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## Synthesis and luminescent properties of ultrasmall colloidal CdS nanoparticles stabilized by Cd(II) complexes with ammonia and mercaptoacetate

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| <b>Abstract:</b>                                     | <p>The synthesis of stable water-soluble ultrasmall 1.8 nm CdS nanoparticles co-stabilized with Cd(II) complexes with NH<sub>3</sub> and mercaptoacetate ions is reported. The CdS nanoparticles emit broad-band photoluminescence with a peak at 2.3 eV and a quantum yield of up to 15%. The photoluminescence decay is strongly non-exponential and characterized by an average radiative life-time increasing from 46 to 105 ns as the emission quantum energy decreases from 2.9 to 1.8 eV. The photoluminescence intensity and life-time decrease to about 50% as the colloid temperature is elevated from 22 to 50 °C. This behavior is completely reversible and assumed to originate from the thermally activated dissociation of Cd(II)-NH<sub>3</sub> complexes on the nanoparticle surface and the formation of Cd(II)-H<sub>2</sub>O complexes acting as the radiationless recombination sites. The strong temperature dependence of the luminescent properties coupled with the small size and reasonably high quantum yields of emission makes CdS nanoparticles co-stabilized with NH<sub>3</sub> and mercaptoacetate attractive for bio-imaging, bio-sensing, and other applications.</p> |
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| <b>Question</b>                                   | <b>Response</b>   |
| Scientific Justification (Available to Reviewers) | <p>The manuscript reports new synthesis of stable water-soluble ultrasmall 1.8-nm CdS nanoparticles co-stabilized with Cd(II) complexes with NH<sub>3</sub> and mercaptoacetate ions. The CdS nanoparticles emit broad-band photoluminescence in the visible range (1.7-2.9 eV) with a quantum yield of 15%. Due to the stabilization with labile Cd (II) complexes the CdS nanoparticles exhibit unusually strong temperature dependence of the luminescent efficiency. Such synthesis has not been reported earlier and can be applied to synthesize other metal-chalcogenide colloidal nanoparticles. We believe that a combination of the strong temperature dependence of the luminescent properties coupled with the small size and reasonably high quantum yields of emission makes CdS nanoparticles co-stabilized with NH<sub>3</sub> and mercaptoacetate attractive for bio-imaging, bio-sensing, and other applications.</p> |

# Synthesis and luminescent properties of ultrasmall colloidal CdS nanoparticles stabilized by Cd(II) complexes with ammonia and mercaptoacetate

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## Abstract

The synthesis of stable water-soluble ultrasmall 1.8 nm CdS nanoparticles co-stabilized with Cd(II) complexes with NH<sub>3</sub> and mercaptoacetate ions is reported. The CdS nanoparticles emit broad-band photoluminescence with a peak at 2.3 eV and a quantum yield of up to 15%. The photoluminescence decay is strongly non-exponential and characterized by an average radiative life-time increasing from 46 to 105 ns as the emission quantum energy decreases from 2.9 to 1.8 eV. The photoluminescence intensity and life-time decrease to about 50% as the colloid temperature is elevated from 22 to 50 °C. This behavior is completely reversible and assumed to originate from the thermally activated dissociation of Cd(II)-NH<sub>3</sub> complexes on the nanoparticle surface and the formation of Cd(II)-H<sub>2</sub>O complexes acting as the radiationless recombination sites. The strong temperature dependence of the luminescent properties coupled with the small size and reasonably high quantum yields of emission makes CdS nanoparticles co-stabilized with NH<sub>3</sub> and mercaptoacetate attractive for bio-imaging, bio-sensing, and other applications.

**Key words:** cadmium sulfide, radiative life-time, temperature dependence, thioglycolate, luminescence quenching

## 1 Introduction

Ultrasmall cadmium chalcogenide nanoparticles (NPs) have recently been recognized as an emerging class of broad-band-emitting nanomaterials with a vast potential of applications in luminescent bio-labeling, sensing, LED technologies, *etc.* (McBride et al. 2010; Kim et al. 2014). Recent studies on the mechanism and dynamics of the photoluminescence (PL) of ultrasmall cadmium chalcogenide NPs (McBride et al. 2010; Dukes III et al. 2011; Zhou et al. 2011; Pennycook et al. 2012; Rosson et al. 2012), especially those performed on single NPs (Dukes III et al. 2011; Pennycook et al. 2012), showed that the large spectral width of the PL band and relatively long PL life-time is not the result of the collective properties of an inhomogeneous NP ensemble but rather of inherent properties of each individual NP. These findings shed light and stimulated further discussions also on the PL mechanism in larger, “regular” NPs.

At the same time, the progress in understanding the unique properties of ultrasmall NPs is retarded by a limited number of reliable synthetic protocols for producing ultrasmall NPs in comparatively mild conditions and polar solvents. In order to produce water-soluble ultrasmall cadmium chalcogenide NPs typically either sulfur-containing stabilizers are used such as cysteine (Xia and Zhu 2008; Park et al. 2010, 2011; Zhou et al. 2011; Pennycook et al. 2012) or mercaptocarboxylic acids (Rogach et al. 2007; Xiao et al. 2008; Chen et al. 2008; Tian et al. 2009; Kalasad et al. 2009; Zhou et al. 2011) or amine-rich dendrimers (Wu et al. 2005; Fahmi et al. 2009) forming strong complexes with Cd atoms on the NP surface.

Recently we reported the “green” synthesis of stable ultrasmall 1.8 nm CdS NPs stabilized in water and ethanol by an amine-rich polyelectrolyte – polyethyleneimine (PEI) (Raevskaya et al. 2010a, 2010b). The CdS-PEI NPs are characterized by a broad-band photoluminescence (PL) peaked at 520 nm with quantum yields of 5–8% in solution and up to 15% in PEI films. It was also found that the synthetic protocol used can be extended to other cadmium chalcogenides – CdSe and CdS<sub>x</sub>Se<sub>1-x</sub> (Raevskaya et al. 2010c) as well as other amine-rich stabilizers such as hyper-branched guanidine-based dendrimers (Grodzyuk et al. 2011). In the latter case the feasibility of using ultrasmall CdS/dendrimer NPs as the electroluminescent component of light emitting diodes was demonstrated. However, the presence of a dielectric layer of the polymeric stabilizers on the surface of CdS NPs requires quite high working voltages to be applied to such LEDs (Grodzyuk et al. 2011) and also complicates their application in bio-labeling and bio-sensing where the covalent attachment of various biomolecules to the NP surface is needed. In this view, the development of new synthetic protocols which allow stable and brightly luminescent ultrasmall NPs to be produced is of special interest. These should be passivated by low-molecular-weight species in order to make their surface readily accessible.

In the present paper we report an approach to the synthesis of water-soluble ultrasmall colloidal CdS NPs using cadmium(II) complexes with two ligands – ammonia and mercaptoacetate anions – as stabilizers. The paper focuses on synthetic aspects allowing the size and PL properties of CdS NPs as well as the PL decay dynamics and influence of temperature on the emission characteristics of such NPs to be tuned.

## 2 Experimental Details

Cadmium chloride,  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , mercaptoacetic acid (MAA), 25% aqueous ammonia solution ( $\text{NH}_4\text{OH}$ ), anthracene (ultrapure) were purchased from Sigma Aldrich and used without any further purification.

Colloidal cadmium sulfide NPs were synthesized in aqueous solutions in a reaction between sodium sulfide and Cd(II) complexes with ammonia and MAA. In a typical procedure, to 8.42 mL of distilled water 0.2 mL 1 M aqueous  $\text{CdCl}_2$  solutions was added followed by 0.3 mL 1 M aqueous MAA solution at vigorous stirring. The addition of the acid resulted in visible turbidity caused by precipitation of Cd(II) mercaptoacetate. To the turbid solution 0.085 mL aqueous ammonia solution was added. As a result the precipitate was completely dissolved yielding a clear and stable solution containing complexes of Cd(II) with ammonia and MAA. To such solution 1.0 mL 0.1 M aqueous  $\text{Na}_2\text{S}$  solution was rapidly injected at intense stirring resulting in the formation of CdS NPs. All procedures were performed at ambient temperature, pressure, and atmosphere. The typical composition of the final solutions was  $[\text{CdS}] = 0.01 \text{ M}$ ,  $[\text{CdCl}_2] = 0.01 \text{ M}$  (excess),  $[\text{MAA}] = 0.03 \text{ M}$ ,  $[\text{NH}_4\text{OH}] = 0.12 \text{ M}$ . The solutions were kept in the dark at room temperature or subjected to thermal treatment at 96–98 °C for 10 min. It should be noted that the 25% ammonia solution changes its concentration with time as a result of  $\text{NH}_3$  evaporation. Thus only fresh  $\text{NH}_3$  solution should be used for the synthesis. Alternatively, a mixture of  $(\text{NH}_4)_2\text{SO}_4$  with NaOH (0.12 M) can be used to introduce ammonia into the solution.

The absorption spectra were registered with a Specord 220 or an HP Agilent 8453 spectrophotometer. The PL spectra and decay profiles were obtained using an Edinburgh Instruments FLS920 photon counting system. In order to acquire PL spectra the samples were excited by 330 nm (3.76 eV) light in standard 10.0 mm quartz cuvettes. The relative PL quantum yields were estimated using solid ultra-pure anthracene as a reference. The PL decay curves were approximated by linear combinations of 3 mono-exponential functions  $I(t) = \sum_i A_i e^{-t/\tau_i}$ , where  $I$  is the PL intensity,  $i = 1..3$ , with the amplitudes  $A_i$  and times  $\tau_i$  being the fitting parameters. The average PL decay time  $\langle \tau \rangle$  was determined as

$\langle \tau \rangle = \frac{\sum_i A_i \tau_i^2}{\sum_j A_j \tau_j}$  (Jones and Scholes 2010). Dynamic light scattering measurements were

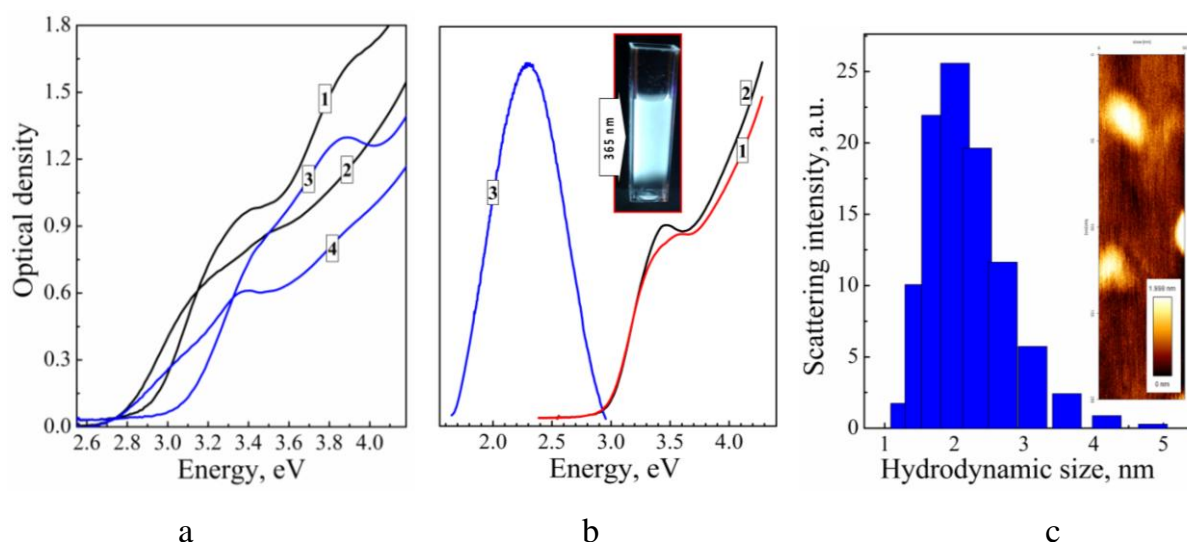
performed with a Zetasizer Nano (Malvern Instruments). Atomic Force Microscopy (AFM) images were acquired with a JPK NanoWizard II from JPK Instruments AG, Berlin. The AFM tip was a NCH Silicon nitride cantilever from NanoWorld with a force constant of 42 N/m and a resonance frequency of 320 kHz. The lateral resolution of AFM was lower than 30 nm.

## 3 Results and discussion

The interaction between Cd(II) chloride and MAA in aqueous solutions results in the precipitation of cadmium(II) mercaptoacetate which can be re-dissolved by introducing a base, particularly ammonia, NaOH or  $\text{N}(\text{C}_2\text{H}_5)_4\text{OH}$ , due to the formation of charged and

water-soluble Cd(II) complexes. The introduction of Na<sub>2</sub>S in such solutions results in the instant formation of colloidal CdS NPs displaying characteristic absorption bands with an edge at 2.9 eV (NaOH, Fig. 1a, curve 1), 3.1 eV (N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>OH, Fig. 1a, curve 3), and 3.0 eV (NH<sub>4</sub>OH, Fig. 1b, curve 1). Large “blue” shifts of the band edges compared to the band gap of bulk cadmium sulfide (2.4 eV) indicates the formation of very small CdS NPs with strong spatial confinement of the photogenerated charge carriers.

Among the three bases studied the ammonia-containing colloids showed an exceptional stability towards either ageing at room temperature or fast ageing by thermal treatment at 96–98°C for 10 min. As can be seen from Fig. 1a, the thermal treatment of NaOH- and N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>OH-containing colloids resulted in a "red" shift of the absorption threshold and a broadening of the band indicating growth and aggregation of CdS NPs (compare curves 1 and 2, 3 and 4, Fig. 1a) as well as in eventual precipitation of CdS NPs. In the case of ammonia-containing CdS colloids no changes in the absorption band edge position or curvature were observed after the thermal treatment (compare curves 1 and 2, Fig. 1b) indicating the high stability of CdS-NH<sub>3</sub>-MAA NPs against ripening and aggregation.



**Figure 1** Spectral and size properties of CdS-NH<sub>3</sub>-MAA NPs ([CdS] = 0.01 M, [MAA] = 0.03 M, [NaOH] = 0.12 M or [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>OH] = 0.12 M).

(a) – absorption spectra of NPs in presence of NaOH (**1**, **2**) or N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>OH (**3**, **4**). (**1**, **3**) before and (**2**, **4**) after thermal treatment (98°C, 10 min).

(b) – absorption (**1**, **2**) and PL (**3**) spectra of NPs at [Cd(II)]/[Na<sub>2</sub>S] = 2 and [NH<sub>3</sub>]/[Cd(II)] = 4. **1-2** – fresh and after thermal treatment (98°C, 10 min), respectively. Inset: luminescence of quartz cuvette with NPs (excitation at 365 nm).

(c) – hydrodynamic size distribution and AFM image of NPs as in (b) with spectrum (2)

On the contrary, the thermal treatment of CdS-NH<sub>3</sub>-MAA NPs results in a sharpening of the absorption maximum at 3.46 eV and imparts the colloidal solutions prolonged (months) stability against precipitation. In the absence of MAA obviously no stable CdS NP colloids can be produced. It can therefore be concluded that not the mere basic medium but rather the availability of nitrogen atoms with free electron pairs capable of forming complexes with Cd<sup>2+</sup> ions is crucial for the formation of stable CdS NPs. Indeed, the

$\text{N}(\text{C}_2\text{H}_5)_4\text{OH}$  base with a bound electron pair on the N atom acts similarly to NaOH and is not capable of stabilizing CdS NPs against thermal ripening. Therefore, MAA and  $\text{NH}_3$  (in the form of  $\text{NH}_4\text{OH}$ ) which both can form complexes with Cd(II) on the surface of CdS NPs apparently act simultaneously as co-stabilizers forming a blocking layer on the NP surface and efficiently prohibiting aggregation and growth of CdS NPs.

The average size  $d$  of CdS- $\text{NH}_3$ -MAA NPs produced after the thermal treatment can be derived from the position of the absorption maximum  $E_1$  using the well-known empiric  $E_1(d)$  correlations, in particular, a calibration curve used by us earlier for PEI-stabilized CdS (Raevskaya et al. 2010). Thus the average size of CdS NPs featuring a maximum at 3.46 eV is 1.8 nm. The absorption maximum can be fitted with a Gaussian curve with a full width at half maximum (FWHM) of 0.28 eV corresponding to a size distribution of CdS NPs of 0.5 nm. The estimated size and its distribution were supported by dynamic light scattering measurements (Fig. 1c) indicating that the average hydrodynamic size and size distribution of colloidal CdS- $\text{NH}_3$ -MAA NPs are around 2 nm and  $\pm 0.5$  nm, respectively. Similar values of  $d$  were obtained by AFM (see Fig. 1c, inset). The AFM image of CdS NPs deposited on mica reveals islands with an average height of around 2 nm, which is close to the  $d$  estimation made from the absorption spectra, and with lateral dimensions of 20–30 nm. The large lateral size can be explained by the formation of monolayer islands of aggregated CdS NPs formed when drying the colloidal solutions on mica as well as limitations in the lateral resolution of AFM.

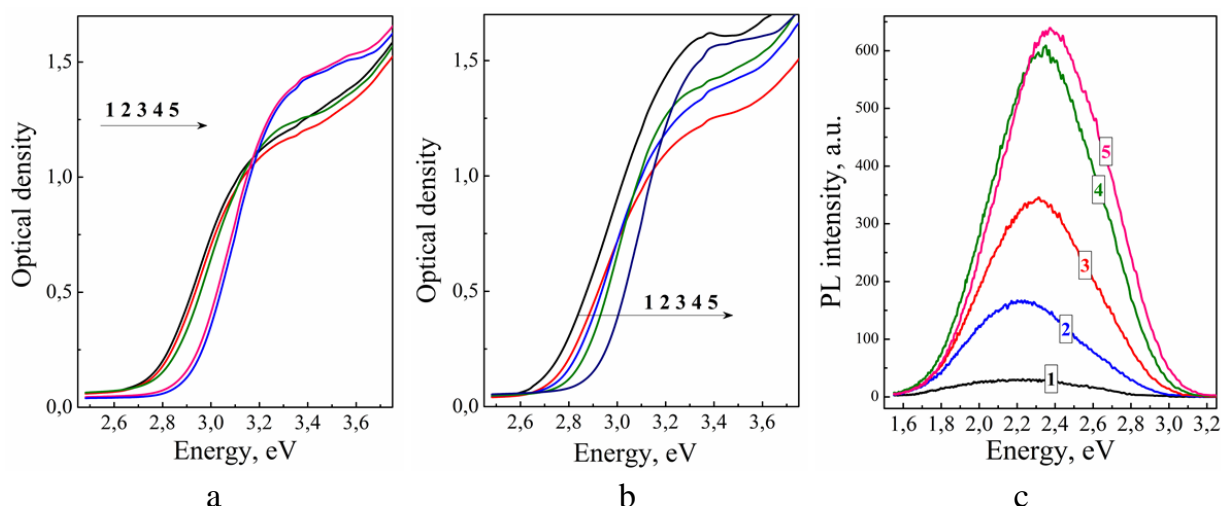
The CdS- $\text{NH}_3$ -MAA NPs possess relatively strong broad-band PL emitted in the range of 1.7–3.0 eV with a maximum at 2.3 eV (Fig. 1b, curve 3) which is close to white light emission (see photo in the inset in Fig. 1b). The large spectral width (FWHM = 0.7 eV) and large Stokes shift of the PL peak (1.16 eV) indicate that the PL originates from the recombination of trapped charge carriers. The quantum yield of PL of CdS- $\text{NH}_3$ -MAA NPs depends on the synthesis conditions and can reach 15%. Similar PL features were also observed earlier by us for PEI-stabilized 1.8 nm CdS NPs [16] as well as by other groups for ultrasmall CdS (Wu et al. 2005) and CdSe NPs (Xia and Zhu 2008; Tian et al. 2009; Park et al. 2010; Rosson et al. 2012) indicating that broad-band PL is a typical feature of ultrasmall cadmium chalcogenide NPs.

The presence of an excess of  $\text{Cd}^{2+}$  over the amount necessary to stoichiometrically bound sulfide ions is a prerequisite for the formation of ultrasmall and stable CdS- $\text{NH}_3$ -MAA NPs. The optical properties of CdS NPs were found to depend on both the ratio between concentrations of Cd(II) and  $\text{NH}_3$ ,  $[\text{Cd}(\text{II})]:[\text{NH}_3]$ , and, at a constant ratio, on the concentration of an excess of cadmium(II) complexes. It should be noted that the amount of MAA was constant in all experiments, 0.03 M, as at a lower concentration the colloids are unstable towards aggregation while an increase of the MAA content higher than 0.03 M has no further effect on the optical properties of CdS NPs.

Figure 2a shows absorption spectra of CdS- $\text{NH}_3$ -MAA colloids synthesized at a  $[\text{Cd}(\text{II})]:[\text{NH}_3]$  ratio varying from 1:1 to 1:6. As can be seen, the increase in the ammonia content ratio results in a “blue shift” of the absorption band edge that saturates at  $[\text{Cd}(\text{II})]:[\text{NH}_3] = 1:4$  and does not change anymore at higher ammonia contents.

At a given ratio  $[\text{Cd(II)}]:[\text{NH}_3]$  of 1:4, the increase of the overall concentration of Cd excess also shifts the absorption band edge to higher energies (Fig. 2b) indicating a reduction of both the average NP size and size distribution. At the same time, an increase in the content of cadmium/ammonia complex has a drastic influence on the PL intensity (Fig. 2c). An increase in the Cd(II) excess content from 20% to 120% results in a 20-fold increase in the PL intensity. Further increase in Cd(II) content only has a minor effect on the emission efficiency (compare curves 4 and 5, Fig. 2c). The PL peak shifts to higher energies concomitantly with a blue shift of the absorption band edge.

Kinetic curves of the PL decay of colloidal CdS-NH<sub>3</sub>-MAA NPs have distinctly non-exponential character (Fig. 3a) and can be satisfactorily fitted with linear combinations of at least three mono-exponential functions with characteristic time constants (fraction in parenthesis) of an order of 1 ns (~20%), 10 ns (~20%), and 100 ns (~60%). The average radiative life-time  $\langle\tau\rangle$  of CdS-NH<sub>3</sub>-MAA NPs depends strongly on the PL registration wavelength  $E_{\text{PL}}$  of the emitted PL quanta and increases from 46 ns at  $E_{\text{PL}} = 2.9$  eV to 105 ns at  $E_{\text{PL}} = 1.8$  eV (Fig. 3b). Such behavior is typical for the ultrasmall cadmium chalcogenide NPs and was observed by us for PEI-stabilized CdS and CdSe NPs (Raevskaya et al. 2010a, 2011).

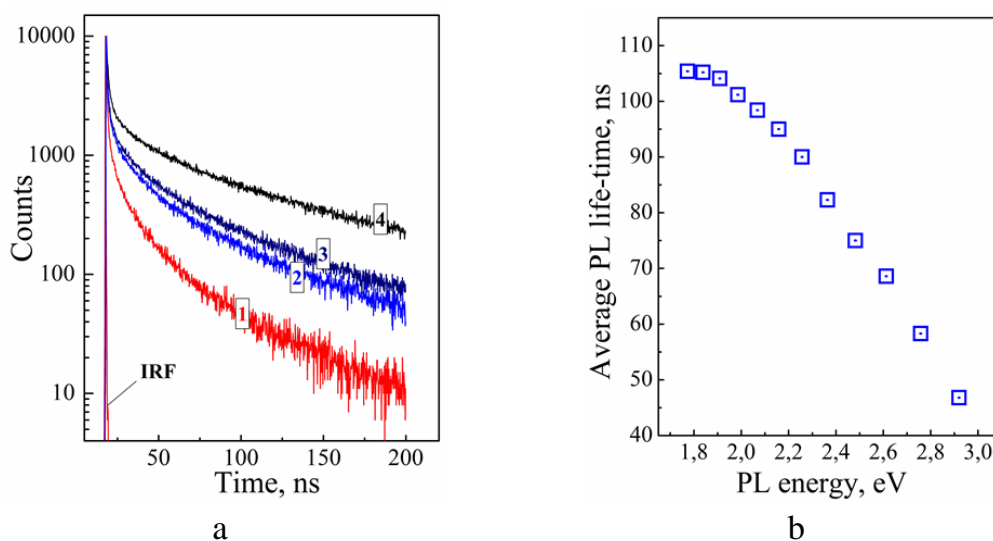


**Figure 2** Spectral properties of CdS-NH<sub>3</sub>-MAA NPs ( $[\text{CdS}] = 8 \times 10^{-3}$  M,  $[\text{MAA}] = 0.03$  M,  $[\text{NaOH}] = 0.12$  M). **(a)** – absorption spectra at  $[\text{Cd(II)}]/[\text{Na}_2\text{S}] = 2$ . **1-5** –  $[\text{NH}_3]/[\text{Cd(II)}] = 0, 1, 2, 4, 6$ , respectively. **(b)** – absorption and **(c)** – PL spectra at  $[\text{NH}_3]/[\text{Cd(II)}] = 4$ . **1-5** –  $[\text{Cd(II)}]/[\text{Na}_2\text{S}] = 1.2, 1.5, 2, 2.2, 2.5$ , respectively. PL excitation at 330 nm (3.76 eV)

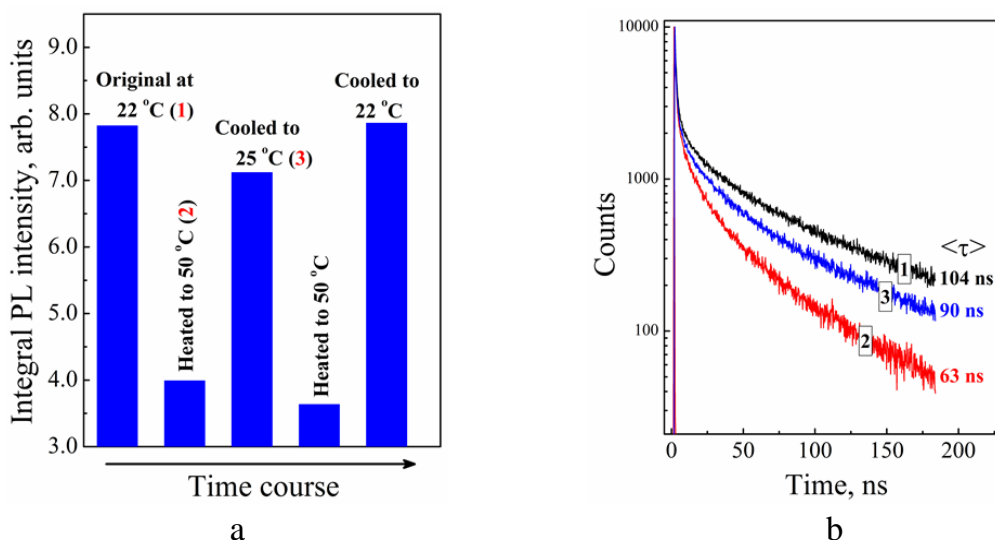
It was suggested earlier (Raevskaya et al. 2010a, 2010b) that the  $\langle\tau\rangle(E_{\text{PL}})$  dependence originates from a competition between the radiative recombination and vibrational relaxation of the charge carriers in the surface layer of the ultrasmall CdS NPs. The longer the NPs remain in the excited state before emitting a PL quantum the lower its energy is due to vibrational energy losses. In this scheme, the large spectral width of the PL band reflects, therefore, not the broad energy distribution of the emitting states in an



ensemble of NPs of different size but rather is an inherent property of each and every single NP in the ensemble.



**Figure 3** Dependence of PL kinetics and life-times of NPs on wavelength. **(a)** 1-4 – registration at 425, 475, 500 and 675 nm. IRF – instrumental response function. **(b)** – the relationship between energy of PL quanta and average life-time



**Figure 4** Dependence of integral PL intensity and kinetics at 550 nm of CdS-NH<sub>3</sub>-MAA NPs solution on cyclic heating/cooling processes. **(a)** – changes of intensity at [Cd(II)]/[Na<sub>2</sub>S] = 2 and [NH<sub>3</sub>]/[Cd(II)] = 4. **(b)** – PL decay profiles of NPs. 1 – kept at 22°C, 2 – heated to 50°C and kept at this T, 3 – cooled to 25°C. The numbers 1–3 in parenthesis in **(a)** refer to the corresponding PL decay curves in **(b)**

The PL intensity and the life-time of CdS-NH<sub>3</sub>-MAA NPs were found to depend strongly and reversibly on the temperature of the dispersive medium. Such dependence may serve as another argument in favor of the assumptions of the surface character of the radia-

tive electron-hole recombination in ultrasmall CdS NPs and of the important role played in this process by the ligands coordinated in the immediate vicinity of the NP surface.

As shown in Fig. 4a, heating of the colloidal CdS-NH<sub>3</sub>-MAA solution from 22 to 50 °C results in an almost 2-fold reduction of the integral PL intensity as well as a radiative life-time shortening from 104 to 63 ns (Fig. 4b, curves 1,2). Subsequent cooling of the colloid is accompanied by the reverse increase of the PL intensity back to the starting value (Fig. 4a) as well as by prolongation of the radiative life-time (Fig. 4b, curves 2,3). Such changes are completely reversible and can be reproduced many times without changes in the absorbance spectra of CdS NPs or losses in their stability against aggregation.

A similar reversible dependence of PL properties on temperature in the range of 18–80 °C were observed earlier by us for ultrasmall CdS NPs stabilized by PEI both in colloidal solutions and incorporated into PEI films (Raevskaya et al. 2012). Simultaneously with the PL changes a reversible red shift of the absorption maximum was observed upon heating of CdS-PEI colloids and films. Such dependences were interpreted in (Raevskaya et al. 2012) as a result of heating-induced dissociation of the complexes between the Cd atoms on the NP surface with amine (imine) groups of PEI and introduction of water molecules into the coordination sphere of Cd atoms. It was supposed that Cd-water complexes on the surface of NPs acted as sites of radiationless recombination decreasing the overall PL intensity.

As the dispersive medium is cooled back the Cd-PEI complexes are restored along with the original PL efficiency. In the case of CdS-PEI NPs such a model is also supported by the fact that the apparent activation energy of T-dependent PL quenching was very close to the typical Gibbs energy of the dissociation of Cd-amine complexes. It can be assumed that similar processes take place in the CdS-NH<sub>3</sub>-MAA system as well, and the PL quenching originates from thermally activated dissociation of Cd-NH<sub>3</sub> bonds and introduction of H<sub>2</sub>O into the formed vacancies. The heating-induced red shift of  $E_1$  observed in (Raevskaya et al. 2012) for CdS-PEI NPs was also interpreted in terms of the Cd-PEI complex dissociation as a result of a decrease of the electron density on the NP surface and weakening of its screening effect on the photogenerated electrons. Here, similar shifts were not observed probably because of the mixed character of surface passivation by Cd(II) complexes with both ammonia and MAA resulting in a lower density of nitrogen electron pairs on the surface of CdS NPs compared to the CdS-PEI system.

#### 4 Conclusions

Stable ultrasmall colloidal CdS NPs were prepared co-stabilized by Cd(II) complexes with ammonia and mercaptoacetate ions. The average size and size distribution of CdS NPs were determined from absorption spectra and dynamic light scattering measurements as 1.8 nm and 0.5 nm, respectively.

The CdS NPs emit white-like broad-band PL with a peak at 2.3 eV and the quantum yields as high as 15%. The PL decay is strongly non-exponential and characterized by an average radiative life-time depending on the registration energy and growing from 46 to 105 ns as the emission quantum energy decreases from 2.9 eV (425 nm) to 1.8 eV (690 nm). The

dependence is supposed to originate not from a distribution of the emissive states by energy but rather to be an inherent property of each single ultrasmall CdS nanoparticle.

The PL intensity and radiative life-time decrease to about a half as the temperature of the solution is elevated from 22 to 50°C. This behavior is completely reversible and can be reproduced many times. The T-dependences of luminescence parameters of CdS NPs are assumed to originate from a reversible, thermally activated dissociation of Cd(II)-ammonia complexes on the surface of CdS NPs and a formation of new complexes with water acting as sites of radiationless recombination. Such strong and reversible T-dependences coupled with the extremely small size, the open surface free of polymeric species, and the relatively high quantum yields of the PL open possibilities for applications in bio-imaging and bio-sensing technologies for the CdS NPs co-stabilized with NH<sub>3</sub> and mercaptoacetate. It should be noted that the stabilization mechanism of CdS NPs by the complexes of Cd(II) with ammonia and mercaptoacetate as well as the exact composition of such complexes passivating the surface of CdS nanoparticles remain open questions and will constitute the subject of a separate study.

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### **References**

- Chen X, Hutchison JL, Dobson PJ, Wakefield G (2008) A one-step aqueous synthetic route to extremely small CdSe nanoparticles. *J Colloid Interface Sci* 319:140-143
- Dukes III AD, Samson PC, Keene JD, Davis LM, Wikswo JP, Rosenthal SJ (2011) Single-Nanocrystal Spectroscopy of White-Light-Emitting CdSe Nanocrystals. *J Phys Chem A* 115:4076-4081
- Fahmi A, Pietsch T, Applehans D, Gindy N, Voit B (2009) Water-soluble CdSe nanoparticles stabilized by dense-shell glycodendrimers. *New J Chem* 33:703-706
- Grodzyuk GY, Rayevskaya AE, Stroyuk AL, Kuchmiy SY, Vortman MY, Lemeshko VN, Shevchenko VV, Chertopalov SV, Kolomzarov YV, Sorokin VM (2011) Optical and electroluminescent properties of CdS nanoparticles stabilized by guanidine-containing dendrimers. *Theoret Experim Chem* 47:346-352
- Jones M, Scholes GD (2010) On the use of time-resolved photoluminescence as a probe of nanocrystal photoexcitation dynamics. *J Mater Chem* 20:3533-3538
- Kalasad MN, Rabinal MK, Mulimani BG (2009) Ambient Synthesis and Characterization of High-Quality CdSe Quantum Dots by an Aqueous Route. *Langmuir* 25:12729-12735
- Kim BH, Hackett MJ, Park J, Hyeon T (2014) Synthesis, Characterization, and Application of Ultrasmall Nanoparticles. *Chem Mater* 26:59-71

- McBride JR, Dukes III AD, Schreuder MA, Rosenthal SJ (2010) On ultrasmall nanocrystals. *Chem Phys Lett* 498:1-9
- Park YS, Dmytruk A, Dmitruk I, Kasuya A, Takeda M, Ohuchi N, Okamoto Y, Kaji N, Tokeshi M, Baba Y (2010) Size-Selective Growth and Stabilization of Small CdSe Nanoparticles in Aqueous Solutions. *ACS Nano* 4:121-128
- Park YS, Okamoto Y, Kaji N, Tokeshi M, Baba Y (2011) Aqueous-phase synthesized small CdSe quantum dots: adsorption layer structure and strong band-edge and surface trap emission. *J Nanopart Res.* doi: 10.1007/s11051-011-0273-7
- Pennycook TJ, McBride JR, Rosenthal SJ, Pennycook SJ, Pantelides ST (2012) Dynamic Fluctuations in Ultrasmall Nanocrystals Induce White Light Emission. *Nano Lett* 12:3038-3042
- Raevskaya AE, Grodzyuk GY, Dzhagan VM, Stroyuk AL, Kuchmiy SY, Plyusnin VF, Grivin VP, Valakh MY (2010a) Synthesis and Characterization of White-Emitting CdS Quantum Dots Stabilized with Polyethyleneimine. *J Phys Chem C* 114:22478-22486
- Raevskaya AE, Stroyuk AL, Grodzyuk GY, Kuchmiy SY, Dzhagan VM, Plyusnin VF, Grivin VP (2010b) Dynamics of the radiative recombination of charge carriers in CdS nanoparticles stabilized with polyethyleneimine. *Theoret Experim Chem* 46:273-278
- Raevskaya AE, Grodzyuk GY, Korzhak AV, Stroyuk AL, Kuchmiy SY, Dzhagan VM, Valakh MY, Plyusnin VF, Grivin VP, Mel'nik NN, Zavaritskaya TN, Kucherenko TN, Plyashechnik OS (2011) Preparation and optical properties of polyethyleneimine-stabilized colloidal CdSe and CdS<sub>x</sub>Se<sub>1-x</sub> quantum dots. *Theoret Experim Chem* 46:416-421
- Raevskaya AE, Grodzyuk GY, Stroyuk AL, Kuchmiy SY, Plyusnin VF (2012) Influence of temperature on optical properties of polyethyleneimine-stabilized CdS nanoparticles. *Theoret Experim Chem* 48:95-101
- Rogach AL, Franzl T, Klar TA, Feldmann J, Gaponik N, Lesnyak V, Shavel A, Eychmüller A, Rakovich YP, Donegan JF (2007) Aqueous Synthesis of Thiol-Capped CdTe Nanocrystals: State-of-the-Art. *J Phys Chem C* 111:14628-14637
- Rosson TE, Clairborne SM, McBride JR, Stratton BS, Rosenthal SJ (2012) Bright White Light Emission from Ultrasmall Cadmium Selenide Nanocrystals. *J Am Chem Soc* 134:8006-8009
- Tian J, Liu R, Zhao Y, Xu Q, Zhao S (2009) Controllable synthesis and cell-imaging studies on CdTe quantum dots together capped with glutathione and thioglycolic acid. *J Colloid Interface Sci* 336:504-509
- Wu XC, Bittner AM, Kern K (2005) Synthesis, Photoluminescence, and Adsorption of CdS/Dendrimer Composites. *J Phys Chem B* 109:230-239
- Xia YS, Zhu CQ (2008) Aqueous synthesis of luminescent magic sized CdSe nanoclusters. *Mater Lett* 62:2103-2105
- Xiao Q, Xiao C, Ouyang L (2008) Strong enhancement of band-edge photoluminescence in CdS nanocrystals prepared by one-step aqueous synthesis method. *J Lumin* 128:1942-1947

Zhou D, Lin M, Chen Z, Sun H, Zhang H, Sun H, Yang B (2011) Simple Synthesis of Highly Luminescent Water-Soluble CdTe Quantum Dots with Controllable Surface Functionality. *Chem Mater* 23:4857-4862