

Spectral Properties of Ultrasmall CdS Nanoparticles Stabilized by Mercaptoacids and Hydrazine

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Abstract — Ultrasmall colloidal CdS quantum dots (QDs) were synthesized in water at room temperature by using a combination of two low-molecular-weight stabilizers – hydrazine and a mercaptoacid, particularly, mercaptoacetic and mercaptopropionic-2 acids. The average size of QDs was found to depend on the Cd-to-S ratio at the synthesis and be as small as 2,5 nm at 80% cadmium(II) excess. The CdS QDs emit broadband photoluminescence in the visible spectrum range with a relative quantum yield of around 5% and the radiative life time of around 100 ns.

I. INTRODUCTION

Highly stable colloidal ultrasmall (1–3 nm) semiconductor nanoparticles or quantum dots (QDs), mostly of cadmium and lead chalcogenides, gained great research potential due to their unique properties which considerably differ from larger nanoparticles and can find promising applications in biolabeling and electroluminescent devices [1–5]. The nature of ultrasmall NP is still a subject of intense research and discussion. The most promising hypothesis appeals to existence of the so-called “magic clusters” possessing unique properties such as monodispersity, strong exciton confinement and broad photoluminescence bands in the visible region. At the same time studies of the ultrasmall QDs are hampered by very limited range of available synthetic methods of producing such nanoscale objects. Only a few papers have reported so far on the synthesis of ultrasmall QDs in mild conditions and in aqueous solutions, which are of great interest from the viewpoint of biosensoric applications. Recently we have reported on the synthesis and unusual properties of ultrasmall CdS QDs stabilized in water and ethyl alcohol by polyethyleneimine [4]. The unique properties of such QDs have been shown to originate from a dynamic character of coordination of amino-groups of the stabilizer to surface Cd atoms. Further search of amine-containing compounds capable of stabilizing luminescent ultrasmall CdS QDs revealed that a series of guanidine dendrimers can be used for this purpose producing 2–3-nm CdS QDs with promising photo- and electroluminescent properties [5]. However, CdS QDs synthesized in the presence of polymers are tightly captured in a polymeric “coat” and, hence, their further functionalization is very difficult.

In the present communication we show that successful stabilization of luminescent ultrasmall CdS QDs in aqueous solutions can be achieved without any

polymeric agents by using a combination of two low-molecular-weight compounds – hydrazine and mercaptoacids, specifically, mercaptoacetic acid (MAA) and mercaptopropionic-2 (MPA-2) acids. The benefit of such stabilization is in that the surface of CdS QDs remains opened for further possible modification and conjugation with biomolecules such as nucleic acids.

II. EXPERIMENTAL SECTION

Cadmium chloride, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, MAA, MPA-2, $\text{N}_2\text{H}_4\cdot \text{H}_2\text{O}$, anthracene were purchased from Sigma Aldrich and used without further purification.

The colloidal cadmium sulfide QDs were synthesized in a reaction between Cd^{2+} and HS^- in the presence of hydrazine and MAA (MPA-2) in water mixtures. In a typical procedure, maximally diluted 0,1 mL 1 M Na_2S solution was added to the solution of 0,2 mL 1 M MAA (MPA-2) and 0,5 mL N_2H_4 . To the resulting solution 0,1 mL 1 M CdCl_2 solution was added at vigorous stirring.

The absorbance spectra were registered with a Specord 220 spectrophotometer. The photoluminescence (PL) spectra were taken on a Perkin-Elmer LS55 luminescence spectrometer at the excitation wavelength of 360 nm. The luminescence decay profiles were obtained using an Edinburgh Instruments FLS920 photon counting system equipped with a EPL-375 picosecond diode laser emitting 60 ps pulses with $\lambda = 375$ nm. The XRD spectra were registered using a DRON-3M diffractometer with a copper K_α irradiation source. Dynamic light scattering spectra were obtained with a Zetasizer Nano, Malvern Instruments. Transmission electron microscopy (TEM) studies were performed on a Selmi PEM-125K at an accelerating voltage of 100 kV.

III. RESULTS AND DISCUSSION

Figure 1 shows normalized absorbance and PL spectra of as-prepared CdS QDs stabilized by two different mercapto acids. Both colloids were synthesized in the presence of 80% excess of molar Cd(II). By comparing the absorbance spectrum of N₂H₄/MAA-stabilized QDs NPs with that of N₂H₄/MPA-2-stabilized QDs, the formation of an ensemble with a narrower size distribution evident from a pronounced absorbance maximum at 360 nm (compare curves 1 and 2, Fig. 1). As the MPA-2-stabilized CdS QDs do not reveal distinct spectral features in this range the band gap of the QDs (determined as an energy corresponding to the cross point between a tangent to the absorption band edge and the abscissa axis, E_g) was used to determine the average size $\langle d \rangle$ of CdS QDs using a well-known empirical $E_g(d)$ relations (see for example [4]). The band gaps of both MAA and MPA-2-stabilized CdS QDs were found to be the same and equal to $E_g = 3,06$ eV corresponding to $\langle d \rangle = 2,5$ nm.

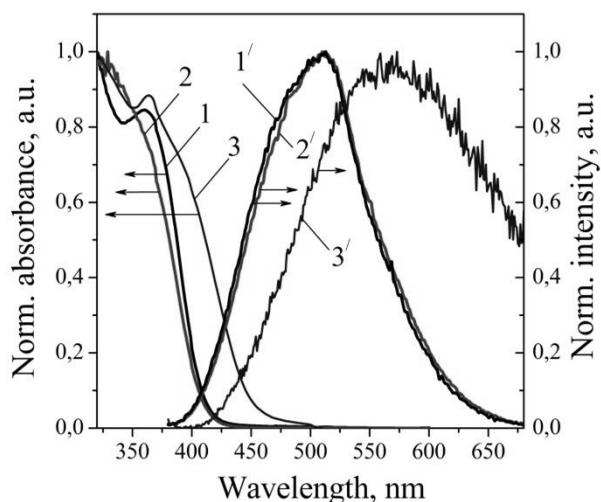


Fig.1. Normalized absorbance (curves 1–3) and photoluminescence (curves 1'–3') spectra of CdS NPs, stabilized by mercaptoacetic (curves 1, 3, 1', 3') and mercapto-propionic-2 acid (curves 2, 2'). CdS QDs were synthesized in the presence an 80% excess of Cd(II) (curves 1, 2, 1', 2') and without Cd(II) excess (curves 3, 3').

If only hydrazine or a mercaptoacid is used in the synthesis, CdS QDs form opalescent aggregates already in the first seconds after the reactant mixing the fact indicating a cooperative effect of N₂H₄ and a mercaptoacid in stabilizing the ultrasmall CdS QDs. The origin and mechanism of such cooperative effect are currently under investigation. Most probably, with both thiol and amine groups present in a combination of MAA and N₂H₄, the stabilization mechanism should resemble that for the recently reported CdSe QDs stabilized with cysteine [2] whose functional groups play a key role in surface passivation, due to their coordination with both surface cadmium and selenium atoms.

As CdS QDs possess very similar optical properties irrespectively of the type of the mercaptoacid used, the MAA-stabilized QDs was chosen for a further detailed

investigation as having a more uniform size distribution and higher stability to aggregation.

A detailed investigation of the influence of various synthesis parameters (precursor concentration and ratio, temperature, post-synthesis heat treatment, pH, etc.) on the band gap and, therefore, the average size of N₂H₄/MAA-stabilized CdS QDs showed that the most crucial parameter potently affecting $\langle d \rangle$ is the presence of an excess Cd(II) in the moment of QD formation. The quantum dots synthesized with no Cd(II) excess present exhibit a considerable red shifts of both the absorption band edge (curve 3, Fig. 1) and the PL band maximum (curve 3', Fig. 1). The average size of such CdS QDs estimated from the absorption spectrum is $\langle d \rangle = 3,5$ nm. The band gap of CdS QDs was found to increase proportionally to an increase in the excess Cd(II) concentration – from 2,77 eV when Cd(II) and S(II) are introduced into solution in the stoichiometric ratio to 3,06 eV at 80% Cd(II) excess (Fig. 2, curve 1). Along with the E_g increase and corresponding decrease of $\langle d \rangle$ a drastic increase in the PL intensity is observed – it grows by a factor of almost 8 at introduction of 80% Cd(II) excess (Fig. 2, curve 2).

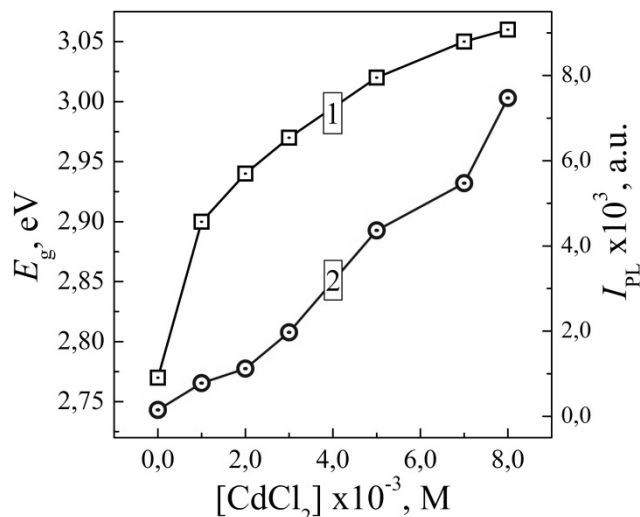


Fig.2. The band gap (curve 1) and PL intensity (curve 2) of N₂H₄/MAA-stabilized colloidal CdS QDs as functions of the content of excessive Cd(II) present at the synthesis.

In case of the N₂H₄/MAA-stabilized CdS QDs prepared with a 80% excess of Cd(II) over the stoichiometric amount, the $\langle d \rangle$ estimation based on the absorption band edge position is supported by results of the TEM (Fig. 3) and the dynamic light scattering (DLS) spectroscopy (Fig. 4). Figure 3a,b shows that the average size of CdS QDs prepared at Cd:S = 1,8:1 is around 3 nm which corroborates the estimations based on the optical data.

As Figure 4 shows, the average hydrodynamic size L_{hd} of N₂H₄/MAA-stabilized CdS QDs prepared with 80% Cd(II) excess is in the range of 2–3 nm agreeing perfectly with $\langle d \rangle$ values derived from absorption spectra and TEM data and indicating that the stabilizer layer on the QD surface is very thin.

A decrease in the average size of CdS QDs in the presence of growing amount of excessive Cd(II) may be

due to several factors. First, the presence of abundant Cd(II) species would create favorable conditions for more primary nuclei to be formed at precursors mixing and, in the end, in formation of smaller QDs.

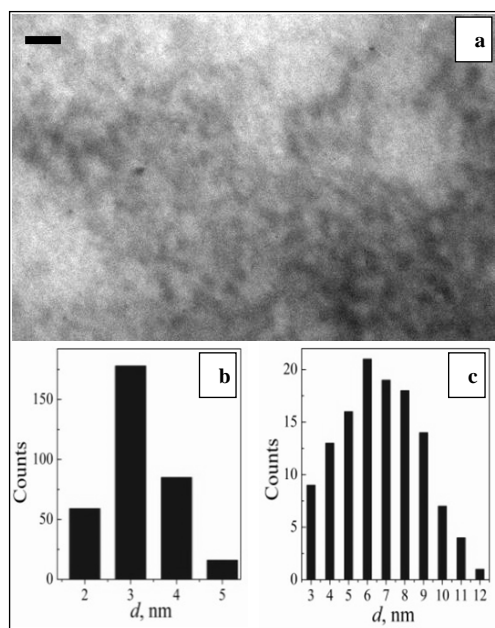


Fig.3. TEM image (a) of N_2H_4/MAA -stabilized CdS QDs prepared in the presence of 80% Cd(II) excess. (b, c) TEM-based size distribution charts for CdS QDs prepared at Cd:S = 1,8:1 (b) and 1:1 (c) (the original TEM image for (c) is not shown here). The scale bar is 10 nm.

Second, adsorption of Cd(II) species or Cd(II)–MAA complexes on the surface of CdS QDs would terminate their growth and arrest post-synthesis QD coarsening. At the same time, there is a limit to the Cd(II) excess which is around 90%. If a higher amount of $CdCl_2$ is introduced into the system before Na_2S addition the formation of CdS QDs is not observed at all.

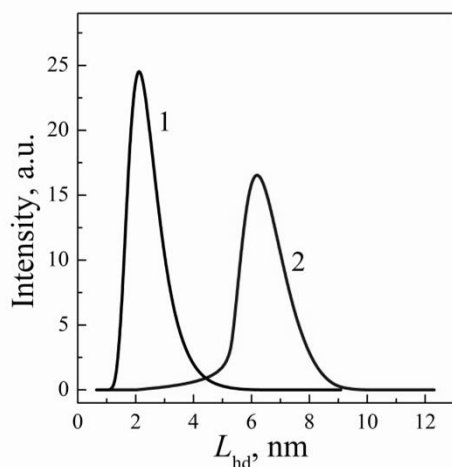


Fig.4. Distribution of the hydrodynamic size of N_2H_4/MAA -stabilized CdS QDs synthesized at a Cd:S ratio of 1,8:1 (curve 1) and 1:1 (curve 2).

In case of larger N_2H_4/MAA -stabilized CdS QDs prepared at the stoichiometric Cd:S ratio the value of $\langle d \rangle$

estimated from the absorption spectrum, 3,5 nm, is considerably lower than the average size determined by the TEM, 5–10 nm, and DLS, 6–7 nm. This discrepancy combined with the fact that TEM and DLS results agrees well with each other, may originate from the aggregation of CdS QDs which are not protected with excessive Cd(II) or their complexes with mercaptoacetate anions. Most probably, aggregates of several (two-four) CdS QDs are observed both in TEM and DLS experiments rather than separate larger QDs.

This assumption is supported by XRD experiments. Fig. 5 shows that the XRD pattern of N_2H_4/MAA -stabilized CdS QDs protected with 80% Cd(II) excess (curve 1) does not reveal any features of a crystalline materials and contains only a halo at $2\theta = 15\text{--}35^\circ$ typical for amorphous matter. On the contrary, the XRD spectrum of the CdS QDs prepared at the stoichiometric Cd:S ratio (curve 2) exhibits perfectly developed set of reflexes typical for cubic cadmium sulfide.

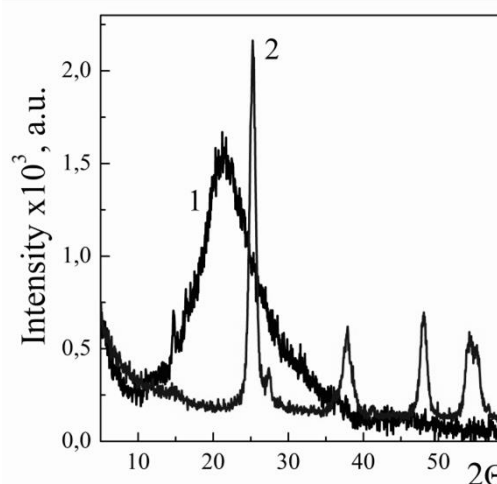


Fig.4. XRD spectra of dry residues from the colloidal solutions of N_2H_4/MAA -stabilized CdS QDs prepared at a Cd:S ratio of 1,8:1 (curve 1) and 1:1 (curve 2).

The crystallite size (the coherent scattering domain size) in the sample prepared at Cd:S = 1:1 (Fig. 4, curve 2) estimated using the well-known Scherer equation was found to be as large as 25–30 nm. This result indicates that solvent evaporation from such CdS colloids results not in mere agglomeration of QDs but rather in QD coarsening and coalescence of original 3–4-nm particles into much larger crystallites. The coalescence requires aggregation of the QDs as a first step and such aggregates may be observed both on TEM images and in DLS spectra instead of separate QDs. At the same time, in such a pre-coalescence state the QDs composing the aggregates do not lose their individuality and behave as separate light-absorbing entities manifesting quantum confinement and a blue shift of the absorption band edge which is not expected to be observed for 25–30-nm CdS crystals.

Figure 1 shows that both N_2H_4/MAA - and $N_2H_4/MPA-2$ -stabilized CdS QDs possess very similar PL properties. In case of colloidal solutions synthesized in the presence of a Cd(II) excess the emission spectra (Fig. 1, curves 1'–3') reveal a broad PL band in the range of 400–650 nm with a non-distinct maximum at 500–520

nm, and a considerable (around 100 nm) Stokes shift separating the absorption band edge from the PL band maximum. As was mentioned before the integral PL intensity increases by an almost order of magnitude when the 80% excess of Cd(II) is introduced at the synthesis. At Cd:S = 1,8:1 the relative PL quantum yields estimated using the solid ultra-pure anthracene as a reference similarly to [4, 5] was found to be around 5%. The CdS QDs synthesized at Cd:S = 1:1 exhibit a red shift of the PL band relative to the sample synthesized at Cd:S = 1:1 (compare curves 2' and 3' in Fig. 1) which is close in terms of energy to the corresponding difference between the band gaps (absorption band edges) of the two CdS QD samples (curves 1 and 3, Fig. 1).

A time-resolved PL study of N₂H₄/MAA-stabilized CdS QDs produced at different Cd:S ratio showed that the radiative electron-hole recombination occurs in a range of hundreds of nanoseconds (Fig. 5). The PL decay profiles are strongly non-exponential and can be satisfactorily fitted with linear combinations of at least four monoexponential functions.

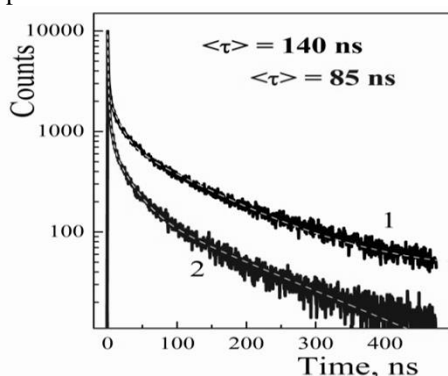


Fig.5. PL decay profiles registered at $\lambda = 500$ nm for colloidal N₂H₄/MAA-stabilized CdS QDs synthesized at a Cd:S ratio of 1,8:1 (curve 1) and 1:1 (curve 2).

The CdS QDs synthesized at Cd:S = 1,8:1 are characterized by a considerably slower PL decay indicating lower contribution of competing radiationless recombination processes. The average radiative life-time $\langle\tau\rangle$ calculated as described in [6] was found to increase from 85 ns for the CdS QDs prepared at Cd:S = 1:1 to 140 ns for the QDs synthesized in the presence of the 80% Cd(II) excess.

As to possible nature of broad luminescence band, it was found that the PL spectra for our CdS NPs could be treated as a superposition (or combination) of components, which corresponded to band-edge emission and surface-trap-state emission. It is considered that magic clusters, i.e. ultrasmall NPs, possess photoluminescence corresponded to charge-transfer state [1–4]. This idea is confirmed by presence of large Stokes shifts and relatively large values of the characteristic radiative life time typical for the trap-state emission.

IV. CONCLUSION

Ultrasmall colloidal CdS quantum dots were synthesized in water at room temperature by using a combination of two low-molecular-weight stabilizers – hydrazine and a mercaptoacid, particularly, mercaptoacetic or mercaptopropionic-2 acids. The

average size of QDs was found to depend on the Cd-to-S ratio at the synthesis and be as small as 2,5 nm at 80% cadmium(II) excess. The average size of CdS quantum dots synthesized at Cd:S = 1:1 was found to be 3,5 nm by UV-Vis absorption data and 6–8 by the TEM and dynamic light scattering data. The discrepancy was interpreted in terms of aggregation and gradual coalescence of CdS quantum dots unprotected by an excess of cadmium(II). The CdS quantum dots were found to emit broadband photoluminescence in the visible range with a characteristic radiative life-time increasing from 85 ns for unprotected CdS quantum dots to 140 ns for the quantum dots produced in the presence of 80% excess of Cd(II). The relative quantum yield of the photoluminescence was found to be around 5%, allowing further applications in biolabeling and LED fabrication.

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