Single Quantum Dots in Silica Spheres by Microemulsion Synthesis

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A new method for the preparation of single quantum dots (QDs) in silica spheres has been developed. The work involves an oil-in-water microemulsion system with cyclohexane as the “oil” phase and Synperonic NP-5 as the surfactant. Reaction parameters such as reactant concentrations, time, and temperature were studied. The method resulted in smooth silica nanoparticles of good monodispersity and high luminescence with single QDs in the center. Elucidating the coating mechanism was attempted. Possible mechanisms include a phase transfer by ligand exchange and a surfactant-supported mechanism. In contrast to sol−gel based methods, this is a straightforward, simple “one-pot” synthesis for such particles. The resulting nanoparticles could be used for further silica growth and assembly of photonic structures, for biolabeling, or for other applications.

Introduction

Recently, nanotechnology drew increasing attention from fields such as electronics, chemical and biotechnology industries, bioanalytics, and others. This attention is caused by the novel mesoscopic properties, which can be observed with nanomaterials in the lower nanometer-size regime. For example, these properties can be used in fields such as optoelectronics,[1−5] catalysis,[6] and biolabeling.[7−9]

Meanwhile, the preparation of monodisperse nanoparticles with several techniques is well-established. For instance, a high-temperature organometallic procedure first published by Murray et al.[10] and subsequently improved by Hines and Guyot-Sionnest[11] led to highly monodisperse, passivated CdSe@ZnS core−shell nanocrystals. Nevertheless, almost any (potential) application of nanoparticles requires a further derivatization of such particles as a prerequisite. Hybrid nanostructures such as biomolecule−nanoparticle conjugates,[9] metal−semiconductor nanohybrids,[12] or polymer−nanocrystal hybrids[13] are important steps toward applications of these nanomaterials.

Encapsulation of single nanoparticles with silica shells is advantageous for applications such as biolabeling, because silica surfaces are easy to functionalize, nontoxic, and protect the surface of the nanoparticles from oxidation. Furthermore, silica particles can be increased in size by “seeded” growth[14] and assembled to bigger aggregates such as photonic crystals.[15] Additionally, silica is chemically inert and optically transparent. A wide variety of silica-coating procedures have been developed for various nanoparticles during the past decade, with a significant progress particularly in metal nanocrystals such as Au and Ag.[16−19]

The methods for covering single nanoparticles with silica can be roughly divided into techniques based on a sol−gel process first published by Stöber et al.[20] (the so-called “Stöber method”) and such on microemulsion synthesis. So far, the Stöber method was used to cover metallic particles,[21,22] insulators,[23−25] organic dyes,[26−28] and semiconductor nano-

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particles.[29] Major disadvantages of the Stöber method for this purpose are the high requirements on purity of the reactants, the difficulty and multiplicity of the preparation steps, and the fact that nanoparticles with nonpolar ligands cannot be coated easily.

Alternatively, a microemulsion approach was used to coat inorganic nanoparticles such as Co,[30] cadmium sulfide,[31−33] silver,[34,35] organic dyes,[36,37] and iron oxide.[38−40] Advantages of the microemulsion method are that it is very "robust" against many reaction conditions, the resulting silica nanoparticles have "smooth" surfaces and display good monodispersity, and last but not least, surprisingly we observed that nanoparticles with nonpolar ligands can be directly coated. To the best of our knowledge, this is the first report of a direct silica coating of nanoparticles with hydrophobic surface ligands via microemulsion synthesis.

The present work describes a simple and straightforward method for the encapsulation of single CdSe@ZnS nanoparticles within monodisperse silica nanospheres. The reaction parameters were investigated, and the encapsulation mechanism was studied. Even though it was not possible to completely elucidate the coating mechanism, there are strong arguments for a ligand-exchange mechanism.

Experimental Section

Chemicals. Tetraethyl orthosilicate (TEOS) 99.999% was purchased from Aldrich, poly(ethylene glycol) nonylphenyl ether (Synperonic NP-5) was purchased from Fluka, and aqueous ammonia solution (33 wt %), cyclohexane, acetone, butanol, propanol, and ethanol were from internal sources. All chemicals were used as received.

The structure, size, and morphology of the resulting nanoparticles were determined by transmission electron microscopy (TEM; Zeiss LEO 912 Omega operating at 120 kV) and UV−visible absorption spectroscopy (J&M TIDAS diode array spectrometer). For the TEM studies, samples were prepared by adding drops of freshly prepared solutions on a carbon film supported on a Cu grid.

Synthesis of CdSe@ZnS@SiO_2 Core/Shell/Shell Structured Particles. CdSe@ZnS nanoparticles were synthesized according to a previously published procedure.[41] A SiO_2 shell was applied as follows: Typically, 10 mL of cyclohexane, 1.3 mL of NP-5, 400 μL of CdSe@ZnS stock solution in chloroform, and 80 μL of TEOS were added in a flask under vigorous stirring. Thirty minutes after the microemulsion system was formed, 150 μL of ammonia aqueous solution (33 wt %) was introduced to initiate the polymerization process. The silica growth was completed after 24 h of stirring. The nanoparticles were isolated from the microemulsion using acetone and centrifuged, and the resultant precipitate of CdSe@ZnS@SiO_2 composite particles was washed in sequence with 1-butanol, 1-propanol, ethanol, and water to remove any surfactant and unreacted molecules. The washing procedure was necessary to completely disperse the precipitate in the corresponding solvent and remove any physically adsorbed molecules from the particle surfaces. Finally, highly luminescent aqueous dispersions of the composite particles were obtained.

Results and Discussion

Osseo-Asare and Arriagada demonstrated that monodisperse SiO_2 spheres can be grown in the size range of 40−70 nm by controlled hydrolysis and condensation of tetraethoxysilane within reverse micelles.[42] The synthesis of colloidal silica by hydrolysis of TEOS in alcohols has been widely studied.[43−47] Because the hydrolysis with water alone is very slow, either an acid or a base catalyst is needed. The former enhances the growth of gel structures, while the latter is a morphological catalyst resulting in spherical particles. Stoichiometrically, the reaction proceeds as

$$Si(OC_2H_5)_4 + 2H_2O \rightleftharpoons SiO_2 + 4C_2H_5OH \tag{1}$$

The reaction is actually a hydrolysis,

$$Si(OC_2H_5)_4 + 4H_2O \rightleftharpoons Si(OH)_4 + 4C_2H_5OH \tag{2}$$

followed by a condensation step,

$$Si(OH)_4 \rightleftharpoons SiO_2 + 2H_2O \tag{3}$$

Polymerization of silicic acid may occur in two ways: In acidic solutions, chainlike or open-branched polymers are initially produced by condensation of silane groups. These polymers are defined as having a specific molecular weight and are not considered as particles. Polymerization in alkaline solutions occurs by internal condensation and cross-linking to give particles in which the interior consists of four silicon−oxygen bonds and the hydroxy groups are attached to the surface of the particles only.

In a typical synthesis, cyclohexane served as the continuous phase in which TEOS, a surfactant (preferably Synperonic NP-5), and hydrophobically ligated quantum dots [QDs; usually with trioctylphosphineoxide (TOPO) ligands] were dissolved. Subsequently, the ammonia catalyst was added. It was found that the size, monodispersity, multiplicity of

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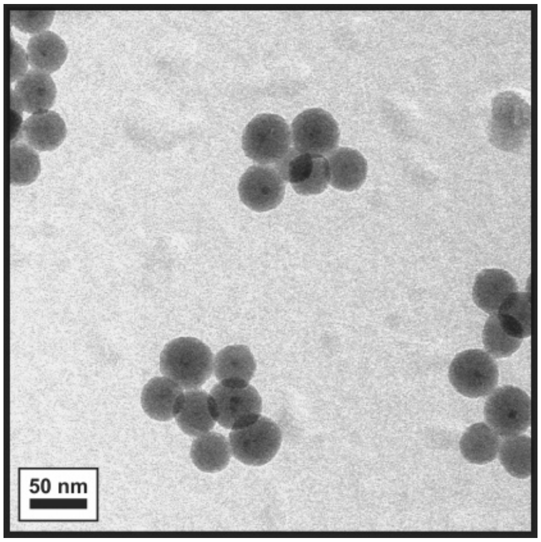

Figure 1. TEM micrograph of core/shell/shell structured CdSe@ZnS@silica particles prepared at the best initial amounts of the surfactant NP-5 (1300 μL).

QDs per silica particle, and overall quality of the resulting QD@silica particles are governed by reaction conditions such as time, temperature, concentration of reactants, and speed of stirring. The influence of these conditions was studied systematically and optimized to yield monodisperse, well-defined particles. Furthermore, elucidating the mechanism of QD incorporation into the silica shell was attempted.

Synperonic NP-5 (NP-5) was chosen as the preferred surfactant because it is nontoxic, is comparatively cheap, and can be handled easily. The concentration of the surfactant turned out to be crucial for the stabilization of the microemulsion system and the resulting nanoparticles. The amount of NP-5 was changed from 900 to 1500 μL, whereas the other reaction conditions were held constant [150 μL of ammonia solution (33 wt %), room temperature, 400 μL of a QD stock solution with a concentration of 8.72×10^{-7} mol/L (concentration was estimated according to the procedure suggested by Yu et al.)].[48] Transmission electron microscope micrographs showed that samples with very low surfactant concentration consisted primarily of agglomerated (almost gelated) small entities of silica. With increasing NP-5 concentration, first polydisperse then monodispere QD@silica nanoparticles appeared (displayed in Figure 1). No clear nanostructure was observable with high surfactant concentrations.

It is known that the ammonia catalyst accelerates the hydrolysis of TEOS proportionally. Rapid hydrolysis is usually preferred, to increase the monodispersity of the resulting particles and prevent competing reactions. Because the pH value of the solution increases with increasing ammonia concentration, the electrostatic stabilization of the colloid should increase. Accordingly, the ionic strength of the solution increases, which destabilizes the microemulsion system.

The influence of the ammonia solution concentration was studied within the range of 50−200 μL of ammonia (aqueous 33 wt % solution), whereas all the other reaction parameters were held constant (as mentioned above). It was observed that with low ammonia concentrations, irregular silica structures were built. With increasing concentration, first polydisperse nanoparticles with multiple QDs and then monodisperse nanoparticles with single QDs appeared (depicted in Figure 2). When the ammonia concentration was further increased, irregular structures were observed besides relatively monodisperse QD@silicas. These observations demonstrate that the monodispersity is lost with low catalyst concentrations because of slow hydrolysis and with high concentrations because of destabilization of the microemulsion.

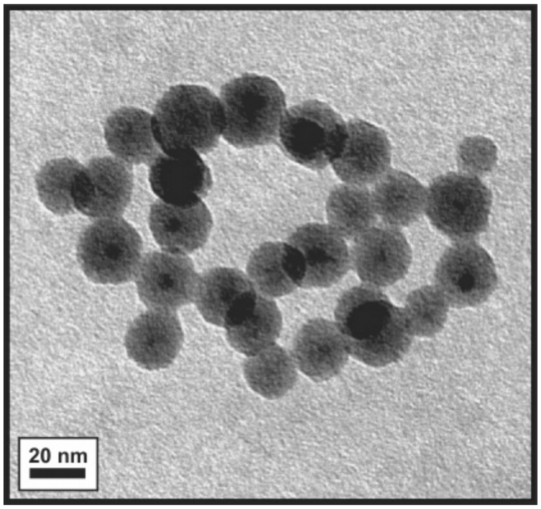

Figure 2. TEM micrograph of core/shell/shell structured silica coated nanoparticles prepared with 150 μL of aqueous ammonia solutions (33 wt %).

The amount of added TEOS is expected to directly influence the size of the resulting nanoparticles. The TEOS was changed from 5 to 150 μL, whereas all other parameters were held constant as described above. It was found that, with an amount below 30 μL, only irregular silica structures were formed. Between 30 and 100 μL of TEOS, single silica coated QDs were found with a proportionally increasing size, dependent on the TEOS concentration. The particles at the limits of this concentration range (viz., 30 and 100 μL) were found to be relatively polydisperse (Figure 3a). The optimal amount of TEOS under these conditions was determined at 80 μL (Figure 3b). With concentrations above 100 μL, again irregular structures were observed (Figure 3c).

Interestingly, it was found that the amount of added QDs not only influences the multiplicity of QDs per silica but also the size and dispersity of the resulting particles. The amount of QDs was investigated from 200 to 600 μL of a stock solution with a concentration of 8.72×10^{-7} mol/L. With QDs below 300 μL it was found that the dispersity was acceptable, but many silica particles without QDs appeared. QD amounts above 500 μL resulted in bigger particles with multiple QDs inside. An intriguing observation was that even when multiple QDs were silica coated, they were found mostly in the middle of the silica particles. Therefore, the QDs seem to act as nuclei for the silica growth and are not "copolymerized" (cf. Figure 4a). With optimal conditions, only one QD was found in the center of a silica particle, like that displayed in Figure 4b.

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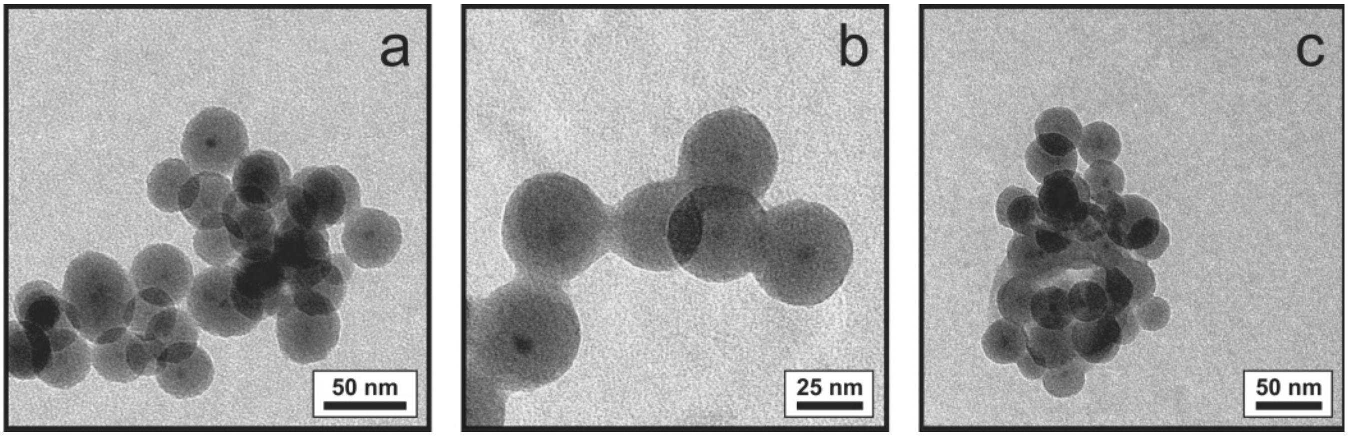

Figure 3. TEM micrographs of core/shell/shell structured CdSe@ZnS@silica particles prepared under different initial amounts of TEOS: (a) 60, (b) 80, and (c) 100 μL.

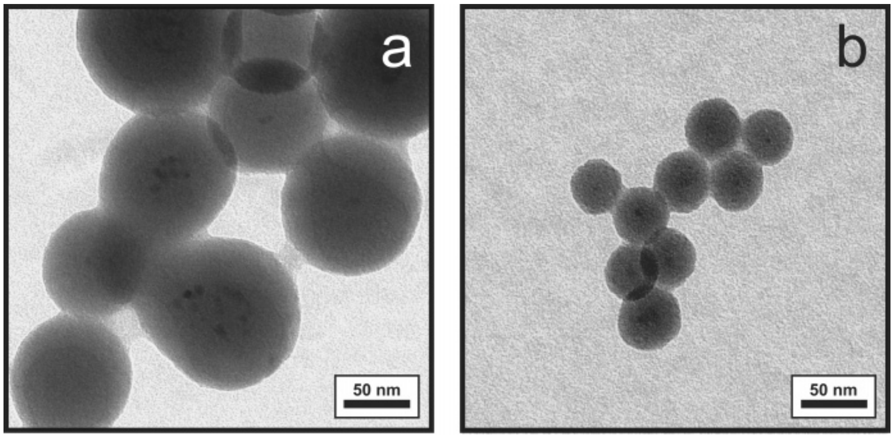

Figure 4. TEM micrographs of core/shell/shell structured nanoparticles prepared under different initial amounts of QD stock solution: (a) 600 and (b) 400 μL.

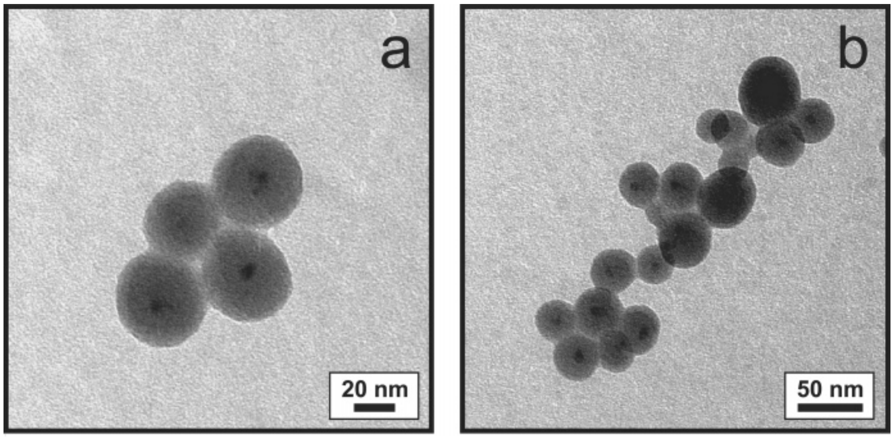

Figure 5. TEM micrographs of core/shell/shell structured CdSe@ZnS@silica composite particles obtained by different reaction times: (a) 24 and (b) 48 h.

It was observed that the reaction kinetics toward silica coated QDs is comparatively slow, even with high (optimal) concentrations of ammonia catalyst. A QD@silica synthesis was performed with the optimized conditions from above, and aliquots were taken in timely intervals. The aliquots were purified according to the procedure described in the experimental section and analyzed by means of TEM. It was observed that small silica coated QDs with rough surfaces were found after 6 h. Shorter reaction times resulted in incompletely coated particles or agglomerates. After 24 h, the growth of the silica shell was completed and the particles were monodisperse with smooth surfaces (depicted in Figure 5a). Further growth led to polydisperse particles (shown in Figure 5 b), most probably as a result of Ostwald ripening.

The influence of the reaction temperature was studied by performing the microemulsion reaction with the optimized conditions from above at elevated temperatures. Syntheses at 308 and 323 K led to polydisperse particles and amorphous material. Therefore, it was concluded that the reaction works optimally at room temperature under these conditions.

Previous publications reported a great influence of the stirring rate on the resulting nanoparticles.[14] Therefore, two

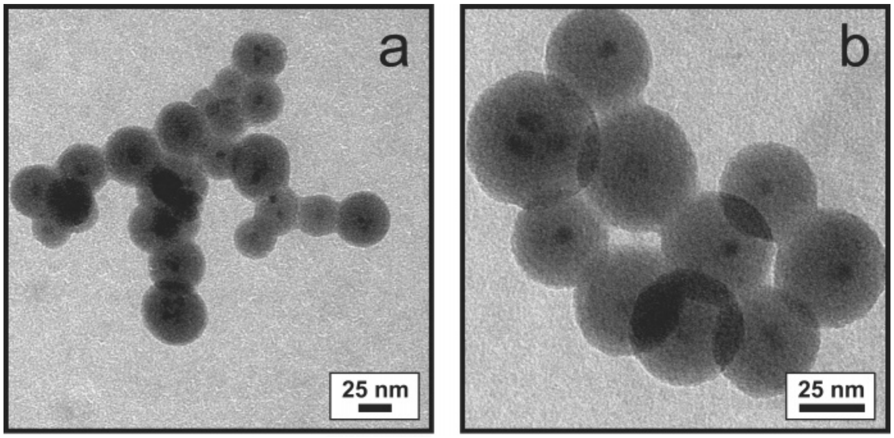

Figure 6. TEM micrographs of core/shell/shell structured CdSe@ZnS@silica nanoparticles obtained by different stirring rates: (a) 1000 and (b) 10 000 rpm.

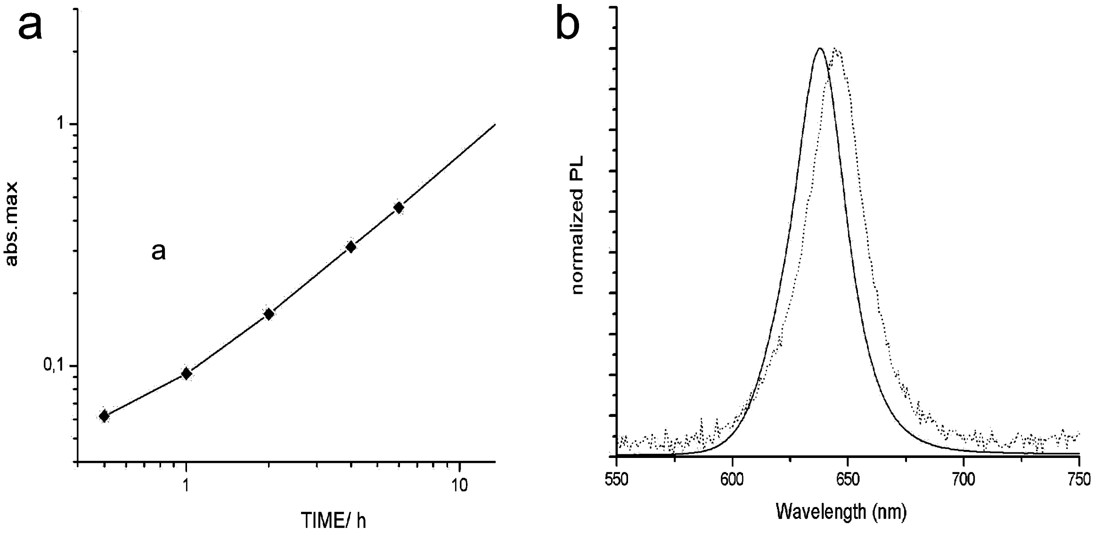

Figure 7. (a) Maximum of the absorbance spectra of colloidal solutions of core/shell/shell structured CdSe@ZnS@silica particles with reaction time at 620 nm and (b) normalized luminescence spectrum for CdSe@ZnS nanocrystals (straight line) and silica coated nanoparticles (dotted line).

identical syntheses were performed with the optimized conditions, except one had a high (above 10 000 rpm) and the other had a low stirring rate (about 1000 rpm). It was observed that the sample with low stirring rate resulted in polydisperse particles and that many particles contained multiple QDs (Figure 6a). A high stirring rate seems to be necessary to form a stable microemulsion (cf. Figure 6b).

The silica coated QDs showed a strong photoluminescence. Figure 7a depicts the increase in absorption at the first excited state of the QDs (620 nm) on preparation of the silica shell. It was observed that the absorption increases almost linearly with the time, indicating a successive growth of the shell. Figure 7b shows the normalized luminescence spectra of nanoparticles before and after silica encapsulation. The silica shell causes a slight red shift of the photoluminescence maximum.

The fact that QDs with hydrophobic ligands (viz., TOPO) are homogeneously silica coated within a microemulsion system is surprising, because the QDs have to undergo a spontaneous phase transfer as a result. This finding can be explained with two hypothetical mechanisms: first, phase transfer without ligand exchange and second, phase transfer with ligand exchange.

QDs with hydrophobic ligands can be easily transferred to water by means of tensides such as, for example, phospholipids.[49] With the first suggested mechanism, the NP-5 could form an “inverse” bilayer around the TOPO-ligated QDs (similar to “inverse” liposomes—hydrophobic ends of the NP-5 are “inside”). On addition of the ammonia catalyst, the silica could grow between the tensid layers (schematically depicted in Figure 8A). This hypothetical mechanism is supported by the observation that not only the QD multiplicity but also the size of the nanoparticles increases on increasing amount of added QDs. Another argument for this mechanism is the slow silica growth rate: TEOS precursors have to be transferred through one tensid layer (rate-determining step) before they are able to hydrolyze on the particle surfaces. The third argument for this mechanism is the fact that the QDs are mostly found exactly in the center of the silica nanoparticles.

With the second suggested mechanism, the TOPO ligands of the QDs are exchanged with, for example, TEOS, and subsequently transferred to the hydrophilic phase of the microemulsion. On addition of the ammonia catalyst, the

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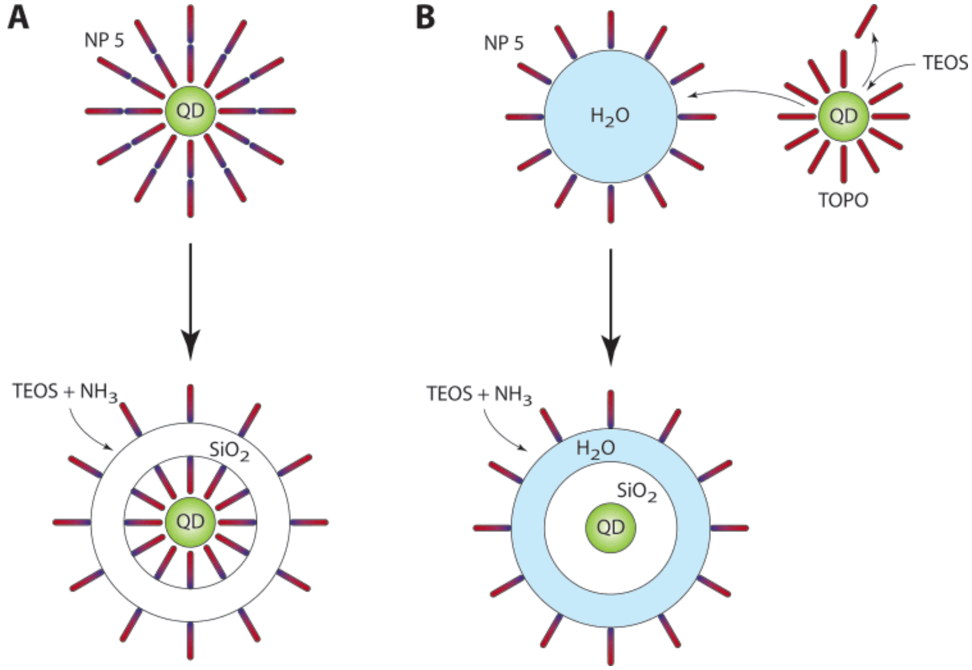

Figure 8. Scheme of the proposed mechanisms for silica growth on QDs: (A) Silica growth without ligand exchange. (B) TOPO is exchanged with TEOS and subsequently transferred into the water pool, and silica is grown on the QD surface.

TEOS is polymerized from the QD surface (shown in Figure 8B). The TEM micrographs do not show any trace of a tensid "transition layer" and, thus, support the second mechanism. Because no ligand exchange is needed with the first mechanism, this observation supports the second. In conclusion, the mechanism could not be clearly elucidated, and more investigation is required; however, in our opinion, the "exchange mechanism" seems more plausible.

Conclusions

In conclusion, a new, straightforward, one-pot method for homogeneous silica coating of single QDs was presented and investigated. Different reaction conditions for the microemulsion synthesis were studied, and it was found that with optimized conditions, highly monodisperse silica coatings can be prepared. In contrast to a previously published, "Stöber"-based method,[29] the procedure is very robust against slight changes with the reaction parameters and the purity of reactants. Furthermore, it can be easily scaled-up and no purification steps are required during preparation of the silica shell. It was not possible to elucidate the encapsulation mechanism completely, but the experimental results point in the direction of a ligand-exchange/phase-transfer mechanism. The resulting nanoparticles could be used for further silica growth and assembly of photonic structures, for biolabeling, or for other applications.

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Supporting Information Available: TEM micrographs and spectroscopic data of core/shell structured CdSe@ZnS particles as well as kinetic data of the TEOS hydrolization. This material is available free of charge via the Internet at http://pubs.acs.org.

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