

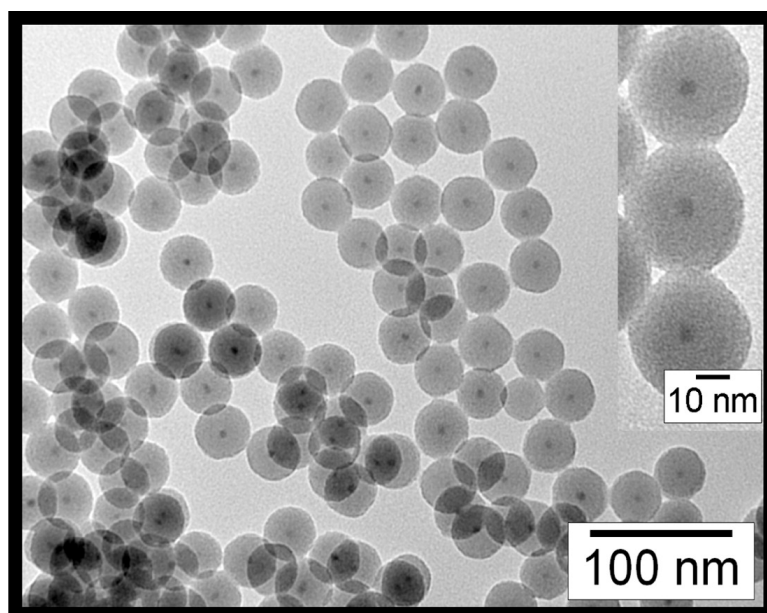
## Article

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# On the Incorporation Mechanism of Hydrophobic Quantum Dots in Silica Spheres by a Reverse Microemulsion Method

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In this work, we show strong experimental evidence in favor of a proposed incorporation mechanism of hydrophobic semiconductor nanocrystals (or quantum dots, QDs) in monodisperse silica spheres (diameter  $\sim 35$  nm) by a water-in-oil (W/O) reverse microemulsion synthesis. Fluorescence spectroscopy is used to investigate the rapid ligand exchange that takes place at the QD surface upon addition of the various synthesis reactants. It is found that hydrolyzed TEOS has a high affinity for the QD surface and replaces the hydrophobic amine ligands, which enables the transfer of the QDs to the hydrophilic interior of the micelles where silica growth takes place. By hindering the ligand exchange using stronger binding thiol ligands, the position of the incorporated QDs can be controlled from centered to off-center and eventually to the surface of the silica spheres. The proposed incorporation mechanism explains how we can have high control over the incorporation of single QDs exactly in the middle of silica spheres. It is likely that the proposed mechanism also applies to the incorporation of other hydrophobic nanocrystals in silica using the same method. In conjunction with our findings, we were able to make QD/silica particles with an unprecedented quantum efficiency of 35%.

## Introduction

In the past decade, the incorporation of metal,<sup>1,2</sup> semiconductor,<sup>3,4</sup> or insulating<sup>5,6</sup> nanoparticles into silica spheres has been studied extensively.<sup>7,8</sup> Silica coated nanocrystals have several advantages over their bare counterparts, especially regarding their end-use in applications. In the first place, silica may provide both chemical and physical shielding from the direct environment, thereby improving the stability. For example, it can prevent aggregation of the nanocrystals, reduce the release of (cytotoxic) ions, or prevent photo-oxidation in the case of quantum dots (QDs).<sup>9–12</sup> Further-

more, the surface chemistry of colloidal silica is well developed and therefore facilitates the solubilization in water or other hydrophilic solvents, enhances the bioapplicability, and allows modifications of the composite particles for further use.<sup>3,13–18</sup> At present, the main application of silica coated nanoparticles ( $< 50$  nm) is their use as biomarkers, where the reduced cytotoxicity, size tunability, and enhanced surface control are the most important features. In addition, silica spheres can contain multiple and different nanocrystals per particle (e.g., gold, magnetite, QDs), which is an ideal starting point for a multimodality contrast agent.<sup>19–21</sup> However, silica coated nanoparticles may also be used for (opto-) electronic devices, as building blocks for photonic crystals, or fundamental single-particle research. In these cases, the

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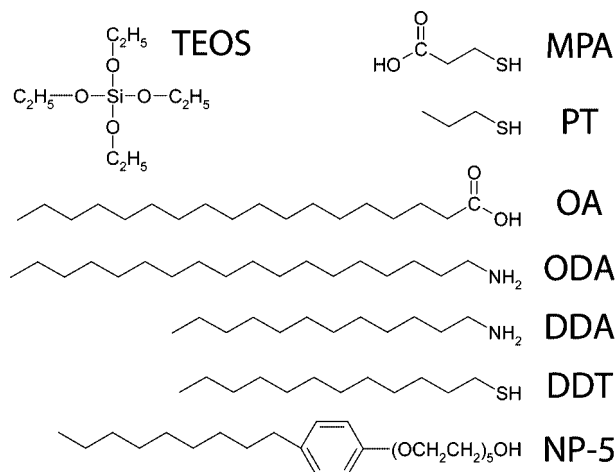
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**Figure 1.** Structural formulas of some of the molecules discussed throughout the article.

robustness, (photo) chemical stability, and high control over the particle size are the most important advantages.

The incorporation of QDs in silica spheres has been accomplished using two different methods. The first method is an adapted “Stöber” approach,<sup>22</sup> where QDs act as seeds for silica growth in an ethanol/water mixture. Typically, the hydrophobically coated QDs have to undergo a ligand exchange to render the QDs hydrophilic, for which MPS (3-mercaptopropyl-trimethoxysilane) is frequently used.<sup>3,4,23</sup> This method yields single or multiple QDs per silica sphere, but the size and size dispersion of the QD/silica particles are not well controlled. The second method uses a water-in-oil (W/O) reverse microemulsion system, where small water droplets are stabilized by a nonionic surfactant (e.g., NP-5, see Figure 1 for an overview of some of the molecules discussed in this article) in a hydrophobic continuous phase (e.g., cyclohexane).<sup>24</sup> Hydrolysis and condensation of the silica precursor (e.g., tetraethyl orthosilicate, TEOS) takes place at the W/O interface or in the water phase, resulting in highly monodisperse silica particles even at small sizes (>25 nm). This system was previously used for the *in situ synthesis* of CdS QDs in silica spheres.<sup>25</sup> Recently, the microemulsion system was also used to *incorporate* both hydrophilic CdTe QDs<sup>12,26</sup> and hydrophobic CdSe/ZnS<sup>9,27</sup> or PbSe<sup>28,29</sup> QDs in silica particles. In comparison with the “Stöber” approach, this method is clearly advantageous because it is less complicated (e.g., no prior ligand exchange is required) and the control over particle size and size dispersion is higher.<sup>27</sup> Hydrophilic CdTe QDs coated with TGA (thioglycolic acid) or MPA (mercaptopropionic acid) are expected to transfer easily into the small water droplets, where silica growth takes place. The silica growth mechanism

for this system was studied in detail, and colloidal stability resulting from the repulsion between the negatively charged QDs explained why only one QD per silica sphere was observed.<sup>12,26</sup> For the hydrophobically coated CdSe or PbSe QDs, the subject of this paper, it is puzzling how the hydrophobic particles end up in the water phase of the microemulsion and are incorporated exactly in the middle of highly monodisperse hydrophilic silica spheres (see Figure 2). Selvan et al. have suggested a ligand exchange of the hydrophobic capping molecules (triethylphosphine oxide, hexadecylamine, oleic acid (OA)) by the nonionic surfactant (NP-5), resulting in a transfer of the QDs to the water phase, but provide no direct evidence for this mechanism.<sup>9</sup> Nann and co-workers have suggested two possible mechanisms for the transfer of hydrophobic QDs to the aqueous phase.<sup>27</sup> The first mechanism assumes an “inverse” bilayer of the surfactants (e.g., NP-5) around the hydrophobic ligands of the QDs, where the silica growth occurs within the bilayer. The second mechanism assumes a ligand exchange, but in this case the hydrophobic ligands (TOPO or OA) are exchanged by TEOS molecules. From their results, no conclusions could be obtained on which of the mechanisms is operative.

It is the aim of this work to elucidate the incorporation mechanism of hydrophobic QDs in silica spheres using the mentioned reverse microemulsion system. Three different types of QDs (CdSe, CdTe, and PbSe) are used to study how the silica shell grows around the QD. The unique advantage of QDs over iron oxide or metal nanoparticles is that changes at the nanocrystal surface frequently affect the optical properties of the QDs. We have therefore used steady state and time-resolved fluorescence spectroscopy to probe the interaction of the QDs with the precursors in the reaction mixture at different stages of the silica synthesis. A ligand exchange mechanism is found to be responsible for the transfer of the hydrophobic QDs into the aqueous phase. On the basis of these results, we were able to control the position of the QD from centered to off-center and eventually to the surface of the silica sphere. Furthermore, we found that the ligand exchange is also responsible for the luminescence quenching that is generally observed when QDs are incorporated in silica. In connection with these findings we were able to obtain a quantum efficiency (QE) of 35% for silica coated QDs which, to the best of our knowledge, is the highest value reported in literature. It is likely that the incorporation mechanism proposed here also applies to the silica coating of hydrophobically coated iron oxide<sup>30</sup> or metal<sup>31</sup> nanoparticles by the reverse micelle method, for which the mechanism has not been resolved yet. In addition, the new insights will facilitate the incorporation of other hydrophobic nanocrystals in silica spheres. Understanding the incorporation mechanism of nanocrystals in silica by this reverse microemulsion method is crucial for further research that has the aim to improve the quality (QE, stability) or control over the final composite particles or to synthesize

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even more complex architectures based on nanocrystals and silica chemistry.

## Experimental Section

Acetone (p.a.), chloroform (p.a.), ammonia (25 wt % in water, p.a.), cadmium oxide (>99%), and zinc oxide (>99%) were purchased from Merck. TEOS (99%) was obtained from Johnson Matthey GMBH Alfa Products. Toluene (anhydrous, 99.8%), methanol (anhydrous, 99.8%), cyclohexane ( $\geq 99\%$ ) poly(5)oxyethylene-4-nonylphenyl-ether (NP-5), OA (90%), dodecylamine (DDA, 98%), octadecylamine (ODA, 97%), propanethiol (PT, 99%), dodecanethiol (DDT, >98%), octadecanol (ODO, 99%), MPA (>99%), ultra pure TEOS (99.999%), butanol (anhydrous, 99.8%), and octadecene (ODE, 90%) were purchased from Aldrich. Sulfur powder (99.999%) was obtained from Alfa Aesar and ethanol (>99.8%) from Riedel de Haën.

CdTe,<sup>32</sup> CdSe,<sup>33</sup> and PbSe<sup>34</sup> QDs were synthesized by organo-metallic syntheses using standard literature procedures. CdTe QDs were purified once by adding 150  $\mu\text{L}$  of methanol to 50  $\mu\text{L}$  of the crude reaction mixture, followed by centrifugation, and redispersing the precipitate in 50  $\mu\text{L}$  of chloroform. To this, 50  $\mu\text{L}$  of DDA or 25  $\mu\text{L}$  of PT or DDT was added to recoat the purified QDs. For MPA coated QDs, 50  $\mu\text{L}$  of the crude CdTe reaction mixture was dispersed in 2.5 mL of chloroform, after which 50  $\mu\text{L}$  of 0.1 M MPA in methanol was added. For transfer to water, 100  $\mu\text{L}$  of a 0.1 M KOH solution in methanol was added, after which 1.5 mL of deionized water (Millipore, 15 M $\Omega$  cm) was added. Upon shaking the mixture formed, the MPA coated QDs were transferred to the water phase.<sup>35</sup> The 1.5 mL aqueous dispersion was separated and partly evaporated to obtain the desired volume for addition to the reverse microemulsion system.

The CdSe QDs were washed by a procedure similar to that of the CdTe QDs but redispersed in ODE. The CdSe QDs were coated with seven monolayers of inorganic shells ( $2 \times \text{CdS}$ ,  $3 \times \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ ,  $2 \times \text{ZnS}$ ) by a SILAR procedure.<sup>36</sup> Addition of these shells was performed by adding precalculated amounts of a 0.1 M precursor solution (Cd oleate, CdZn oleate, Zn oleate, and sulfur in ODE) to CdSe QDs dispersed in ODE at 230 °C. Each monolayer was allowed to grow for 10 min before the next precursor solution was added. The CSS QDs were purified by precipitation in a chloroform/acetone mixture followed by redispersion in chloroform two times, after which they were dispersed in cyclohexane. The ligand exchange by DDT was performed by mixing an appropriate volume of a 1:100 DDT/cyclohexane (v/v) solution (0.042 M) or pure DDT to 1.8 nmol of CdSe CSS QDs in 1 mL of cyclohexane. Addition of 650 DDT molecules per QD was assumed to be equivalent to one monolayer coverage. The mixture was allowed to stand for 24 h, after which it was added to the reverse microemulsion system.

The PbSe QDs were purified by precipitation and redispersed in a toluene/butanol mixture two times. For incorporation in silica, PbSe QDs were dispersed in chloroform.

For a typical reverse microemulsion synthesis, 1.3 mL of NP-5 was dispersed in 10 mL of cyclohexane and stirred for 15 min (850

rpm). Subsequently, 1–2 nmol of QDs dispersed in chloroform (100  $\mu\text{L}$ ), cyclohexane (1 mL), or water (50  $\mu\text{L}$ ) was added, after which 80  $\mu\text{L}$  of TEOS and 150  $\mu\text{L}$  of ammonia were added. Between the additions, the reaction mixture was stirred for 15 min (850 rpm). The order in which the chemicals were added was varied for the experiments as described in Figure 6. After the last step, the mixture was stirred for 1 min, after which it was stored in the dark at room temperature for 1 week. Finally, the QD/silica particles were purified by adding 3 mL of ethanol to the reaction mixture and centrifuging this for 10 min at 1800g. After removal of the supernatant, 10 mL of ethanol was added, and the silica particles were sedimented again by centrifugation at 1800g for 20 min. This was repeated once more for 40 min after which the QD/silica particles were redispersed in ethanol. The purified QD/silica samples were used for making transmission electron microscopy (TEM) images or ODO coating (see below).

To determine the QE of the silica coated QDs, the particles were coated by ODO. This was performed in a nitrogen-purged glovebox by adding 2.5 g of ODO dispersed in 5 mL of ethanol to a dispersion of 1.8 nmol of QD/silica particles in 5 mL of ethanol. After heating this mixture to 100 °C for 1 h to evaporate all ethanol, the temperature was increased to 170 °C for 3 h to covalently link the ODO to the silica spheres by a condensation reaction.<sup>37</sup> The ODO coated particles were purified by precipitation and centrifugation in a cyclohexane/ethanol mixture (repeated two to three times) and redispersed in chloroform. To quantify the QE, the integrated emission of the QDs was compared with that of both Rhodamine 6G (QE = 90%) and Rhodamine 101 (QE = 95%).

Emission spectra were recorded using the monochromator of a Spex Fluorolog spectrometer (double-grating, 0.22 m, SPEX 1680) and a 450 W Xe lamp as the excitation source. The luminescence spectra were recorded by a Princeton Instruments CCD camera (liquid nitrogen cooled) and a 0.25 m Acton Research monochromator with a grating of 150 lines/mm blazed at 550 nm. Photoluminescence decay curves were obtained by time-correlated single-photon counting. The setup consisted of a pulsed PicoQuant laser (2.5 MHz,  $\lambda_{\text{ex}} = 406$  nm, pulse width = 55 ps) in combination with a monochromator (1350 lines/mm blazed at 500 nm), a Hamamatsu photomultiplier tube (H5738P-01), and a Time Harp 200 computer card.<sup>33,38</sup>

## Results and Discussion

Following a synthesis procedure adapted from Nann and co-workers (see Experimental Section for details), we have incorporated 6.4 nm CdSe core/shell/shell (CSS) QDs in silica spheres by the reverse microemulsion method.<sup>27</sup> The resulting silica particles of 37.2 nm are highly monodisperse (4% size dispersion) and have one QD incorporated exactly in the center of the sphere (Figure 2A and inset). The control over the number of QD per silica particle is high: 96% of the particles contains a single QD in the center, 3% is empty, and only 1% contains two QDs per particle. The CSS QDs were coated with ODA and dispersed in chloroform or cyclohexane before addition to the microemulsion system. The amount of CSS QDs that was added (1.8 nmol) was estimated from the initial amount of CdSe core QDs before shell growth. The number of initial CdSe QDs was determined by using the experimentally determined

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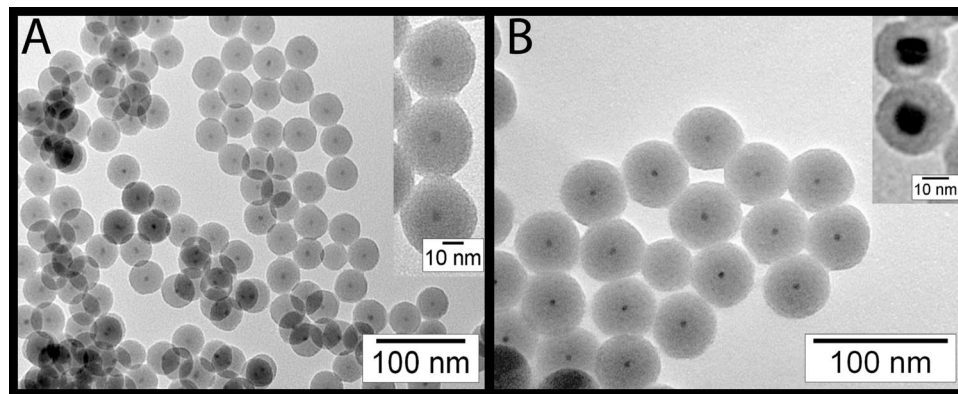
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**Figure 2.** TEM images of (A) CdSe CSS QDs ( $6.4 \pm 0.8$  nm, ODA coated) in silica spheres of  $37.2 \pm 1.5$  nm in diameter; inset shows a magnification of the same sample. (B) PbSe QDs ( $6.8 \pm 0.3$  nm, OA coated) in silica spheres of  $47.0 \pm 3$  nm; inset in panel (B) shows a TEM image of cubic PbSe QDs ( $11.1 \pm 0.6$  nm, OA coated) coated with a thin layer of silica ( $6.4 \pm 1.0$  nm).

size-dependent extinction coefficient of CdSe QDs.<sup>39</sup> For comparison, the number of silica particles can be calculated, given the final size of the particles, the size of the incorporated QDs, and the amount of TEOS molecules used (assuming that all TEOS has reacted). For the QD/silica particles shown in Figure 2A this calculation yields 1.1 nmol of QD/silica particles (or slightly more when a lower density for porous silica is assumed),<sup>40</sup> which is in fair agreement with the 1.8 nmol mentioned above.

To investigate the general applicability of the method, also OA coated PbSe QDs (6.8 nm) were incorporated in silica spheres using the same method. This resulted in 47.0 nm silica spheres with one PbSe QD incorporated in the middle (Figure 2B). The final particles are 10 nm larger than the CdSe CSS QDs in silica, which is explained by the lower amount of PbSe QDs that was used for the synthesis. We did not encounter problems regarding the dissolution of the PbSe QD using ammonia as base catalyst, as was reported earlier.<sup>28</sup> The quality of our silica coated PbSe QDs is unprecedented, particularly regarding the size dispersion and homogeneity (single QD per particle) of the samples.<sup>28,29</sup> Cubic shaped PbSe QDs (11.1 nm) were also incorporated in silica spheres, as is illustrated in the inset of Figure 2B. In this case, the reaction was stopped after 2 h, which resulted in a thin but homogeneous shell (6.4 nm) around the PbSe QDs.

The size of the final QD/silica particles changed if the amount of CdSe CSS-QDs added to the reaction mixture was varied within a certain range. Smaller (25 nm) and thus more silica spheres resulted when twice the amount of CSS-QDs (3.5 nmol) was used, whereas the number of silica spheres with two or more QDs per silica spheres increased with only 10%. Vice versa, larger silica particles (>40 nm) were formed when less QDs were used, without the number of empty silica spheres changing significantly. These observations together with their central position in the silica spheres indicate that the QDs act as efficient nucleation sites for silica growth. Below this range (e.g., 1.3 nmol), the amount of empty silica particles increased (see, for example, Figure 5A), whereas an excess of QDs (>3.5 nmol) resulted in predomi-

nantly multiple QDs per silica particle. Figure 3A,B shows TEM images of silica particles with multiple QDs incorporated, as a result of adding 7.2 nmol or 9 nmol of QDs to the reaction mixture respectively (four and six times the quantity used for the particles shown in Figure 2A). At these high concentrations of QDs the micellar system becomes unstable, resulting in an aggregation of the QD/silica nuclei. Aggregation at an early stage of the silica growth results in little or no spacing in between the QDs, whereas aggregation at a later stage causes a certain distance between the QDs. Both small and larger interdot distances are observed in Figure 3A. The latter is particularly interesting because it may open up a new route to colocalize different types of nanocrystals within one silica sphere (to study for instance exciton-plasmon coupling), by adding a second type of nanocrystal at a later stage of the silica synthesis. When even more QDs are added (Figure 3B), the QDs clearly form chains within the silica particles. This suggests a directional force on the particles during aggregation, which may be explained by the presence of a permanent dipole moment in semiconductor nanocrystals.<sup>41–43</sup>

As is shown in Figure 2, the incorporation of hydrophobically coated QDs in silica spheres by the reverse microemulsion method gives a high degree of control and indicates that the QDs act as nucleation centers. This control is surprising because the silica nucleation and growth occurs within the small water droplets of the microemulsion, where one would expect the hydrophobic QDs to agglomerate or not to be present at all. To study the influence of the hydrophobic nature of the capping layer in more detail, we have also used CdTe QDs with different ligand coatings for the incorporation in silica. Figure 4A shows the result for DDA coated CdTe QDs. These were incorporated, albeit in more polydisperse silica spheres with a larger spread in the number of QDs per silica particle. When the same CdTe QDs were coated with an excess of PT (see Experimental Section), the nanocrystals were not incorporated in silica spheres, as

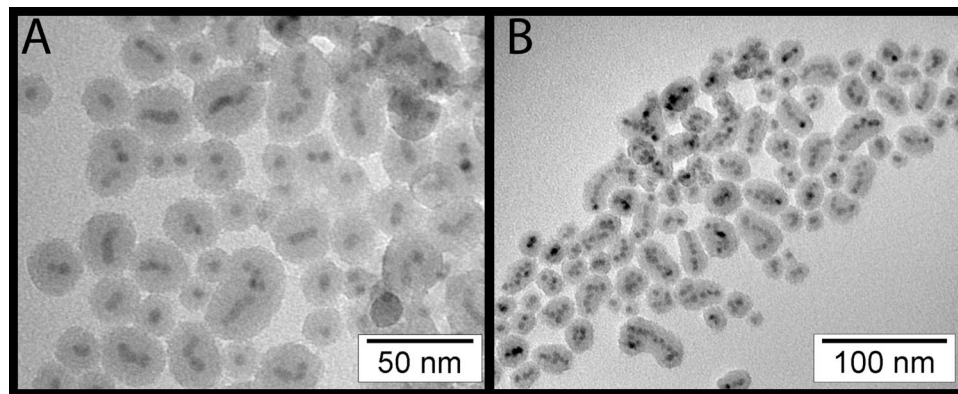
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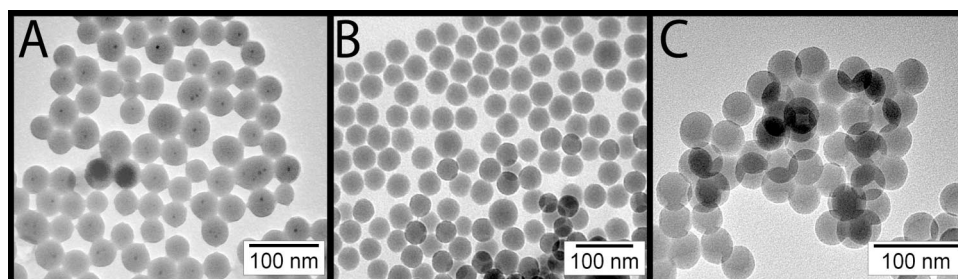
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**Figure 3.** TEM images of silica particles with multiple CdSe CSS QDs (ODA coated) incorporated. The particles were obtained by adding (A) four times (7.2 nmol) or (B) six times (9 nmol) the number of CdSe CSS QDs used for the particles shown in Figure 2A.



**Figure 4.** TEM images of resulting silica spheres when (A) DDA coated and (B) PT coated CdTe QDs in chloroform or (C) MPA coated CdTe QDs in water are added to the microemulsion system.

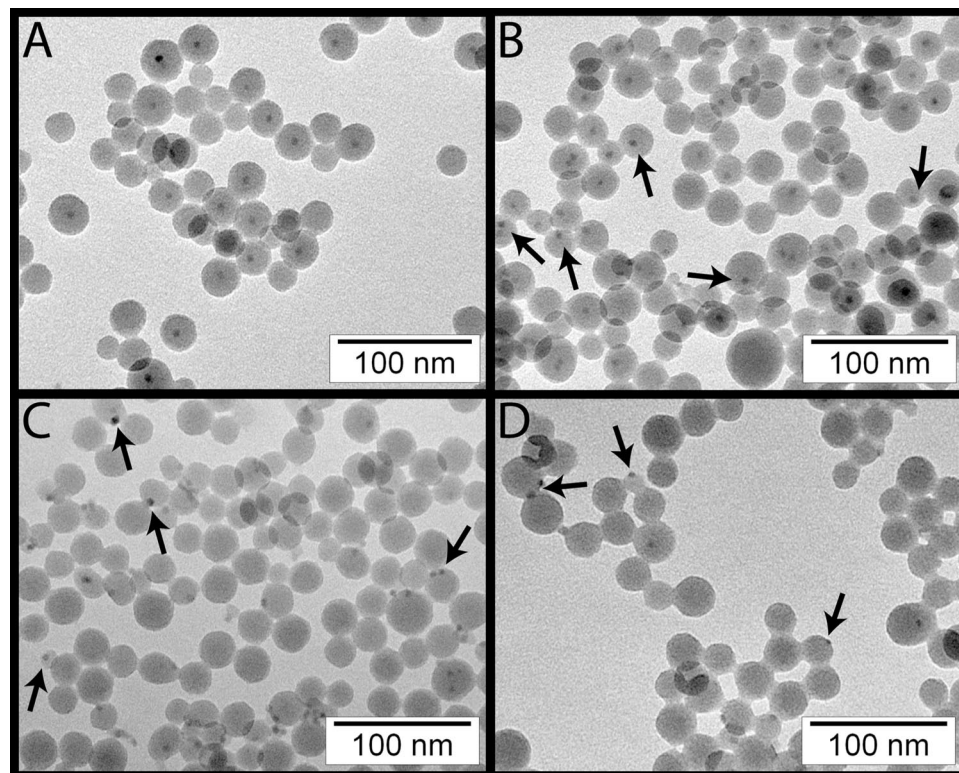
is clearly illustrated in Figure 4B. We have performed the same experiment with DDT coated CdTe QDs, which gave a similar result (no incorporation). In addition, the CdTe QDs were coated with MPA and transferred to water as described previously.<sup>35</sup> When the water soluble MPA coated QDs were added to the standard microemulsion system, no incorporation was observed (Figure 4C). The same experiment was conducted for MPA coated CdTe QDs that were not transferred to water but still dispersed in chloroform (not deprotonated), which did not result in incorporation in silica either (not shown). It has been reported earlier that hydrophilic coated CdTe QDs dispersed in water do incorporate in silica using the same procedure, but we were not able to reproduce these results.<sup>12,26</sup>

The results described above indicate that CdTe QDs coated with either hydrophobic or hydrophilic thiolated ligands are not incorporated in silica spheres using the reverse microemulsion method, whereas the incorporation of amine coated CdTe QDs is successful. We have therefore systematically investigated the influence of thiol-coating of CdSe CSS QDs on their incorporation in silica spheres. A variable amount of DDT was added to the CSS QDs, 24 h before addition to the microemulsion system. For these experiments, a significantly smaller amount of QDs was used (1.3 nmol), to avoid multiple QDs per particle. This explains the higher number of empty silica spheres in the case where no DDT was added (Figure 5A) as compared to Figure 2A. When an amount of DDT corresponding to a 10-fold excess of the number of molecules that is required for one monolayer (assuming 650 DDT molecules per QD, see Supporting Information) is added, the QDs are still incorporated into silica but are

positioned off-center (Figure 5B). When an amount corresponding to 100 monolayers of DDT is added, some QDs are incorporated off-center, but most of the QDs are attached to the surface of the silica spheres (Figure 5C). In the case of an amount for 500 monolayers DDT, the QDs are also attached to the outside of the silica particles, and the number of QDs associated with silica spheres decreases significantly (Figure 5D). TEM images of samples where concentrations corresponding to 1 or 50 monolayers of DDT were used are in line with the trend that the CSS QDs are “pushed” to the outside of the silica spheres when more thiolated ligands are added. These results show that the position of the QD in the silica sphere can be controlled by changing the amount of DDT molecules.

In the experiment described above, the relative number of DDT molecules compared to TEOS or NP-5 is low. The number of DDT molecules at 10 monolayers is still a factor 50 and 410 lower as compared to the number of TEOS and NP-5 molecules, respectively (an overview of the relative amount of molecules present in the microemulsion system is given in Table S1 of the Supporting Information). Therefore, we assume that the relatively low number of DDT molecules does not significantly influence the actual microemulsion system, which is confirmed by the fact that the shape or size of the silica spheres themselves is not changed upon addition of DDT. Nevertheless, the effect on the incorporation of the QDs is clearly visible already at 10 monolayers of DDT.

The original ODA coating of the CdSe CSS QDs is easily replaced by the DDT molecules, because the thiolated ligands bind much stronger to the QD surface than the amine groups



**Figure 5.** TEM images of silica particles when an amount of DDT corresponding to (A) 0, (B) 10, (C) 100, or (D) 500 monolayers is added to the CdSe CSS QDs (originally ODA coated), 24 h before addition to the microemulsion system.

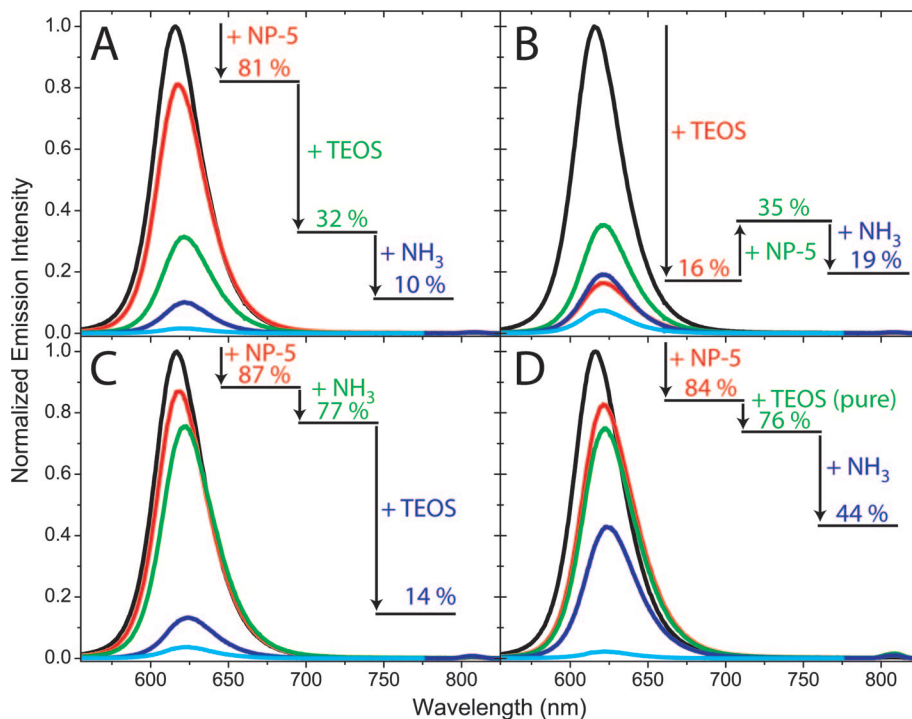
of ODA.<sup>35,44</sup> The observation that DDT coated QDs are not incorporated in silica cannot be explained by the first mechanism proposed by Nann and co-workers, where silica growth takes place in a bilayer of NP-5 molecules around the hydrophobic QDs.<sup>27</sup> This mechanism should still be possible when ODA ligands are replaced by DDT, because both coatings result in a hydrophobic coating of the QDs. On the other hand, the observations in Figure 5 do support a ligand exchange mechanism, where ODA or DDT is replaced by either NP-5 or TEOS, enabling the transfer of the QDs to the small water droplets.<sup>26,27</sup> The stronger binding of DDT to the QD surface reduces this ligand exchange and hinders the incorporation of the QDs, explaining the trend observed in Figure 5. Without any DDT present, the QDs are coated by ODA which is easily replaced by TEOS and/or NP-5 (Figures 2A and 5A) resulting in a central incorporation in silica. At a relatively low amount of DDT molecules, an incomplete or delayed ligand exchange can still result in incorporation in silica spheres, albeit off-center. At higher DDT concentrations, ligand exchange occurs only locally (or not at all), resulting in QDs that are attached to the outer surface of the silica spheres (or not associated at all).

To provide additional evidence for the ligand exchange mechanism, (time-resolved) fluorescence spectroscopy experiments were performed on the reaction mixture at different stages of the silica synthesis. The optical spectroscopy elucidates by which ligands (and to what extent) the ODA is exchanged, allowing us to propose a detailed picture of

the incorporation mechanism. The emission spectra of CdSe CSS QDs (initial QE of 60%) at different stages of the reverse microemulsion synthesis are shown in Figure 6. To 10 mL of a QD dispersion in cyclohexane were added NP-5, TEOS, and ammonia in different sequences. After each addition, the reaction mixture was stirred for 15 min, directly followed by the optical measurement. Figure 6A shows a decrease to 81% of the initial emission intensity upon addition of NP-5, followed by a decrease to 32% and 10% upon addition of TEOS and ammonia, respectively. After 1 week, the emission intensity had decreased to approximately 2% of the initial intensity. When TEOS is added first (Figure 6B), a drastic decrease in emission intensity is observed (to 16%), followed by an intriguing increase to 35% upon addition of NP-5. Finally, the emission decreased to 19% of the initial intensity when ammonia was added. Figure 6C shows that addition of ammonia in the absence of TEOS does not cause a significant decrease in emission intensity. However, the emission intensity drastically decreases to 14% when TEOS is subsequently added.

Figure 6A,C clearly shows that both NP-5 and TEOS (in a hydrolyzed form, as will be shown below) have affinity for the QD surface, as is concluded from the quenching of the QD emission. This provides direct evidence for the ligand exchange mechanism, that is, the replacement of ODA ligands by hydrolyzed TEOS and/or NP-5 molecules. If TEOS is added after NP-5 (Figure 6A), the NP-5 is partly replaced by TEOS, as can be concluded from the drastic additional decrease in emission intensity. The fact that (hydrolyzed) TEOS quenches the QD emission significantly stronger than NP-5 can be attributed to a higher affinity of

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**Figure 6.** Emission spectra of CdSe CSS QDs (ODA coated) at different stages of the reverse microemulsion synthesis ( $\lambda_{\text{exc}} = 406$  nm). In panels (A–C), NP-5, TEOS, and  $\text{NH}_3$  were added in different orders, as indicated by the arrows in each panel. The synthesis shown in panel (D) was identical to the synthesis in panel (A), except for the use of ultra pure and water-free TEOS. The emission spectra are corrected for the significant dilution factor upon addition of NP-5, and percentages represent the integrated emission intensity. The emission spectra in “cyan” were measured 1 week after the synthesis.

TEOS for the QDs (i.e., more TEOS molecules attached), to an intrinsic higher quenching efficiency of TEOS, or both. In this context, it is important to note that there is approximately 8 times more NP-5 present in the reaction mixture than TEOS (see Table S1 of the Supporting Information). Importantly, the increase in emission intensity in Figure 6B after addition of NP-5 can be explained by an exchange of TEOS attached to the QD surface by NP-5, implying that NP-5 quenches the QD emission less efficiently than TEOS. The values of 32% and 35% after addition of both NP-5 and TEOS (Figure 6A,B) indicate that a similar equilibrium is reached, regardless of the order in which they were added.

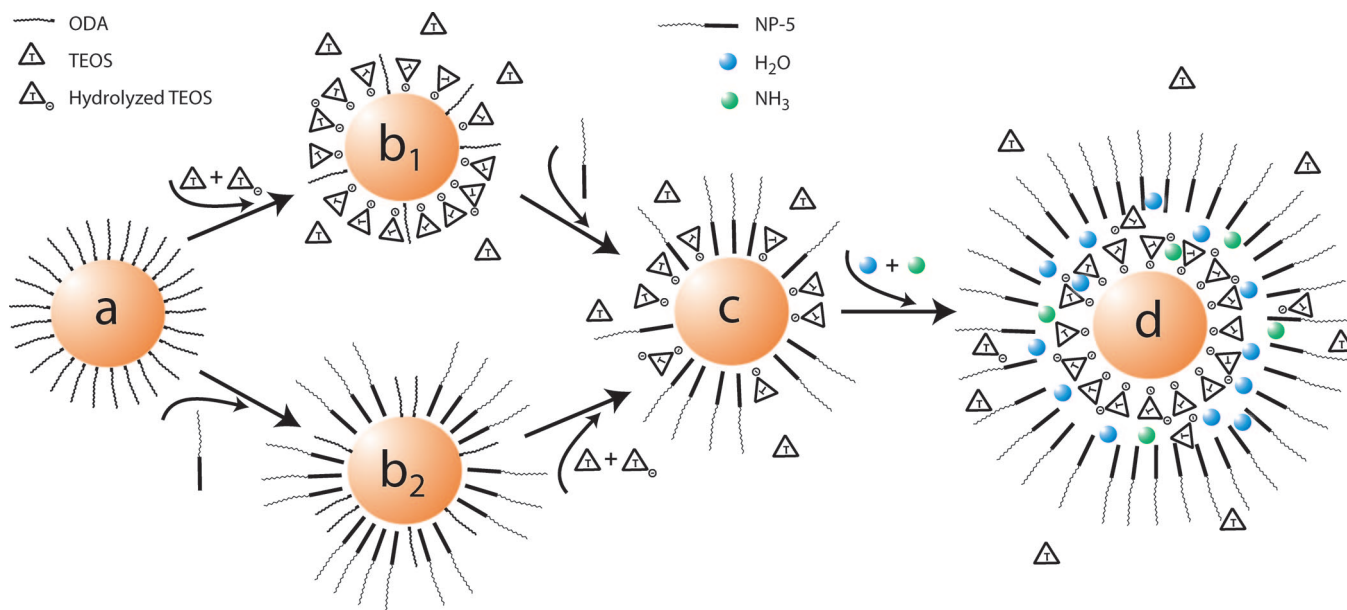
In a simplified model, the relative quenching efficiency and binding affinity of NP-5 and (hydrolyzed) TEOS molecules can be (roughly) quantified. Because the number of NP-5 and TEOS molecules per QD is rather high ( $3.6 \times 10^5$  and  $2.1 \times 10^6$  respectively, see Table S1), we assume that 100% of the QD surface sites is occupied by TEOS or NP-5 molecules after addition to the QDs in cyclohexane. When NP-5 is added only, the quenching is 16% on average, while the quenching is 84% when the QDs are fully covered by TEOS. It can thus be calculated that TEOS quenches the QD emission a factor of 28 more efficiently than NP-5 (see Supporting Information). When NP-5 is added to TEOS coated QDs (Figure 6B), the emission intensity increases from 16% to 35%. It can be calculated that this is due to the replacement of 64% of the TEOS molecules by NP-5 (see Supporting Information). This means that in the equilibrium situation, 64% of the QD surface is coated by NP-5, while 36% of the surface is coated by TEOS. Taking into consideration that there is an 8-fold excess of NP-5 with

respect to TEOS, it may be concluded that TEOS has a factor of four to five times higher affinity for the QD surface than NP-5. It must be stressed that this calculation assumes a 100% (or at least equal) coverage of the QD surface when TEOS or NP-5 is added only, for which we cannot provide direct evidence. The calculated values must therefore be regarded as rough estimates.

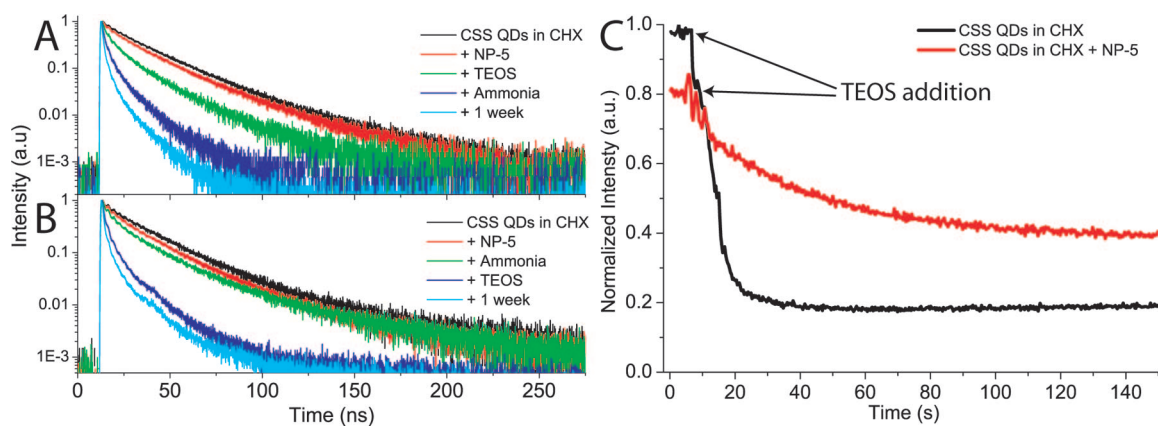
Figure 6D shows the emission spectra measured on a QD/silica synthesis similar to the synthesis depicted in Figure 6A, except for the fact that ultra pure and water-free TEOS (99.999%, stored in glovebox) was used. As can be seen, there is a clear difference in the degree of quenching upon addition of ultra pure water-free TEOS (decrease of 8%) as compared to the 99%-pure TEOS used in the other experiments (decrease of 49%). The 99%-pure TEOS was stored outside the glovebox and therefore contained more hydrolyzed TEOS as compared to the ultra pure and water-free TEOS. The difference in degree of quenching between part A and part D of Figure 6 therefore implies that it is hydrolyzed TEOS in particular that attaches to the QDs and causes the emission quenching. When TEOS is (partly) hydrolyzed, the resulting Si–OH or Si–O<sup>−</sup> groups can bind to the QD surface. The calculated affinity of TEOS relative to NP-5 (vide supra) should therefore be regarded as the lower limit, because only a (small) fraction of the TEOS molecules will be initially hydrolyzed. The further decrease in emission intensity upon addition of ammonia (Figure 6A,B,D) can now be explained by the enhanced hydrolysis of TEOS, which leads to a shift in the NP-5/TEOS equilibrium. That is, the increased number of hydrolyzed TEOS molecules will eventually replace all NP-5 molecules that are



**Scheme 1. Schematic Representation of the Incorporation Mechanism of Hydrophobic CSS QDs (in orange) in Silica Spheres by the Reverse Microemulsion Method<sup>a</sup>**



<sup>a</sup> (a) Illustrates the ODA coated CSS QDs dispersed in cyclohexane. Upon addition of TEOS or NP-5 the ODA is largely replaced, resulting in TEOS (b<sub>1</sub>) or NP-5 (b<sub>2</sub>) coated QDs. When subsequently NP-5 or TEOS is added, the same equilibrium is obtained (c), where the QDs are coated by (hydrolyzed) TEOS and NP-5. Upon addition of ammonia, TEOS is further hydrolyzed, and replaces all NP-5 (d). Water and ammonia molecules are present in between the TEOS coated QD and the micelle that is formed by NP-5.



**Figure 7.** (A and B) Fluorescence decay curves of CdSe CSS QDs (ODA coated) at different stages of the reverse microemulsion synthesis ( $\lambda_{\text{exc}} = 406$  nm,  $\lambda_{\text{em}} = 620$  nm). The order in which the precursors were added (indicated from top to bottom) differs for the two panels. (C) Evolution of the emission intensity of CdSe CSS QDs as a function of time, after addition of TEOS (at time = 0). Ten spectra per second were recorded, and the intensity at the emission maximum (620 nm) was plotted as a function of time.

attached to the QD surface and thereby even further decrease the emission intensity. After 1 week, the emission intensity in Figure 6D has decreased to approximately 2%, similar to the result in Figure 6A. The initial smaller decrease in emission intensity upon addition of the ultra pure TEOS has apparently no effect on the final emission intensity, which can be explained by the fact that eventually all TEOS will be hydrolyzed as a result of the presence of ammonia. The similar final emission intensities in Figure 6A,D also suggest that possible other impurities in the 99%-pure TEOS do not play an important role. The mechanism described above is illustrated in Scheme 1.

Fluorescence decay curves for the CdSe CSS QDs were measured at the different stages of the silica synthesis (Figure

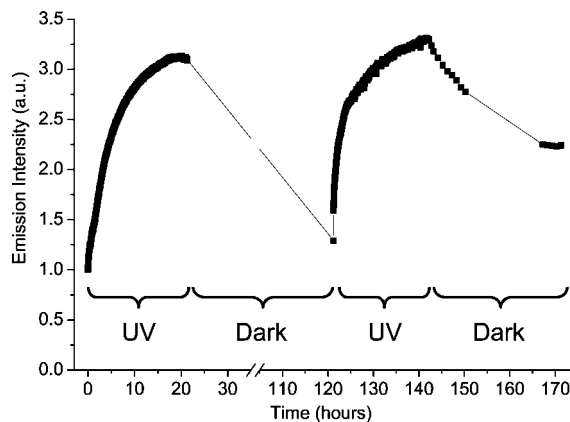
7A,B). The QDs dispersed in cyclohexane display a nearly single-exponential decay ( $\tau = 22$  ns), in good agreement with the high initial QE (60%). When NP-5 is added, no significant change in the decay curve is observed (Figure 7A,B), even when this is followed by the addition of ammonia (Figure 7B). However, when TEOS is added, the fluorescence decay becomes significantly faster and nonexponential. This effect is stronger when ammonia is present (Figure 7B), as compared to the situation where ammonia is absent (Figure 7A). Faster fluorescence decay indicates the presence of additional nonradiative recombination pathways of the exciton, resulting in a lower overall QE. These results are in good agreement with the changes in emission intensities observed in the spectra of the same samples in

Figure 6A,C. It can be concluded that the attachment of hydrolyzed TEOS molecules to the QD surface causes quenching and corresponding faster decay of the QD emission.

To follow the kinetics of the ligand exchange, we have followed the emission intensity of the CdSe CSS QDs over time, upon addition of TEOS (Figure 7C). When TEOS is added to the QDs dispersed in cyclohexane, the emission decreases rapidly to 18% of the initial intensity, which is in good agreement with the decrease to 16% in Figure 6B upon addition of TEOS only. The fast decrease demonstrates the rapid association of hydrolyzed TEOS to the QDs. The emission intensity of a dispersion where NP-5 is present before TEOS addition was initially 19% lower compared to the cyclohexane dispersion, which is in good agreement with the decrease observed upon addition of NP-5 in Figure 6A. When TEOS is added to this mixture, a significantly slower decrease in emission intensity is observed. The final emission intensity is 39%, again in good agreement with the emission decrease in Figure 6A,B when both TEOS and NP-5 are added.

The slower decrease in emission intensity when NP-5 is present provides additional evidence for the partial replacement of NP-5 by TEOS, which is hindered because of the large excess of NP-5 (see Table S1). However, it still takes only about 2 min before the NP-5/TEOS equilibrium on the QD surface is reached. This rapid exchange and equilibration of the TEOS and NP-5 can explain the exact central incorporation of the QDs in the silica spheres. It is well-known that the silica nucleation and growth in the reverse microemulsion system (and even in the Stöber approach) is relatively slow (slower than minutes) and rate limited by the (first) hydrolysis of TEOS.<sup>45,46</sup> Because this process is much slower than the complete TEOS exchange and subsequent TEOS/NP-5 equilibration time, systems (c) and (d) as depicted in Scheme 1 will act as effective and isotropic nucleation sites for the growth of silica. If, because of the presence of DDT, the ligand exchange is hindered and therefore not complete or delayed, the QDs are incorporated off-center (as illustrated in Figure 5B) as a result of anisotropic silica growth. In the presence of an excess of DDT, only a fraction of the ligands will be eventually exchanged, which will force the hydrophobic QDs to reside at the interface of the micelle. In this case, silica growth takes place only on a part of the QD surface, which results in QDs attached to the outside of silica spheres, as illustrated in Figure 5C,D.

The emission intensity of the final QD/silica particles after 1 week of silica growth is typically only a few percent of the initial intensity (Figure 6). This dramatic decrease in QE is ascribed to the attachment of fully hydrolyzed and subsequently condensed TEOS (i.e., silica) to the QD surface causing emission quenching. We observed that this decrease is partly reversible, although only temporarily, by illumina-



**Figure 8.** Evolution of the emission intensity of CSS-QD/silica particles dispersed in ethanol as a function of time, under UV illumination and in the dark. Note the time break between 35 and 95 h.

tion of the samples after synthesis. Figure 8 shows the evolution of the emission intensity over time, when the sample is illuminated with an intense 406 nm light source (450 W Xe lamp, slits of the spectrometer fully opened). An increase in emission intensity by a factor of 3 is observed within 24 h, which decreases to the initial intensity when the sample is stored in the dark. When exposed to the light source again, a similar photoactivation is observed.

The quenching mechanism when hydrolyzed TEOS attaches to the QD surface remains unclear, but we can think of two possibilities. First, the hydrolyzed TEOS can act as an efficient hole or electron acceptor, which introduces new nonradiative decay pathways for the exciton. This would increase the total fluorescence decay rate, as observed in Figures 7A,B. Another explanation may be the presence of charges such as Si-O<sup>-</sup> groups, hydroxyl ions, or ammonium ions which are likely to be found in the close vicinity of the QD. It is known that the presence of a single charge close to the QD surface can generate an electric field that is sufficiently large to cause significant quenching<sup>47</sup> and/or a red-shift<sup>48</sup> of the QD emission, as observed in Figure 6. Photoactivation has been reported for QDs in organic or aqueous solvents,<sup>49</sup> monolayers in air,<sup>50</sup> films,<sup>51</sup> polymers,<sup>52</sup> or physiological conditions.<sup>53</sup> Surface passivation by water, or photoactivated rearrangement of the surface and/or surfactants, are proposed as possible mechanisms responsible for the enhanced luminescence upon UV illumination. Because the quenching mechanism by the silica layer is unclear, it is difficult to assign the photoactivation that is observed for the QDs to one of the explanations mentioned above.

Regardless of the mechanism, the quenching by hydrolyzed TEOS and its condensed form, silica, will be dependent

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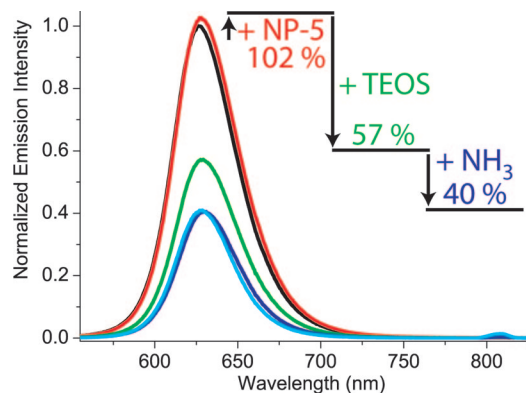
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**Figure 9.** Emission spectra of CSS CdSe QDs (ODA coated) with a thicker inorganic shell ( $7.7 \pm 0.9$  nm in diameter), at different stages of the reverse microemulsion synthesis.

on the distance between the luminescent CdSe core and the quenching groups. To reduce the quenching to obtain more efficiently luminescing QDs in silica, we have incorporated CSS QDs with a thicker inorganic shell ( $7.7 \pm 0.9$  nm in diameter) in silica spheres using the same method. The decrease in the emission intensity at the different stages of the silica synthesis was significantly lower using these QDs (see Figure 9). As can be seen, NP-5 no longer influences the emission intensity, and subsequent addition of TEOS to the reaction mixture results in a decrease to 57%, as compared to 32% in Figure 6A. Addition of ammonia leads to a reduction to 40%, which is maintained after one week. This decrease in intensity is much lower than that observed for CdSe CSS QDs with thinner shells (to 10% and 2% respectively, see Figure 6A). The final emission intensity of the QD/silica particles directly after synthesis was 40% of the initial intensity, which implies a final QE of approximately 24% (the initial QE was 60%). The QD/silica particles were subsequently coated with ODO (see Experimental Section) to render them hydrophobic. The hydrophobic QD/silica particles could be dispersed in chloroform, of which the refractive index is well matched to that of ODO coated silica.<sup>37,54</sup> The scattering-free dispersions allow a reliable determination of the QE of the QDs in silica when a dye is used as a reference, in contrast to QD/silica particles dispersed in, for example, ethanol. We observed that the hydrophobic coating increases the QE of the QD/silica particles, which may be ascribed to the heating step to 170 °C that is involved in this procedure. In this manner, we

have measured a final QE of the QDs in hydrophobic silica spheres dispersed in chloroform of 35%, which to the best of our knowledge is the highest value reported.

## Conclusions

In conclusion, we have found strong experimental evidence in favor of the proposed incorporation mechanism of hydrophobic QDs in silica spheres by a reverse microemulsion system on the basis of a nonionic surfactant (NP-5) in hexane, in addition with TEOS and ammonia that are used to cover the QDs with silica. We show by (time-resolved) fluorescence spectroscopy that hydrolyzed TEOS molecules (and initially also NP-5 molecules) replace the original hydrophobic amine ligands of QDs in this reverse microemulsion system. The replacement facilitates the transfer of the QDs into the hydrophilic interior of the micelles, where silica growth takes place. For QDs coated with (stronger binding) thiol ligands, the replacement by TEOS or NP-5 is hindered, which results in QDs that are incorporated off-center, attached to the outer surface of the silica spheres or not incorporated at all, depending on the fraction of thiol-ligands at the QD surface. On the basis of these results, we can now explain the highly controlled incorporation of hydrophobic CdSe CSS and PbSe QDs exactly in the middle of monodisperse silica spheres by this reverse microemulsion synthesis. In conjunction with these findings, we were able to make QD/silica particles with a final QE of 35%. It is likely that the mechanism proposed here also applies to the incorporation of other hydrophobic nanoparticles in silica (such as iron oxide, gold, or iron–platinum nanocrystals) by a reverse microemulsion method. Multiple QDs per silica can be achieved by increasing the QD concentration, which implies the possibility of colocalizing different types of nanocrystals in silica at a tuneable distance.

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**Supporting Information Available:** Calculation of the relative affinity and quenching rate of TEOS and NP-5 and Table S1 giving the relative amount of molecules involved in the reverse microemulsion synthesis (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.