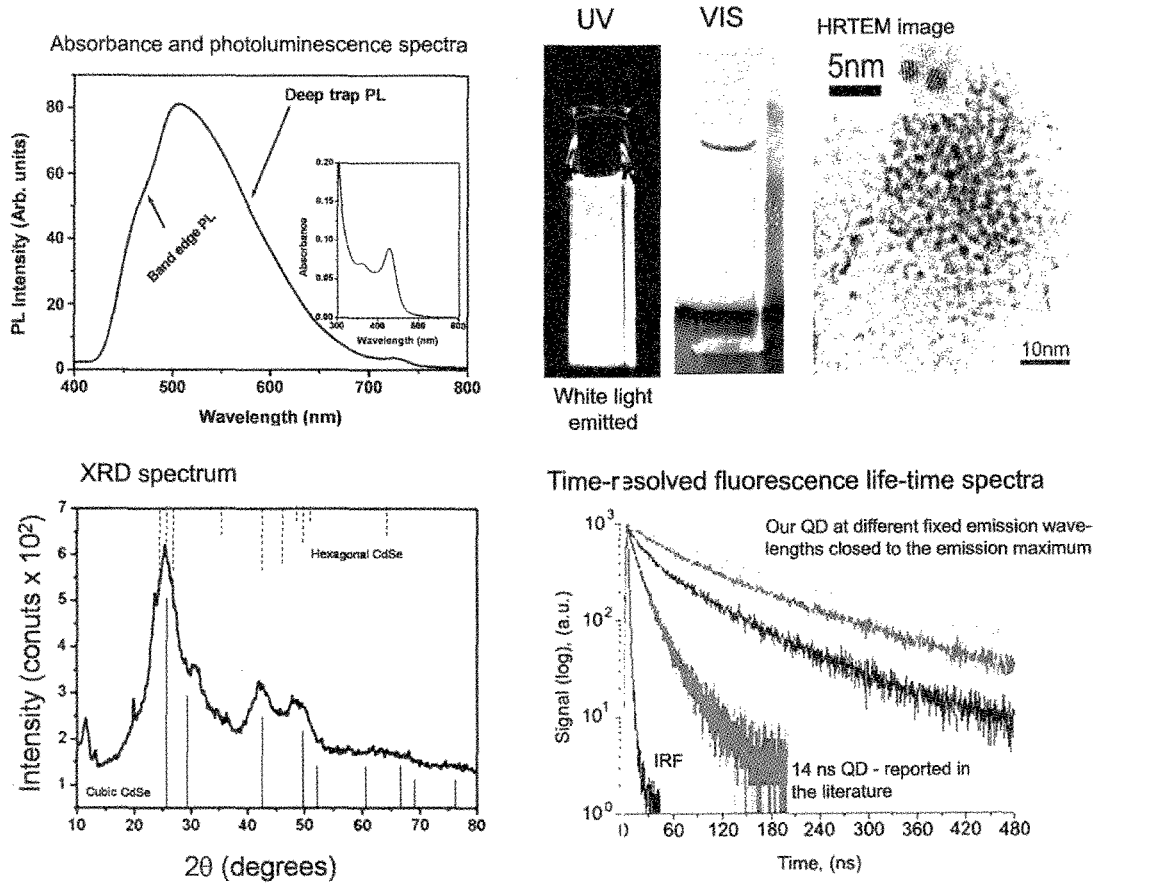
XRD measurements show that in the described synthetic protocol CdSe seems to crystallize in a cubic close packed (zinc blende) structure. The characteristic zinc blende planes of 111, 220, and 311 located at 25.38°, 42.06°, and 49.76° in the 2θ range of 20° to 70° for CdSe were observed. There are also weak peaks representing wurtzite facets observed in the XRD patterns. Presumably, the formation of cubic phase of CdSe in our synthetic procedure is attributed to the low temperature of synthesis (~22 °C). However, in some cases at low temperature of synthesis, the observed X-ray diffraction patterns can be explained also by the presence of zinc blende stacking faults along the (002) direction that is very typical for wurtzite II-VI nanocrystals.

Density functional theory (DFT) calculation at B3LYP/Lanl2dz level was employed to understand the structural geometry of the CdSe

QDs synthesized at RT (Figure 4). Time-dependent DFT calculation for singlet excited states reproduced the experimental absorption spectra and size-dependent shift in HOMO-LUMO transitions. Theoretically estimated spectra of CdSe QDs revealed red-shifted (~250 meV) oscillator strengths from HOMO-LUMO transitions and the most likely structural geometry is shown in Figure 4D.

The RT synthesized CdSe QDs were easily solubilized in aqueous solutions using mercaptosuccinic acid as a surface modifying agent (Figure 5). The quantum yield of water-soluble CdSe core QDs was impressively high (~50% in buffer – higher than in chloroform). Moreover, the same QDs possessed a high fluorescence life-time: ~120 ns in organic solvents and 90 ns in aqueous solutions vs 10-14 ns reported in the literature (Figure 3). This long PL life-time makes them appropriate for time-resolved spectroscopic analyses.

In conclusion, the present study undoubtedly demonstrate that the single changes in the synthetic condition (e.g., temperature, coordinating ligands, Cd:Se ratio) results in a significant changes of PL and structural characteristics of CdSe quantum dots, as well as in their water-solubility with preservation of high quantum yield without additional organic coatings.



Temporal evolution of UV-Vis absorption and emission spectra of CdSe nanocrystals during the synthesis. The spectra were recorded after dispersion of aliquots from the reaction mixture in 1-butanol. The PL-spectra were recorded at an excitation wavelength of 365 nm.

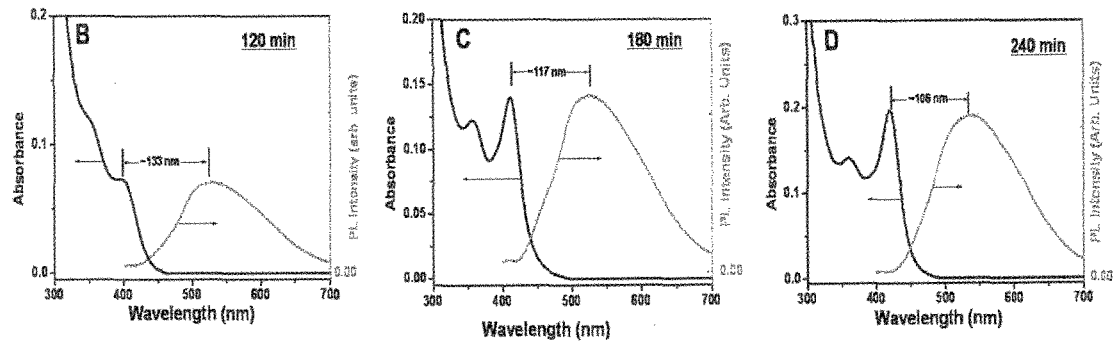


Fig. 3. Spectral characteristics and HRTEM images of CdSe QDs synthesized at room temperature at Cd:Se ration 1:1.

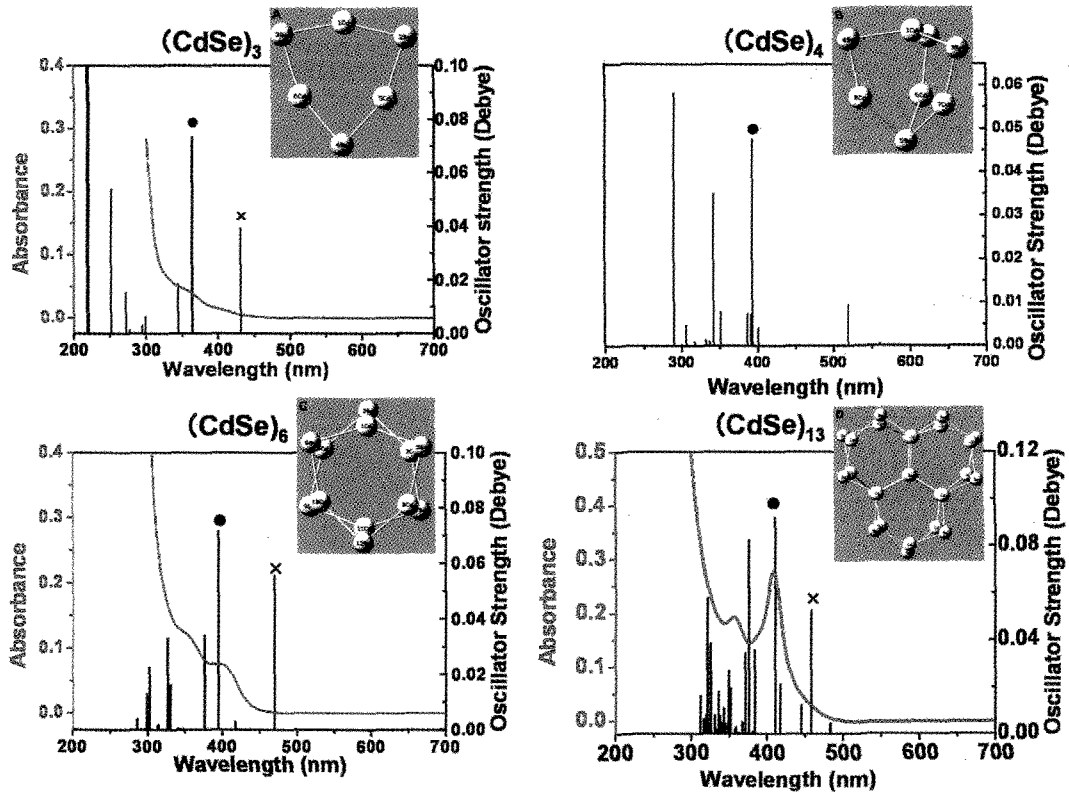


Fig. 4. Optimized geometries of $(CdSe)_3$ (A), $(CdSe)_4$ (B), $(CdSe)_6$ (C), and $(CdSe)_{13}$ clusters. Comparison between calculated transition oscillator strengths and experimental UV-VIS absorption spectrum of (CdSe)3, (CdSe)4, (CdSe)6, and (CdSe)13 clusters. The oscillator strengths marked with "•" are HOMO-LUMO transitions and those with "x" are assumed to arise from surface trap.

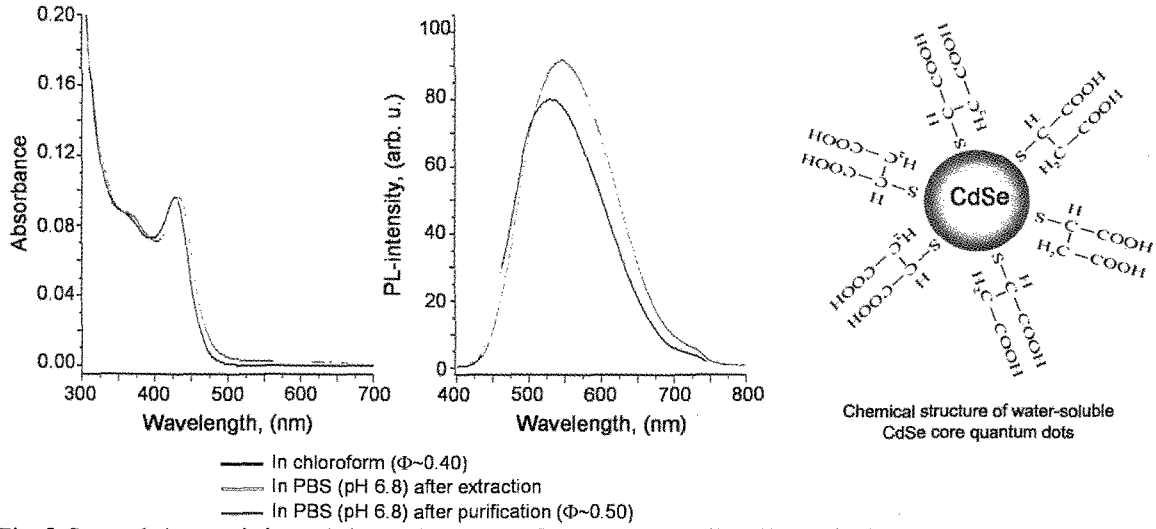


Fig. 5. Spectral characteristics and chemical structure of water-soluble CdSe QDs synthesized at room temperature.

4. ACKNOWLEDGEMENT

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References

[1] R. Bakalova, H. Ohba, Z. Zhelev, T. Nagase, R. Jose, M. Ishikawa and Y. Baba, Nano Lett. **4**, 1567-73 (2004).

[2] R. Bakalova, H. Ohba, Z. Zhelev, M. Ishikawa and Y. Baba, Nature Biotechnol. **22**, 1360-1 (2004).

[3] Z. Zhelev, H. Ohba, R. Bakalova, R. Jose, S. Fukuoka, T. Nagase, M. Ishikawa and Y. Baba, Chem. Commun. (Camb.), **15**, 1980-82 (2005).

[4] R. Bakalova, Z. Zhelev, H. Ohba and Y. Baba, J. Am. Chem. Soc., **127**, 9328-9 (2005).

[5] R. Bakalova, Z. Zhelev, H. Ohba and Y. Baba, J. Am. Chem. Soc., **127**, 11328-35 (2005).

[6] Z. Zhelev, R. Jose, T. Nagase, H. Ohba, R. Bakalova, M. Ishikawa and Y. Baba, J. Photochem. Photobiol. B, **75**, 99-105 (2004).

[7] Z. Zhelev, R. Bakalova, H. Ohba, R. Jose, Y. Imai and Y. Baba, *Anal. Chem.*, **1**, 321-330 (2006).

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