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Synthesis and Characterization of CdS Nanoparticles Stabilized by Double-Hydrophilic Block Copolymers

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ABSTRACT

A novel and simple preparation method for single monodisperse CdS nanoparticles with controllable size and stability against oxidation is presented. Double-hydrophilic block copolymers consisting of a solvating poly(ethylene glycol) PEG block and a poly(ethylene imine) PEI binding block have been used as effective stabilizers for the solution synthesis of high-quality CdS nanoparticles in water and methanol. Absorption, fluorescence spectroscopy, and transmission electron microscopy were employed for characterization, which revealed that the prepared CdS nanoparticles had a well-resolved cubic structure and were monodisperse in size. It was also found that the CdS nanoparticles were dispersed in solution as single entities and showed a very good resistance against oxidation for months, according to their polymer shell. The particle size was controllable in the range between 2 and 4 nm by adjusting the polymer concentration and choice of the solvent.

Introduction. Semiconductor nanoparticles have attracted much interest during the past decade due to their unique size-dependent chemical and physical properties.[1−5] Many synthetic methods, which normally include arrested precipitation in homogeneous solution and synthesis in confined reaction vessels such as reverse micelles[6] and vesicles,[7] have been developed for the chemical preparation of relatively monodisperse nanoparticles of various semiconductor materials. Specifically, high-quality nanoparticles of CdS, a typical semiconductor material, have been synthesized via arrested precipitation from simple inorganic ions using polyphosphate[8] and low molecular weight thiols[9,10] as stabilizers, from dimethylcadmium in trioctyl phosphine using trioctyl phosphine oxide as a stabilizer,[11] and from cadmium 2-ethylhexanoate in dimethyl sulfoxide (DMSO) using ethylhexanoate as a stabilizer.[12]

Recently, polymers carrying functional groups have been used as specific stabilizers for the solution synthesis of CdS nanoparticles with varied properties. For example, polyester chains with a thiol end group were used as a covalently attached stabilizer for the preparation of stable CdS nanoclusters in dimethylformamide (DMF) and tetrahydrofuran (THF), which were further used for the preparation of homogeneous dispersions of CdS particles in a polymer matrix.[13] Interestingly, a blue-emitting CdS/dendrimer nanocomposite was synthesized by the arrested precipitation of CdS nanoclusters in the presence of Starburst (PAMAM: poly(aminoamine)) dendrimers[14] and CdS/polyamine nanocomposites, which can be further immobilized in a sol−gel glass, were prepared using Starburst dendrimers and their linear analogues, polyethylenimine (PEI), as stabilizers.[15] More recently, amino-derivatized polysaccharides (aminodextrans or Amdex) were employed as a stabilizer for the preparation of stable aqueous dispersions consisting of CdS nanoparticles, and the resultant Amdex-CdS nanoparticle complexes could be activated and conjugated with an antibody.[16] Due to the fact that the CdS/dendrimer nanocomposite underwent further aggregation in solution to produce micrometer-scale composite flocs and that each CdS/PEI or CdS/Amdex nanocomposite particle contains more than one nanoparticle attached to each polymer molecule, individual CdS particles cannot be isolated in these CdS/polymer nanocomposites. Therefore, it remains a challenge to produce single well-dispersed, monodisperse, and size adjustable CdS nanoparticles by arrested precipitation in aqueous solution at room temperature using appropriate polymers as stabilizers. A further challenge, especially from the application point of view, is the CdS protection from photooxidation. A combination of these requirements could so far not be achieved by any reported synthesis method for CdS nanoparticles.

Our recent investigations have revealed that the so-called double-hydrophilic block copolymers,[17] which consist of one hydrophilic block interacting strongly with appropriate inorganic materials and another hydrophilic block mainly

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promoting solubilization in water, can exert a strong influence on the crystallization of inorganic crystals such as $CaCO_3$,[17,18,20] $BaSO_4$,[21] and calcium phosphate.[22] Here, we use double-hydrophilic block copolymers, such as PEG-*b*-PEI that consist of a binding PEI block and a solvating PEG block, as stabilizers for the controlled synthesis of CdS nanocrystals. It will turn out that stable colloidal solutions consisting of well-dispersed, monodisperse CdS nanoparticles can be facially synthesized in aqueous solution at room temperature with very high quality, as revealed by optical experiments and high-resolution electron microscopy.

Experimental Section. *Materials.* $CdCl_2$ and Na_2S were purchased from Fluka and Aldrich, respectively. Poly(ethyleneglycol)-*block*-poly(ethyleneimine)-branched (PEG_{5000}-*b*-PEI_{700}-branched), Poly(ethylene glycol)-*block*-poly(ethyleneimine)-linear (PEG_{5000}-*b*-PEI_{400}-linear) and Poly(ethyleneglycol)-*block*-poly(ethyleneimine)-poly(acetic acid) (PEG_{5000}-*b*-$PEIPA_{1800}$) were synthesized according to ref 18. Furthermore, PEG_{5000} monomethyl ether (Aldrich) was connected to a Starburst dendrimer of the 2nd generation (Aldrich, $M = 1430$ g/mol) via coupling of the epoxidated PEG by a chemistry analogeous to that described in refs 17 and 18) to give, poly(ethyleneglycol)−Starburst (PEG_{5000}−$Starburst_{1400}$) with statistically one PEG per dendrimer.[19]

Synthesis of CdS Nanoparticles. The synthesis of CdS nanoparticles in the solutions of various double-hydrophilic block copolymers was conducted at room temperature (∼20 °C). First, 2 mM stock solutions of $CdCl_2$ and Na_2S in the appropriate solvent (water or methanol) were prepared freshly. Then, a 5.0 mL portion of the $CdCl_2$ stock solution was added to 10.0 mL of a certain polymer solution in the corresponding solvent, followed by the addition of 5.0 mL of the Na_2S stock solution in the corresponding solvent under stirring, giving a final CdS concentration of 0.5 mM. The resulting stable CdS colloidal solutions were stored at 10 °C in the dark and were characterized normally after 24 h of aging because our preliminary optical measurements showed that the absorption and fluorescence characteristics of the obtained colloidal dispersions show a minor change within the first 24 h and then remained essentially unchanged for at least 2 months.

Characterization. UV−vis spectra were recorded using a UVIKON 940/941 dual-beam grating spectrophotometer (Kontron Instruments) with a 1-cm quartz cell. Steady-state fluorescence spectra were obtained on a Spex Fluorolog-2 (Model FL-2T2) spectrofluorometer with an excitation wavelength λ_{exc} of 400 nm (for aqueous solutions) or 340 nm (for methanolic solutions). The excitation and emission bandwidths were both 1 nm. Dynamic light scattering was employed on a laboratory-built goniometer with an ALV/SO−SIPD single-photon detector, a ALV 5000/FAST digital correlator (ALV Langen), and an INNOVA 300 argon ion laser operated at a wavelength of 488 nm. Analytical ultracentrifugation (AUC) was carried out using a Beckman Optima XL-I ultracentrifuge (Beckman Coulter, Palo Alto, CA) at 25 °C and 30 000 rpm applying UV−vis absorption detection at wavelengths between 270 and 290 nm. Transmission electron microscopy (TEM) was performed on a DSM 940 A (Carl Zeiss, Jena) microscope operating at 200 kV, and high-resolution transmission electron microscopy (HRTEM) was carried out on a Philips CM 12 microscope operating at 120 kV (equipped with an EDAX 9800 analyzer). Grids were prepared by depositing a droplet of the colloidal solution onto a carbon-coated copper grid and removing excess solvent with a paper tip.

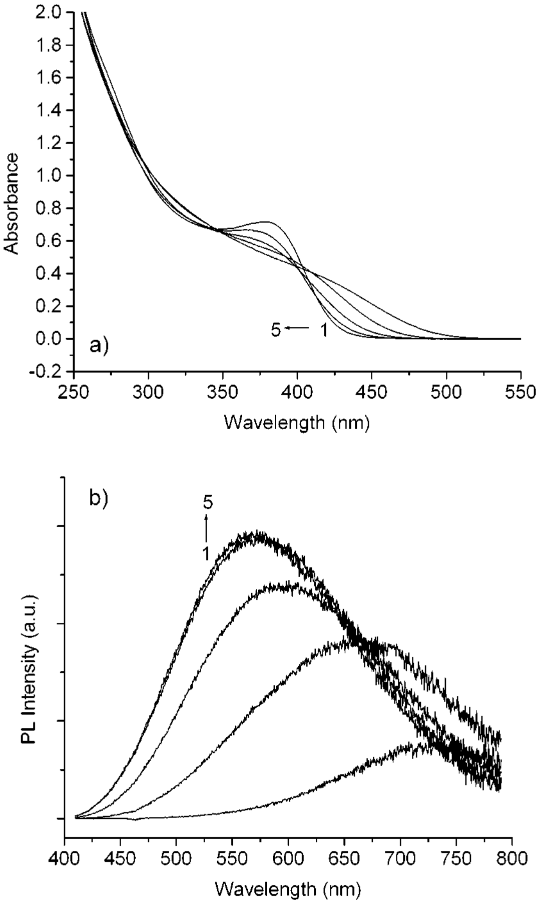

Figure 1. Absorption (a) and photoluminescence (b) spectra of CdS nanoparticles prepared in (1) 0.05, (2) 0.1, (3) 0.25, (4) 0.5, and (5) 1 g/l aqueous solution of branched PEG_{5000}-*b*-PEI_{700}.

Results and Discussion. PEG-*b*-PEI is a typical double-hydrophilic block copolymer carrying a branched PEI block that can bind to CdS particles through its chelating nitrogens. It is known that the homopolymer PEG does not stabilize CdS nanoparticles in water, whereas high-molecular-weight PEI was already used as a stabilizer for the preparation of CdS nanoparticles. In these experiments, one PEI molecule however tends to attach simultaneously to several CdS nanoparticles[15]. Figure 1 presents the absorption and photoluminescence (PL) spectra of CdS nanoparticles prepared in aqueous PEG_{5000}-*b*-PEI_{700}-branched solutions with a series of concentrations.

As shown in Figure 1a, the CdS particles obtained at a PEG_{5000}-*b*-PEI_{700}-branched concentration of 0.05 g/L exhibited an absorption edge of 490 nm, which is considerably blue-shifted relative to the absorption onset of bulk CdS (515 nm), indicating quantum confinement. With increasing the concentration of PEG_{5000}-*b*-PEI_{700}-branched from 0.05 to 1 g/L, the absorption edge of the obtained CdS nanoparticles was decreased gradually from 490 to 425 nm, suggesting that smaller CdS clusters were produced at a higher polymer concentration. According to the experimental correlation between the absorption edge and the particle diameter for CdS,[23] the particle sizes of the CdS nanoparticles obtained at polymer concentrations of 0.05 and 1 g/L were estimated to be 4.0 and 2.3 nm, respectively. It is worth noting that accompanying the decrease of the particle size, the exciton peaks became sharper as the polymer concentration was increased. At a polymer concentration of 1 g/L, a relatively sharp exciton peak at 388 nm was observed, the width of which is comparable to that for the monodisperse CdS nanocrystals prepared using reverse micelles as microreactors[6] and using phosphatidylcholine vesicles as reaction compartments,[7] indicating a narrow size distribution and good crystal quality.[6,7,9]

The PL spectra of the prepared CdS nanoparticles upon excitation at 400 nm suggest that with increasing the PEG_{5000}-*b*-PEI_{700}-branched concentration from 0.05 to 1 g/L, the relatively broad PL band blue-shifts gradually from 728 to 568 nm accompanying a gradual increase in the intensity of the PL emission (Figure 1b). The observed broad PL peak is commonly attributed to the recombination of charged carriers trapped in the surface states and is related to the size of CdS nanoparticles, i.e., the PL emission blue-shifts with decreasing particle size.[12,13,24] Compared with the CdS nanoparticles prepared using Starburst dendrimer and linear PEI as stabilizers,[14,15] the CdS nanoparticles stabilized by PEG_{5000}-*b*-PEI_{700}-branched showed PL emission at higher wavelengths, corresponding to somewhat larger particles, but the shape of the PL band for the particles is simpler, indicating particles with fewer defects.[14]

TEM was employed to obtain direct information about the size and structure of the produced CdS nanoparticles. Figure 2a presents a typical TEM image of representative CdS nanoparticles obtained at a PEG_{5000}-*b*-PEI_{700}-branched concentration of 0.05 g/L. It shows that practically monodisperse particles with an average size about 4 nm were loosely distributed on the grid (note that significant uncertainties exist in the measurement of the particle size with TEM due to fuzzy particle boundaries). The fact that no large dense flocs were observed in the TEM image already indicates that the prepared CdS nanoparticles were well-dispersed in the solution. This result is consistent with our DLS measurement, which showed that the scattering intensity of all the solutions was so weak that no reliable particle sizes can be obtained, excluding the presence of aggregates larger than 10 nm in the solutions. AUC also revealed the absence of aggregates for all samples and furthermore yielded a particle polydispersity of ~20%, which however is mainly due to the polydispersity of the stabilizing polymer shell and not of the nanoparticles themselves.

A typical HRTEM image is presented in Figure 2b, showing that the nanoparticles exhibit clearly resolved lattice fringes with the interplanar spacing of 0.33 nm assigned to the (111) plane of the cubic CdS structure,[12,25] indicating the formation of high-quality cubic CdS nanocrystals. The cubic (zinc blende) stucture of the produced CdS nanoparticles was further evidenced by the observation that a lattice spacing of 0.36 nm, which is found only for hexagonal CdS, was not observed in any of our samples.

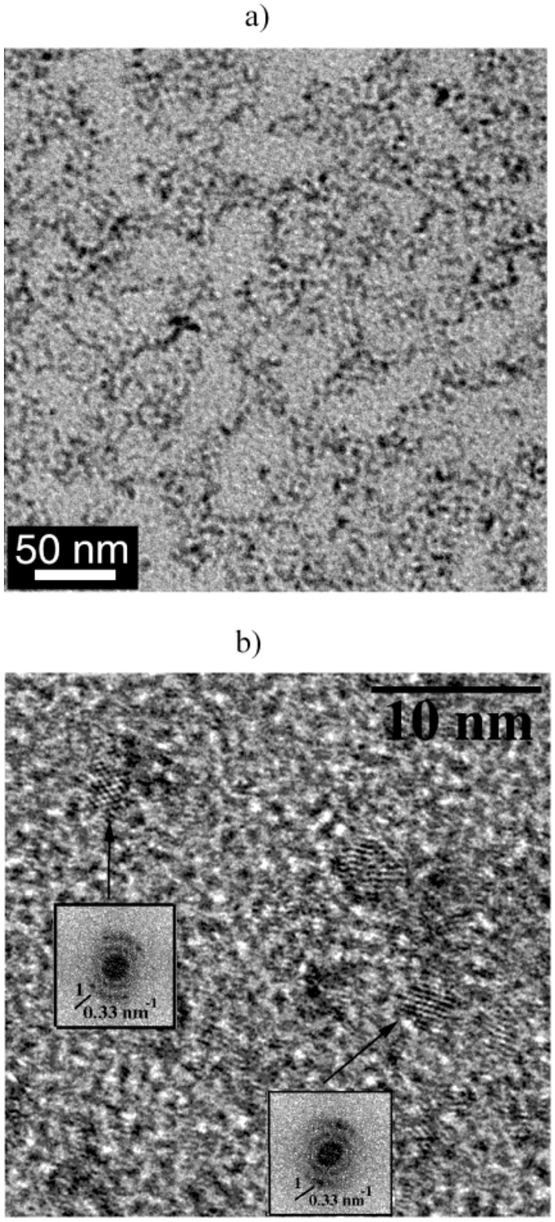

Figure 2. TEM (a) and HRTEM (b) images of CdS nanoparticles prepared in 0.05 g/L of aqueous solution of PEG_{5000}-*b*-PEI_{700}.

These results suggest that because of the separation of the binding PEI moiety on one side of the macromolecule and the solvating PEG moiety on the other, PEG_{5000}-*b*-PEI_{700}-branched acted as a very effective stabilizer for the preparation of a stable colloidal solution consisting of well-dispersed, monodisperse CdS nanocrystals.

Several double-hydrophilic block copolymers with various molecular architectures were also used as stabilizers to prepare CdS nanoparticles in aqueous solution to examine the effect of molecular architectures. As shown in Figure 3, the CdS nanoparticles prepared in the presence of PEG_{5000}-*b*-PEI_{400}-linear showed an absorption edge of 471 nm, larger than that of its branched counterpart PEG_{5000}-*b*-PEI_{700}-branched (429 nm), and a broad PL band centered around

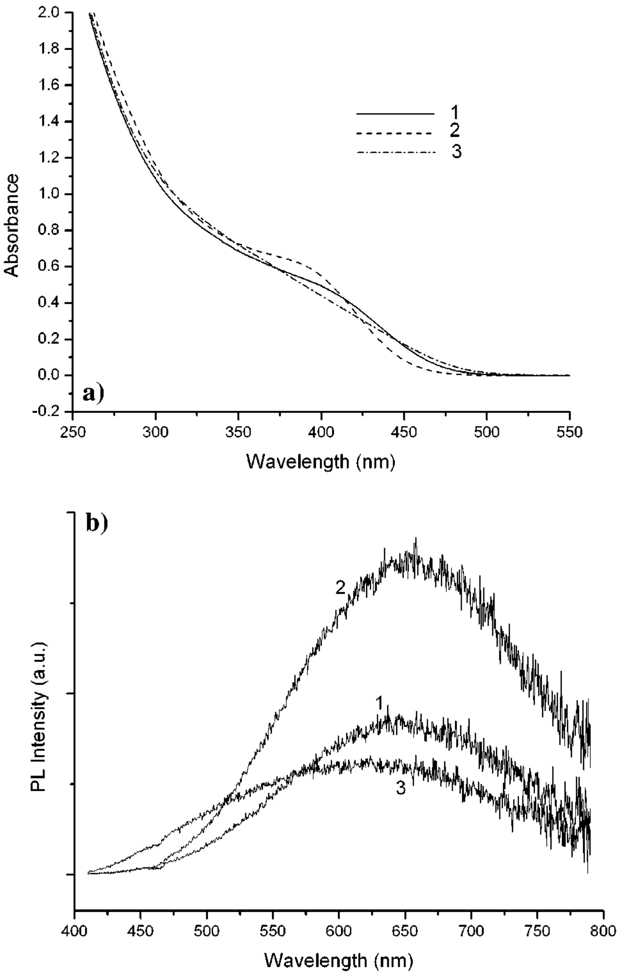

Figure 3. Absorption (a) and photoluminescence (b) spectra of CdS nanoparticles prepared in 0.5 g/L of aqueous solution of (1) linear PEG$_{5000}$-*b*-PEI$_{400}$, (2) PEG$_{5000}$-*b*-Starburst$_{1400}$, and (3) PEG$_{5000}$-*b*-PEIPA$_{1800}$.

649, also larger than that of PEG$_{5000}$-*b*-PEI$_{700}$-branched (575 nm). This result suggests that the linear PEI block was less effective than the branched PEI block in controlling the CdS particle size, resulting in the formation of larger CdS nanoparticles under otherwise identical conditions. It has been suggested that the high local concentration of basic nitrogens on PEI chelate the introduced Cd(II) ions and effectively capture the growing CdS particles upon sulfide addition, which means that a polymer having a higher local concentration of basic nitrogens would be more effective in controlling the particle size.[15] Generally, the local concentration of basic nitrogens in the branched PEI block is higher than that on the linear PEI block, which would largely contribute to the formation of smaller CdS particles. When PEG-Starburst was used as a stabilizer, the absorption edge and PL peak were shifted to 452 and 654 nm, respectively indicating smaller particles than obtained for linear PEG$_{5000}$-*b*-PEI$_{400}$ but still bigger than for branched PEG$_{5000}$-*b*-PEI$_{700}$ possibly due to the lower accessibility of all amine groups in the more regular dendrimer structure (as compared to the branched PEI). Also, the dendritic structure can be considered as the most rigid one compared to linear and branched PEI, although it has the highest local functional group concentration. These results clearly show that an optimum of an effective functional group accesibility exists between molecular flexibility and functional group density so that the branched PEI is the optimum sticker block in that respect.

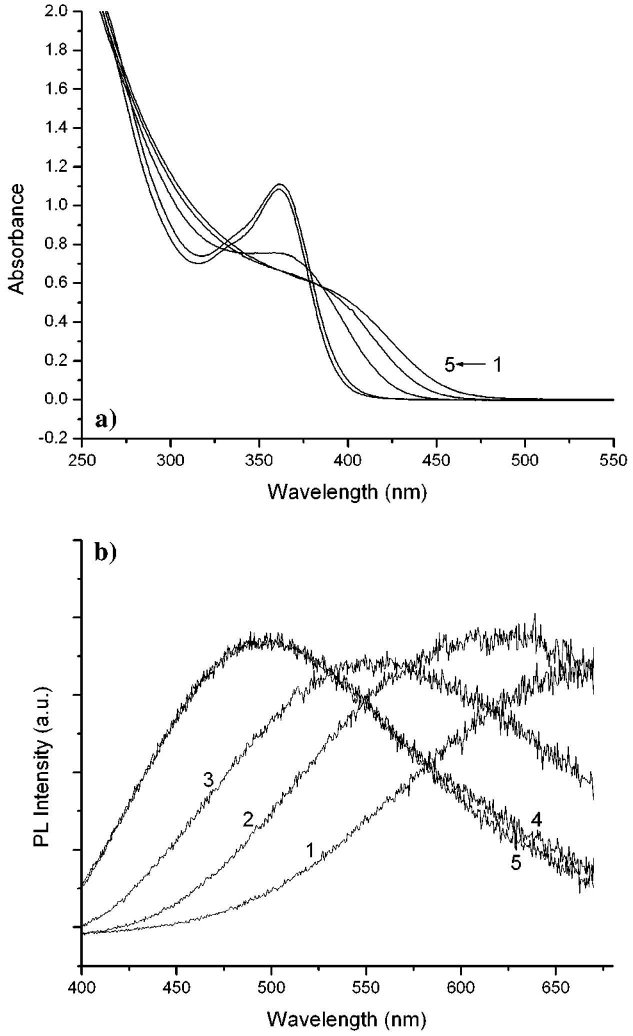

Figure 4. Absorption (a) and photoluminescence (b) spectra of CdS nanoparticles prepared in (1) 0.05, (2) 0.1, (3) 0.25, (4) 0.5, and (5) 1 g/L of methanolic solution of branched PEG$_{5000}$-*b*-PEI$_{700}$.

If the branched PEG$_{5000}$-*b*-PEI$_{700}$ was modified with carboxylic acid groups, the obtained CdS nanoparticles exhibit a much less structured absorption spectrum with an absorption onset of 479 nm and a much broader PL band centered around 620 nm, suggesting that the modification of chelating nitrogens of PEI with carboxylic acid groups and the coupled transformation of the polycationic into a polyanionic block worsen the stabilization of the CdS nanoparticles (see Figure 3).

Finally, the synthesis of CdS nanoparticles was employed in methanolic solution of PEG$_{5000}$-*b*-PEI$_{700}$-branched to examine the effect of solvent, and the corresponding absorption and PL spectra are displayed in Figure 4. Similar to the case of water as a solvent, the absorption edge was decreased gradually with increasing polymer concentration from 0.05 to 1 g/L, and the PL peak ($\lambda_{exc} = 340$ nm) blue-shifted gradually, suggesting that smaller CdS nanoparticles were produced at higher polymer concentration. However, it can be noted that the particle size was smaller than that for the particles prepared in water under otherwise identical conditions. For example, at a PEG_{5000}-*b*-PEI_{700}-branched concentration of 1 g/L, the CdS nanoparticles showed an absorption edge of 392 nm with a sharp exciton peak of 365 nm, corresponding to an average particle size of 2.0 nm,[23] considerably smaller than the 2.3 nm obtained in water. This result is in agreement with data from the synthesis of CdS nanoparticles using Starburst dendrimers as stabilizers.[14] The smaller particle size in methanol can be explained by the change from the complexing solvent water where the polymeric ligand stands in concurrence with the solvent to a non complexing solvent. Therefore, the particle-ligand bond in methanol is tighter than in water, which leads to a slower particle growth at the same nucleation rate compared to water and thus to the observed smaller particles.

It is worth mentioning that all samples show a very prolonged stability against oxidation: solutions kept under athmospheric conditions for at least 2 months show practically the identical photoluminescence efficiency as the original samples. This means that the usually occurring oxidation of CdS to $CdSO_4$ is supressed. This is speculatively attributed to the strong binding of the chelating PEI block which obviously blocks all surface oxidation sites.

Conclusions. This work demonstrates a facile one-step solution synthesis of high-quality CdS nanoparticles in water by using simple double-hydrophilic block copolymers as effective stabilizer, which consist of a solvating PEG block and a PEI binding block. The produced monodisperse CdS nanoparticles, which have a well-resolved cubic structure, were found to be dispersed in solution as single entities and show high colloidal stability. The particle size was controllable in the range between 2 and 4 nm by adjusting the polymer concentration and the solvent. The prepared CdS nanoparticles coated with the polymer show a very good resistance against oxidation and, according to their polymer shell, can additionally be processed as a typical polymer, i.e., can be directly used to prepare thin films of CdS/polymer nanocomposites,[14] immobilized into silicate glasses,[15] or incorporated into bulk polymers or silica.[26] This inheritance of the polymer stabilizer significantly simplifies the use of such species in some of the exciting applications of semiconductor nanoparticles.

In summary, apart from the easy CdS synthesis in water or methanolic solution and the defined nature of the synthesized nanoparticles, the long term stability (at least > 2 months, possibly longer) of the stabilized CdS against oxidation is remarkable and most important from the application viewpoint. Obviously, the interacting PEI groups with their nitrogen electron donor atoms successfully protect the surface of the CdS core from oxidation, a feature that has already been reported before for other nitrogen electron donors, but never for unaggregated and defined particles. Thus, the anticorrosive function of the nitrogen donors in the PEG-*b*-PEI block copolymers in aqueous or methanolic solution combined with the stabilizing function of the PEG shell is unique for a double hydrophilic block copolymer due to the separation of stabilizing and interacting moieties combined with the possibility of tailoring each of the blocks.[27] Therefore, the reported novel approach of the synthesis of single monodisperse, colloidally and oxidation stable quantum sized CdS colloids in aqueous environments can be expected to have a significant impact for various applications of these semiconductors, where up to now, defined deposition and photocorrosion are the most serious obstacles.

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