Size Control of Cadmium Sulfide Nanoparticles in Polyvinyl Alcohol and Gelatin by Polyethyleneimine Addition

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ABSTRACT

A simple method of controlling the size and photoluminescence of CdS nanoparticles stabilized by gelatin and polyvinyl alcohol in water by introducing small amounts of polyethyleneimine at the moment of nanoparticle formation is reported. It was found that by adding 0.01–0.10 w.% polyethyleneimine the size of CdS nanoparticles can be changed in the range of 3.8–6.6 nm. The luminescence efficiency and radiative life time of polyvinyl alcohol-stabilized CdS nanoparticles were found to increase four-, fivefold with increasing the polyethyleneimine content at the moment of CdS nanoparticles synthesis. A more complex behavior was observed for gelatin-based media, where the interaction between the polyethyleneimine and gelatin can have a detrimental effect of on the size distribution and luminescence properties of CdS nanoparticles.

INTRODUCTION

Cadmium chalcogenide nanoparticles (NPs) stabilized in aqueous solutions by water-soluble polymers, for example, gelatin and polyvinyl alcohol (PVA) attract considerable attention as promising materials for the luminescent biodiagnostics, photocatalysis, non-linear optics, light-emitting devices, etc. [1-5]. The main challenges at the synthesis of aqueous CdS colloids are low photoluminescence (PL) efficiency, and the limited means of exerting control over the size and the size distribution of CdS NPs [1-3]. Recently we have reported on the synthesis of ultra-small, ~2 nm (with ~10% size dispersion), colloidal CdS nanoparticles (NPs) stabilized by polyethyleneimine (PEI) in water and ethanol [6]. The CdS-PEI NPs exhibit excellent chemical and photo-chemical stability and PL emitted in a broad band at λ = 400-700 nm with the quantum yields up to 20-30% and a life-time of 60-70 ns [6]. However, though producing CdS NPs with superior PL efficiency and size distribution to those stabilized by gelatin or PVA, this approach does not allow varying the NP size without concomitant deterioration of PL properties [6]. Here we report on a simple method of controlling the average size and PL properties of CdS NPs stabilized by gelatin and PVA in water by introducing small amounts of PEI at the moment of NP formation.

EXPERIMENTAL DETAILS

Polyethyleneimine (50 wt% aqueous solution, molecular weight 50.000 g/mole), $CdSO_4$, Na_2S, gelatin, polyvinyl alcohol of reagent grade quality were supplied by Sigma-Aldrich.

Aqueous colloidal CdS solutions were prepared by interaction between $CdSO_4$ and Na_2S in the presence of gelatin [7, 8], PVA [7, 9] and PEI [6] alone or a mixture of PEI with gelatin or PVA. In a typical procedure, 0.8 mL 0.1 M aqueous $CdSO_4$ solution was added to 9.2 mL of aqueous solution containing gelatin (or PVA) and PEI at vigorous stirring. The concentrations of CdS and gelatin (PVA) were 8×10^{-3} M and 2.0 wt%, respectively, while the PEI content was varied from 0.01 to 0.1 wt%. To this mixture 0.8 mL of 0.1 M aqueous Na_2S solution was added drop-wise at vigorous stirring resulting in formation of colloidal CdS NPs. Then an additional PEI amount was added to the colloidal solutions so that the final PEI concentration was 0.10 w.% in all the synthesized samples. The colloidal solutions were used to prepare polymer films on the microscope glass substrates. The glass plates were cleaned by into the piranha solution and keeping in an ultrasonic bath. The polymer films were prepared by depositing of 1.0 mL colloidal solution onto a 2.5×2.5 cm glass plate followed by drying at ambient temperature till complete evaporation of the solvent. The final films had a thickness of 0.2-0.3 mm and contained 3.5 wt% CdS.

The absorbance spectra were registered with an HP Agilent 8453 spectrophotometer. The photoluminescence (PL) spectra and PL decay profiles were taken on an Edinburgh Instruments FLS920 luminescence spectrometer equipped with a photon counting system based on a EPL-375 picosecond diode laser emitting 60 ps pulses with $\lambda = 375$ nm. The average PL life time $<\tau>$ was determined after deconvoluting the decay curves into four monoexponential functions with the characteristic time constants τ_i and amplitudes A_i as $<\tau> = \sum_i \dfrac{A_i \tau_i^2}{\sum_j A_j \tau_j}$ [10].

DISCUSSION

Absorbance spectra of CdS NPs incorporated into the gelatin- and PVA films reveal broad bands with non-distinct edges at around 455 and 470 nm, respectively (Fig. 1a,b, curves 1), shifted to shorter wavelengths as compared to the bulk CdS [1, 3], indicating the presence of an ensemble of quantum-sized NP with a broad size distribution. The size of CdS NPs, d, can be estimated using well-known empirical correlations between d and NP band gap, E_g [1, 3, 6]. As the absorbance band edge is formed by a fraction of larger NPs in the ensemble, the band gap energy determined by plotting the tangent to the absorption band slope (absorption threshold energy, see inset in Fig. 1a), E_t, can be used to find the upper NP size limit, d_{max}, while the energy corresponding to the minimum of the first derivative of the absorbance spectrum, E_d (see the inset in Fig. 1b), characterizes the average size of NP in the ensemble, $<d>$ [1]. A difference between d_{max} and $<d>$ may be used as a measure of the NP size distribution, Δd (Table I).

As can be seen from Fig. 1 and Table I addition of PEI to polymer solutions before CdS NPs formation results in a "blue" shift of the absorption threshold of CdS NPs formed in such solutions and appearance of a distinct maximum at 360-370 nm. The changes are the more pronounced the higher is the PEI concentration. At the same time, an additional amount of PEI

added to solutions after formation of CdS NPs in order to achieve equal PEI concentration in all the samples, 0.10 w.%, does not influence the optical properties of NPs.
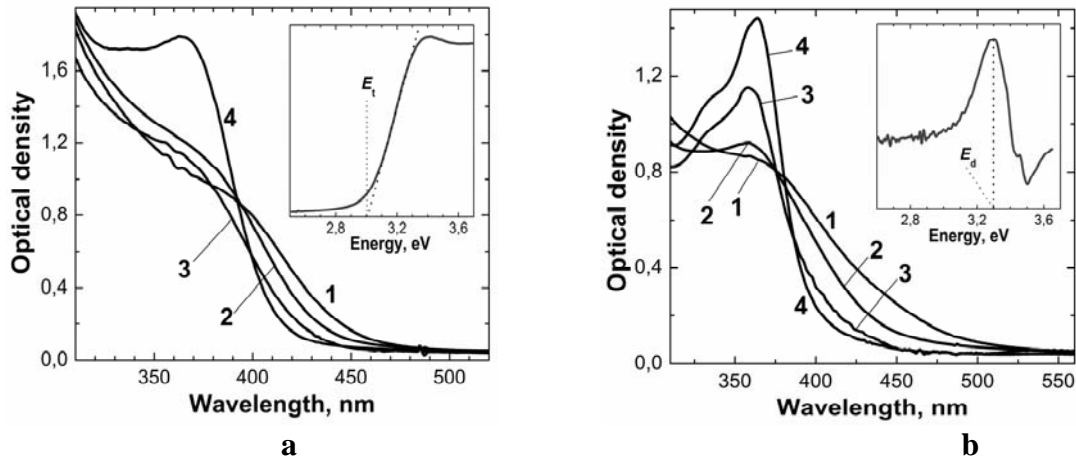
Figure 1. Absorbance spectra of CdS NPs in polymer films composed of PEI and gelatin (a) and PEI and PVA (b) at various content of PEI during the NP formation in original colloidal solutions – no PEI (curves 1), 0.02 w.% PEI (curves 2), 0.04 w.% PEI (curves 3), and 0.10 w.% PEI (curves 4). Insets: examples of determination of E_t and E_d from the absorption spectra.

Estimations based on spectral data show introduction of PEI and increase of its concentration from 0.02 to 0.10 w.% result in decreasing d_{max} from 6.6 nm to 3.8 nm in case of PVA and from 2.9 to 2.0 nm in case of gelatin (Table I). As can be seen from the table, PEI addition allows focusing considerably the size distribution of CdS NPs – from 70% to 10% in case of PVA and from 30% to 15% in case of gelatin. It should be noted that in the latter case Δd first grows when 0.02 w.% PEI is introduced into solution, then, at higher PEI content, it begins to decrease.

Table I. Energy of the absorption threshold (E_t) and the minimum of first derivative of the absorption spectrum (E_d), size determined from E_t (d_{max}) and E_d ($<d>$), size distribution Δd, integral PL intensity I_{PL}, PL band maximum position (λ_m) and the average PL life time of CdS incorporated into polymer films of gelatin, PVA and PEI of different composition.

Polymer	PEI, w.%	E_t, eV	E_d, eV	d_{max}, nm	$<d>$, nm	Δd, %	I_{PL}, 10^{-7}, a.u.	λ_m, nm	$<\tau>$, ns
PVA	–	2.65	3.10	6.6	3.8	70	0.88	495	6
	0.02	2.87	3.27	5.0	3.7	40	1.44	475	13
	0.04	3.07	3.34	4.0	3.6	20	1.58	480	30
	0.10	3.14	3.30	3.8	3.5	10	3.67	490	43
Gelatin	–	2.74	2.98	5.7	4.7	20	2.64	560	50
	0.02	2.83	3.07	5.0	4.0	30	1.49	530	45
	0.04	2.90	3.13	4.8	3.8	25	1.80	505	40
	0.10	3.03	3.20	4.2	3.8	15	4.78	500	50
PEI	–	3.40	3.45	2.0	1.8	10	7.16	475	70

Notes: the experimental errors are 0.01 eV for E_d and E_t, 1×10^4 a.u. for I_{PL}, 1 ns for $\langle\tau\rangle$.

PL spectra of gelatin- or PVA-stabilized CdS NPs reveal broad PL bands in the range of 400–700 nm centred at around 550–560 nm (Fig. 2a) typical for the surface-trap-state-related radiative recombination [1, 2, 10]. The two polymer stabilizers react differently on the PEI addition (Fig. 2b). While in case of PVA introduction of PEI results in an increase in PL intensity (Fig. 2b, curve 1) at an almost constant maximum position (Table I) and FWHM of the PL band, in the gelatin-based systems PEI addition at low concentrations inhibits the radiative recombination efficiency (Fig. 2b, curve 2). At the same time, CdS NPs synthesized at PEI content higher than 0.05–0.06 w.% are superior by PL intensity as compared to those prepared using the gelatin alone.

a   b
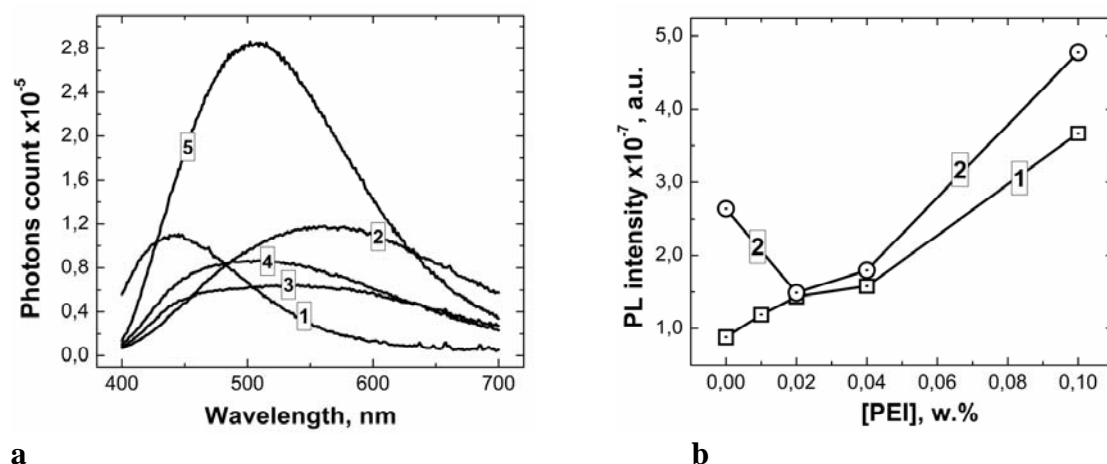
Figure 2. (a) PL spectra of pure gelatin film (curve 1), gelatin film with CdS NPs (curve 2), and mixed gelatin–PEI films with CdS NPs containing different amount of PEI: 0.02 w.% (curve 3), 0.04 w.% (curve 4), and 0.10 w.% (curve 5). (b) Integral intensity of PL bands of CdS NP in pure PVA and gelatin films, and in mixed PVA–PEI films (curve 1) and gelatin–PEI films (curve 2) as a function of PEI content.

The PL kinetic profiles of gelatin- and PVA-stabilized CdS NPs have prominently non-exponential character (Fig. 3a, curve 1) typical for the trap-state-related emission [1, 2, 10] with the average time constants of 50 and 6 ns, respectively (Table I). A much higher radiative life time of gelatin-stabilized CdS NPs indicates the more efficient passivation of the surface states responsible for the radiationless recombinative processes, as compared with PVA. This fact as well as a much higher PL efficiency of the stationary PL, a lower NP size and a narrower size distribution evidence a superior ability of gelatin to stabilize and passivate colloidal CdS NPs in water. The difference can be accounted for by a different nature of the interaction between the two polymers and the surface of CdS NPs. In contrast to PVA, the gelatin molecules contain terminal carboxyl and amine groups and a lot of peptide –CONH– fragments [11] capable of efficient bounding to the under-coordinated Cd atoms on the surface of CdS NPs and passivating the sites of the radiationless processes.

Similarly to the case of stationary PL, increase in PEI content has a different influence on the PL decay kinetics of CdS NPs stabilized by PVA and gelatin (Fig. 3b, Table I). In the first case a monotonous increase in the radiative life time is observed (Fig. 3a, curves 2,3, Fig. 3b, curve 1) while in the gelatin-based systems $\langle\tau\rangle$ first decreases when PEI is introduced to the system and then, at higher PEI content, increases almost to the original value (Fig. 3b, curve 2).

a   **b**
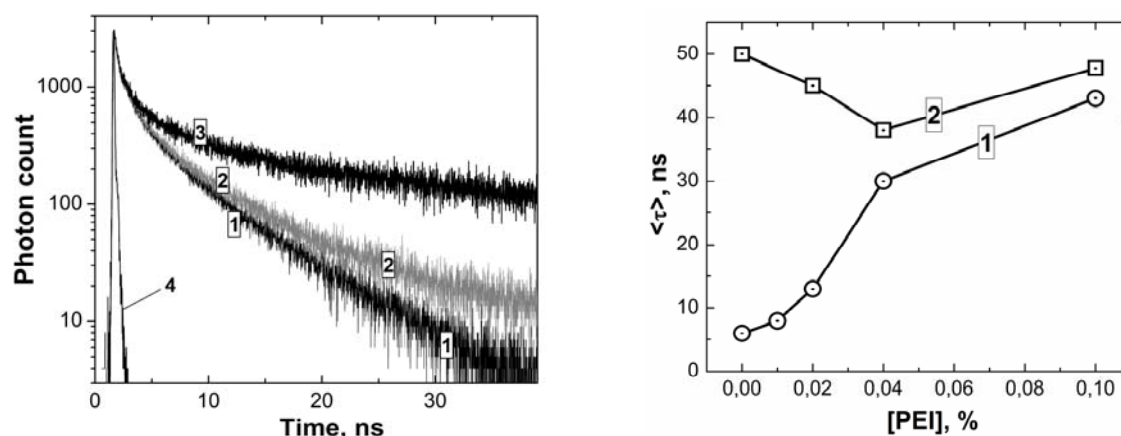
Figure 3. (a) PL decay profiles for CdS NPs incorporated in PVA film (curve 1), and PVA–PEI films with 0.02 w.% PEI (curve 2) and 0.10 w.% PEI (curve 3). Curve 4 – instrumental response function. (b) Average PL life time for CdS NPs incorporated in pure PVA and gelatin films, and mixed PVA–PEI films (curve 1) and gelatin–PEI films (curve 2) as a function of PEI content.

In summary, the CdS NPs stabilized by PVA alone are characterized by the largest size, the most broad size distribution, the lowest PL efficiency and the shortest life time. As the PEI is introduced to the system, the former containing a lot of amine groups capable of formation of comparatively strong coordination bonds with the Cd atoms on the surface of forming CdS NPs, the size and its distribution decrease, while the PL efficiency and time constants of the charge recombination grow monotonously with increasing the PEI content. At the same time, similar gelatin-based systems reveal quite a different behavior. In particular, addition of PEI affects the NP size and its distribution for the gelatin-stabilized CdS NPs to a lesser extent as compared to the PVA-based systems. The changes of the size distribution, the PL intensity and the life time with increasing PEI content are of a non-monotonous character and reach extremes at 0.02-0.04 w.% PEI. From the facts one can conclude that in this concentration range some interaction between the gelatin and PEI occurs that prevents them from effectively bounding to the surface of CdS NPs. A possible reason for the observed irregular dependences can be related to the formation of the well-known polyionic complexes between the gelatin and PEI molecules. Polyethyleneimine is a well-known polyelectrolyte due to the protonation of the amine nitrogen of PEI at the expense of water dissociation. The gelatin is reported to reveal mild polyanionic properties as a result of dissociation of terminal carboxyl groups [11]. When both polymers are present in the system a polyionic complex can form between the positively charged PEI chains and negatively charged gelatin molecules prohibiting them from stabilizing and passivating CdS NPs. At higher PEI concentrations only a fraction of PEI gets involved into the formation of such polycationic complexes while the rest of PEI molecules can interact with the surface of forming CdS NPs and stabilizing them in water.

CONCLUSIONS

A simple method of controlling the size and photoluminescence of CdS NPs stabilized by gelatin and PVA in water by introducing small amounts of PEI at the moment of NP formation has been reported. It was found that by adding 0.01–0.10 wt% PEI, the size of PVA-stabilized CdS NPs can be tuned from 6.6 nm to 3.8 nm, while the dispersion Δd narrowed from 70% to 10%. In the case of gelatin a size decrease from 5.7 nm to 4.2 nm but only a modest size distribution narrowing from 30 to 15 % can be achieved. The PL efficiency of PVA-stabilized CdS NPs increases more than 4-fold upon introduction of 0.10 wt% PEI. The averaged PL life-time $<\tau>$ was found to increase from 6 ns to 43 ns when 0.10 wt% PEI is added to PVA solution before the formation of CdS NPs, indicating efficient elimination of the radiationless recombination sites by complexation of amino-groups of PEI with the Cd(II) on the surface of CdS NPs. A more complex behavior was observed for gelatin-based media, where PEI introduction results in a decrease of $<\tau>$ at low PEI content and an increase of $<\tau>$ upon further increase of PEI content to 0.10%. The detrimental effect of small PEI additives upon the size distribution and PL properties of gelatin-stabilized CdS NPs is tentatively ascribed to the formation of polyionic complexes between the dissociated carboxyl-groups of gelatin and protonated amino-groups of PEI.

ACKNOWLEDGEMENTS

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