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Colloidal CdS/SiO$_2$ Nanocomposite Particles from Charged Colloids of CdS and Silica

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Colloidal CdS/SiO$_2$ nanocomposite particles were prepared from soluble negatively charged silica particles (d = 150 nm) and positively charged ligand-stabilised CdS particles (d = 3 nm). The positively charged ligand shell of the CdS particles is constituted of thiocholine [TC, trimethyl(2-sulfanylethyl)azanium chloride]. As a quaternary nitrogen atom carries the charge in this ligand, the positive charge on the particles is basically independent of the pH value of the solution. A neutral pH value was chosen for the deposition of the CdS particles on the larger silica particles which already contain a significant negative charge under these conditions. The obtained nanocomposite particles were characterised by optical spectroscopy, gel electrophoresis and electron microscopy.

Introduction

The preparation and investigation of nanocomposite systems are very generally motivated by the idea of a superior combination of different property profiles brought to the nanocomposite by its individual components. Different types of systems can be considered nanocomposites in this context: small nanoparticles that are embedded in a macroscopic polymeric or oxidic matrix,[1–5] loose assemblies of nanoparticles and silica spheres[6] or isolated spherical structures consisting of chemically different components such as silica-coated quantum dots[7,8] or silica spheres decorated with smaller nanoparticles. With this last type of composite structure, a desired combination of properties such as photoluminescence and solubility in water[7] or magnetism combined with optical emission[9] can be realised. When water solubility together with either magnetic or optical properties is required, silica particles are frequently the component of choice as they are optically inactive and are soluble in water up to a much bigger particle size than most other nanoparticles.[10] Consequently, nanocomposites containing silica particles in combination with particles of II/VI compound semiconductors,[11] of noble metals[12] or of other oxides[13] were described. Ideally, the nanocomposite will exhibit the properties of the smaller particles in the quantum size regime such as blueshifted photoluminescence, plasmon bands or superparamagnetism together with the convenience in handling that the larger silica particles can provide. Regarding the attachment of the semiconductor particles or metal particles on silica, several modes of connectivity were described in the literature. The two most prominent methods to attach smaller functional particles on silica are the coordinative binding of salts or other precursors with subsequent formation of the desired particles on the silica surface[14] and the deposition of preformed small particles on the surface of the silica. The latter concept has the advantage that monodisperse functionalized particles can be used whereas the formation of small particles directly on the surface of the silica support yields quite polydisperse and aggregated products[11a,14,15] because no protecting agent surrounds the primary grains at the moment of their formation. When preformed monodisperse quantum dots such as CdS particles are deposited on a silica support, this can either be done on functionalised silica with a modified surface covered by, for example, thiol groups[3,4] or by the use of appropriately functionalized small particles that are deposited on pure silica spheres. As silica spheres are negatively charged at neutral pH, the application of polycationic polymers as mediators for an attachment of neutral particles proved successful.[16] As an additional variant of such nanocomposites, embedded small functional particles that are covered by an additional silica layer on the original silica sphere were introduced recently.[17] The direct addition of oppositely charged particles as it is applied for the production of ordered superstructures of polymer spheres or semiconductor particles[18] is much less common for the deposition of particles in nanocomposite synthesis. Here, we present the preparation of CdS/SiO$_2$ nanocomposite structures with monodisperse CdS particles and without the need of additional reagents.

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Results and Discussion

Colloidal nanoparticles of cadmium sulfide CdS capped with a thiocholin (TC) shell were prepared from cadmium chloride, hexamethyldisilathiane $(Me_3Si)_2S$ and freshly prepared thiocholine in an experimental procedure similar to the one described by Barglik-Chory et al.[19] (Scheme 1).

Instead of a mixture of water and ethanol, ultrapure water was used as a reaction medium and the reaction time was shortened to 15 min. This protocol yielded colloidal CdS particles with a mean diameter of 2.9 nm after dialysis at a pH value of 7. The stability of the resulting colloid was significantly improved by the use of ultrapure water and by previous extensive rinsing of all glassware with ultrapure water. Whereas colloids in glassware without prior treatment precipitated within a few days, those in rinsed glassware could be stored at 4 °C for at least three months without precipitation. However, even with this precaution taken, strongly diluted colloid solutions precipitated within 24 h because the equilibrium of the cooordinated thiocholin ligand and its uncoordinated form is shifted away from a stabilising coordination. The resulting precipitation was found to be irreversible.

The stable colloids of thiocholine-capped CdS particles were characterized by UV/Vis spectroscopy and by transmission electron microscopy (TEM). The UV/Vis absorption spectrum of the colloidal particles in aqueous solution (Figure 1) shows an absorption maximum at $\lambda_{\max}$ = 369 nm. This value indicates a mean diameter of the particles of 2.8–3.0 nm.[20] This particle size was confirmed by TEM images of the stabilized particles (Figure 2). An overview of the CdS particles (Figure 2a) shows that they are not agglomerated but evenly distributed on the TEM grid. A high resolution TEM image (Figure 2b) shows individual particles of 3 nm size. For some particles, the lattice planes of CdS are also visible.

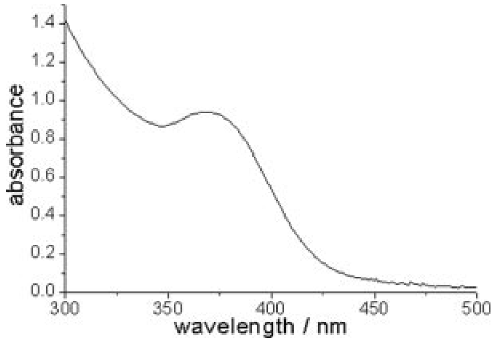


Figure 1. UV/Vis absorption spectrum of thiocholine-capped nanoparticles of CdS ($\lambda_{\max}$ = 369 nm).

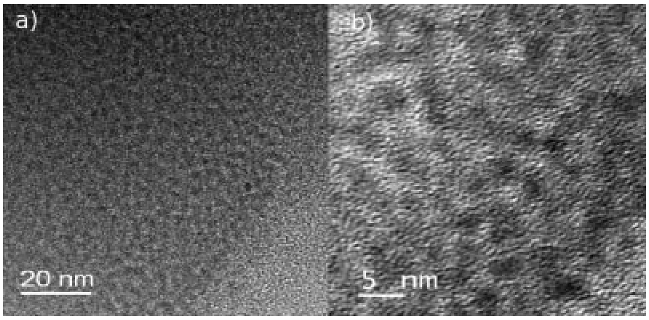


Figure 2. (a) Overview TEM image of thiocholine-capped CdS nanoparticles (d = 3 nm); (b) high resolution TEM image of the particles.

To give evidence for a charged ligand shell on the particles in solution, the CdS particles were subjected to gel electrophoresis. To compare the charge and the mobility of the thiocholine-capped particles with similar charged colloids, we ran solutions of colloidal particles with ligand shells of 11-mercaptoundecanoic acid (MUDA), reduced glutathione (GSH) and dimethylaminoethanethiol (DMAET) as well as negatively charged particles of SiO_2 in parallel. The results are depicted in Figure 3. As expected, the silica particles and the CdS particles with ligand shells of MUDA and GSH were found to move towards the anode in the gel. In contrast, the particles covered by ammonium-functionalized ligands such as DMAET or TC moved towards the cathode. This shows that the TC colloid is sufficiently stable at pH 7 and that it can be used as a

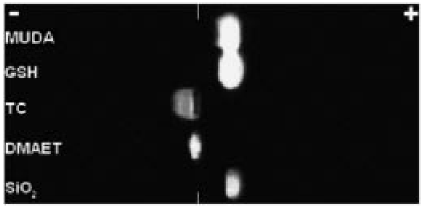
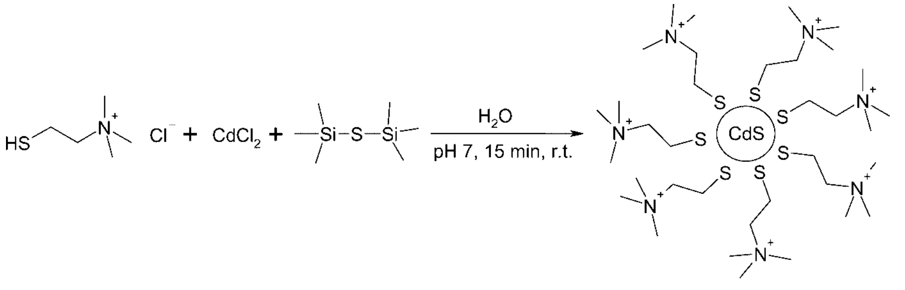


Figure 3. Agarose gel of colloidal nanoparticles of CdS with capping shells of mercaptoundecanoic acid (MUDA), glutathione (GSH), thiocholine (TC) and dimethylaminoethanethiol (DMAET) as well as of silica particles.



Scheme 1. Preparation of colloidal nanoparticles of CdS with a thiocholine shell.

carrier of a permanent positive charge on the shell in nanocomposite synthesis.

Starting from these stable, positively charged particles of CdS and soluble negatively charged particles of silica, we prepared colloidal nanocomposites of SiO_2/CdS where the smaller CdS particles are deposited on the surface of the anionic silica particles at neutral pH value. As the negative charge is situated directly on the particle surface, not on a ligand covering the silica particles, no ligand exchange of oppositely charged ligands of the two types of particles can occur. The silica particles used for the formation of SiO_2/CdS composite particles have a diameter of 150 nm which is much larger than the diameter of only 3 nm of the CdS particles with the thiocholine shell. Thus, no regular packing of spheres as in ordered superstructures of particles of similar size, but a coverage of the bigger particles with a large number of small ones is to be expected. An investigation of the nanocomposite particles by UV/Vis spectroscopy, by TEM and by gel electrophoresis confirmed this picture. In the TEM images (Figure 4) of the nanocomposite particles it can be seen that the surface of the big silica spheres is covered by a large number of darker CdS particles of a few nanometres size. This confirms a significant interaction between the oppositely charged particles making the formation of a stable nanocomposite possible.

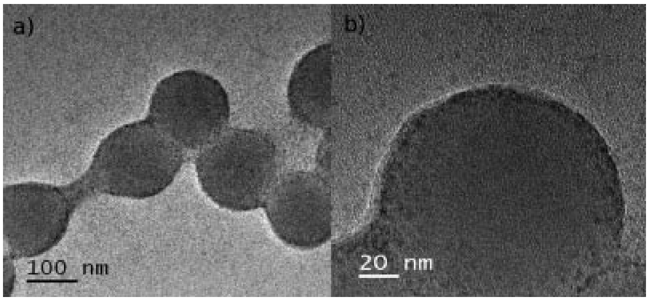


Figure 4. (a) TEM overview image of SiO_2/CdS nanocomposite particles; (b) TEM image of a single SiO_2/CdS nanocomposite particle, which shows the small CdS particles on the surface of the silica sphere.

It was shown by gel electrophoresis that the degree of coverage of the silica spheres with CdS particles is determined by electroneutrality. In contrast to the pure silica particles, which moved towards the anode (Figure 3), and the thiocholine-capped particles of CdS, which moved towards the cathode (Figures 3 and 5), the nanocomposite particles acted as neutral species (Figure 5). For comparison, anionic CdS particles with shells of MUDA and GSH were run in the gel.

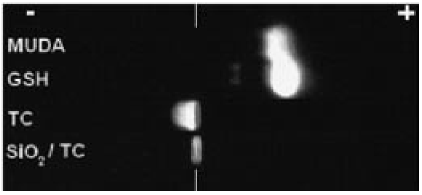


Figure 5. Agarose gel of pure CdS nanoparticles with capping shells of 11-mercaptoundecanoic acid (MUDA), glutathione (GSH) and thiocholine (TC) as well as of SiO_2/TC nanocomposite particles.

Additional evidence for the formation of nanocomposite particles of SiO_2/CdS with a relatively close coverage of the silica surface comes from UV/Vis absorption spectroscopy on aqueous solutions of the particles. The absorption band of the TC-capped CdS particles (Figure 6) is shifted after the deposition from an absorption maximum of λ_{max} = 369 nm to a value of λ_{max} = 400 nm and it is significantly broadened. Both effects are expected for a closer contact of CdS particles on the surface of the silica particles. The shift of the absorption band towards lower energy can be attributed to dipolar interaction between the CdS particles as well as between the CdS particles and the silica. Changes in the electronic structure of the CdS due to their close contacts with each other are known to lead to a broadening of the absorption band.[21]

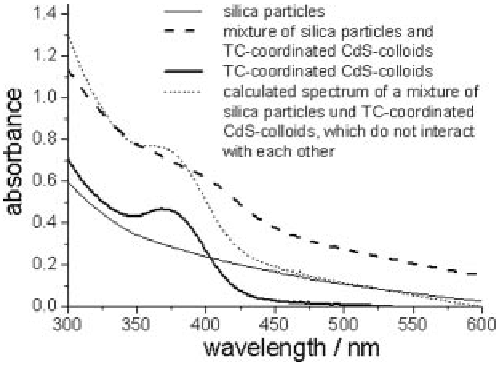


Figure 6. UV/Vis absorption spectra of aqueous solutions of nanoparticles of TC-capped CdS, SiO_2 and the SiO_2/CdS nanocomposite.

Summary and Conclusions

The addition of thiocholine-capped CdS nanoparticles to a colloidal solution of larger silica particles at pH 7 leads to a deposition of the cationic CdS particles on the negatively charged surface of the silica until neutrality of the composite particles is reached. The optical properties of the CdS particles are altered by the deposition, and the absorption maximum is shifter to longer wavelengths. The SiO_2/CdS particles can be handled as a colloidal solution under neutral aqueous conditions. Thus, it was shown that the direct deposition of positively charged nanoparticles of CdS with a thiocholine shell on anionic silica particles as a support is well feasible and leads to a soluble nanocomposite material with the mechanical properties of the larger silica spheres but with the optical characteristics of small quantum confined systems.

Experimental Section

General: For the syntheses and for rinsing all glassware, ultrapure water taken from a purifier of the type Seralpur Pro 90 CN was used. Cadmium chloride $CdCl_2 \cdot 2.5H_2O$ and hexamethyldisilathiane $(Me_3Si)_2S$ (HMDST) were purchased from Acros. Glutathione

(GSH), *N*,*N*-dimethylaminoethanethiol·HCl (DMAET·HCl), tetramethylammonium hydroxide solution (TMAH, 25 wt.% in methanol) and an aqueous suspension of silica particles (d = 150 nm) were purchased from Fluka. 11-Mercaptoundecanoic acid (MUDA) and *S*-acetylthiocholine chloride (S–Ac–TC) were obtained from Sigma–Aldrich. All chemicals were used as received.

Preparation of Thiocholine-capped CdS Particles: In an argon-flooded Schlenk flask, S–Ac–TC (0.188 g, 0.95 mmol, 5 equiv.) was dissolved in ethanol (10 mL). After the addition of concentrated hydrochloric acid (20 mL), the reaction mixture was stirred for 3 h at 80 °C. The solvent was then removed under vacuum at 70 °C, and the residue was dissolved in pure water (40 mL). Subsequently, $CdCl_2{\cdot}2.5H_2O$ (43 mg, 0.19 mmol) was added and as much TMAH as was needed to reach a pH value of 7.0 was also added. Fast addition of HMDST (36 µL, 0.19 mmol) resulted in a yellowish solution. After 15 min, the reaction solution was transferred to dialysis tubing and dialysed against pure water (3 × 600 mL). The resulting slightly cloudy solution was filtered through a 0.2 µm filter to give a clear yellowish solution that was stable at 4 °C for several weeks. ^1H NMR (300 MHz, D_2O, 25 °C): $\delta = 2.92$ (m, 2 H, CH_2), 3.12 (s, 9 H, CH_3), 3.52 (m, 2 H, CH_2) ppm.

Preparation of Glutathione-capped CdS Particles: A sample of GSH (0.544 g, 1.80 mmol, 3 equiv.) and $CdCl_2{\cdot}2.5H_2O$ (0.135 g, 0.59 mmol) was dissolved in pure water (30 mL) in an argon-flooded Schlenk flask and stirred at room temperature for 5 min. TMAH (1.4 mL, 3.4 mmol) and pure water (53 mL) were then added. After an additional 10 min of stirring, HMDST (124 µL, 0.59 mmol) was quickly added. After 15 min, the reaction solution was transferred to dialysis tubing and dialysed against pure water (4 × 300 mL). The resulting slightly cloudy solution was filtered through a 0.2 µm filter to give a clear yellowish solution that was stable at 4 °C for several weeks.

Preparation of MUDA-capped CdS Particles: A sample of MUDA (0.500 g, 2.30 mmol, 1.9 equiv.) and $CdCl_2{\cdot}2.5H_2O$ (0.285 g, 0.59 mmol) was suspended in pure water (60 mL) in an argon-flooded Schlenk flask. After the addition of TMAH (2.5 mL, 5.9 mmol) and 10 min of stirring, MUDA completely dissolved and HMDST (263 µL, 1.24 mmol) was quickly added. After 15 min, the reaction solution was transferred to a dialysis tube and dialysed against pure water (4 × 400 mL). The resulting slightly cloudy solution was filtered through a 0.2 µm filter to give a clear yellowish solution that was stable at 4 °C for several weeks.

Preparation of DMAET-capped CdS Particles: A sample of DMAET·HCl (0.533 g, 3.77 mmol, 6 equiv.) and $CdCl_2{\cdot}2.5H_2O$ (0.143 g, 0.62 mmol) was dissolved in pure water (38 mL) in an argon-flooded Schlenk flask and stirred at room temperature for 5 min. TMAH (0.9 mL, 2.1 mmol) was then added. After an additional 10 min of stirring, HMDST (132 µL, 0.62 mmol) was quickly added. After 30 min, the reaction solution was transferred to dialysis tubing and dialysed against pure water (4 × 300 mL). The resulting slightly cloudy solution was filtered through a 0.2 µm filter to give a clear yellowish solution that was stable at 4 °C for several weeks.

Preparation of SiO_2/CdS Nanocomposite Particles: An aqueous suspension of silica particles (10 µL) and a concentrated aqueous solution of thiocholin-capped CdS colloids (250 µL) were added one after the other to pure water (1 mL). This procedure ensures an excess of CdS colloids in the mixture. The resulting suspension was diluted and dropped on a grid without further purification.

Transmission Electron Microscopy: TEM images were taken with a JEOL JEM 3010 electron microscope operated at an accelerating voltage of 300 kV. All samples were deposited on a carbon foil covering a copper grid. The colloids were diluted by a factor of ca. 30 before they were transferred to the grid.

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