

**CdSe/TiO₂ core-shell nanoparticles produced in AOT reverse micelles:
applications in pollutant photodegradation using visible light**

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Abstract

CdSe quantum dots with a prominent band-edge photoluminescence were obtained by a soft w/o AOT microemulsion templating method with an estimated size of 2.7nm. The CdSe particles were covered with a TiO₂ layer using an intermediate SiO₂ coupling reagent by a sol-gel process. The resulting CdSe/TiO₂ core/shell nanoparticles showed appreciable photocatalytic activity at $\lambda=405\text{nm}$ which can only originate from electron injection from the conduction band of CdSe to that of TiO₂.

Keywords: CdSe, TiO₂, quantum dots, core-shell nanoparticles, photodegradation methylene blue.

Introduction

Over the last decade, nanostructured semiconductor materials have been the focus of intense research efforts [1]. The striking feature of a nanometric solid is that conventionally detectable properties are no longer constant, but are tunable by simply controlling its shape and size and this has originated a revolution in materials science and device technology. Their photophysics shows high luminescence with tunable emission maxima and narrow bandwidth. Semiconductor nanocrystals (CdSe, ZnS, ...), metallic nanocrystals (Ag, Au, ...) and magnetic nanocrystals (Ni, Fe₃O₄, ...) can be prepared by templating with the aqueous cavities existent in self-organized structures of water-in-oil microemulsions [2]. The main aspects that control structure of these nanoparticulate systems are the nucleation and growth processes, which are determined by the microemulsions dynamics, the interaction between nanoparticle surface and surfactant molecules and, if needed, by the presence of metal complexing agents. Core-shell nanoparticles (CdSe/ZnS) have also been made by templating techniques [2], opening the range of possibilities for tailoring the material to specific needs of application and improving its biocompatibility. In this work we succeeded in the production of CdSe quantum dots (QDs) with ~2.7nm size emitting with high quantum yield at 545nm with a halfwidth of 30nm using AOT reverse micelles as templates and polyselenide, Se_n²⁻, as selenium source. We have grown a titanium dioxide shell above the cadmium selenide core. The observed huge decrease of the photoluminescence quantum yield of the resulting particles indicates the formation of core-shell CdSe/TiO₂ nanoparticles as it was reported a photoinduced electron transfer from CdSe to TiO₂ in a linked arrangement [3]. This process can thus capacitate the TiO₂ outer layer for electron transfer reactions with adsorbed or surrounding molecules. TiO₂ can originate this photocatalytic process by itself but, due to a high band gap, UV radiation is needed with $\lambda < 387\text{nm}$. The advantage of the prepared nanoparticles is the possibility of efficient use of visible light for the same purpose.

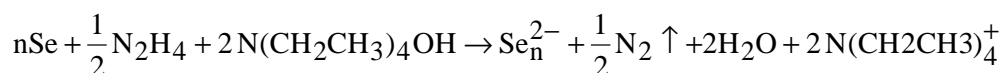
Experimental

Chemicals

All solutions were prepared using spectroscopic grade solvents. Selenium powder (99.5%) was obtained from ACROS. Cadmium nitrate tetrahydrate (98%), sodium sulphide (98%), sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 99%), hydrazine, 25%(w/w) solution of tetraethylammonium hydroxide in methanol, (3-mercaptopropyl)trimethoxysilane (95%), tetra-n-butylorthotitanate were obtained from Sigma-Aldrich. Titanium dioxide P25 was kindly supplied by Degussa. All reagents were used as received.

Preparation of CdSe quantum dots

Two w/o microemulsions are prepared by injecting a given amount of precursor solutions to a 0.2M solution of AOT in cyclohexane. The injection is performed under strong vortexing. In one microemulsion a cadmium nitrate aqueous solution is injected into the AOT solution followed by an 1M aqueous solution of sodium sulphide. A solution of polyselenide in DMF was chosen as the precursor for the other microemulsion. This was prepared by a procedure reported by H. Eggert et al [4], in which hydrazine is added to an appropriate amount of selenium powder dispersed in DMF, as a reduction agent, combined with 25% solution of tetraethylammonium hydroxide as an organic base. The process is described by the following equation



from which one can see that the relation between Se and the organic base determines the type of polyselenide that is formed. The resulting homogeneous solution has a dark green colour. For the preparation of the second microemulsion first a given amount of water is injected, then the sodium sulphide solution and finally the polyselenide/DMF solution. The resulting microemulsion solution acquired a very slight rose coloration. The total aqueous volume is similar to that of the first microemulsion. The final concentration of Cd and Se was $2 \times 10^{-4}\text{M}$. The used molar ratios were $\text{Cd}/\text{SO}_3^{2-}=0.1$, $\text{Se}/\text{hydrazine}=0.5$, $\text{Se}/\text{organic base}=1.5$, $\text{Se}/\text{SO}_3^{2-}=0.1$.

The second microemulsion is added drop by drop to the first one with vortexing. The resulting solution is apparently colourless. After heating at $\sim 80^\circ\text{C}$ during 1h an orange like colour appears that corresponds to the formation of CdSe QDs. The photoluminescence is seen with naked eye using an UV lamp in a dark room (see figure 1).

Preparation of CdSe/TiO₂ nanoparticles

A 1:10 mixture of a 3-(mercaptopropyl)trimethoxysilane (MTMS) and tetra-n-butylorthotitanate (TBOT) was directly added to the solution of CdSe QDs in AOT. This allowed the covalent coupling of the QDs surface with silicon alkoxide through its -SH group. The existing water in the microemulsion allows a sol-gel process that results in a small initial layer of SiO₂ followed by an

outer shell of TiO₂. The solution turned turbid and slightly gelatinous and the fluorescence previously observed for the CdSe QDs disappeared. After heating at 60°C during 45min a coloured precipitate settled in the bottom. The colourless supernatant was removed with a pipette and the solid was washed several times with ethanol to remove the remaining AOT surfactant molecules. The used molar ratios were MTMS/Cd=1, TBOT/Cd=10.

Spectroscopic measurements

Absorption spectra were recorded in a Shimadzu UV-3101PC UV-Vis-NIR spectrophotometer. Fluorescence measurements were performed using a Fluorolog 3 spectrofluorimeter, equipped with double monochromators in both excitation and emission. Fluorescence spectra were corrected for the instrumental response of the system.

Irradiation experiments

The irradiation setup is based on a 150W Xe arc lamp from Lot-Oriel with appropriate interference filters (340nm or 405nm with 10nm halfwidth) placed before the cuvette holder. A focusing lens was used so that the cuvette could be placed in focus at a distance of 42.5cm from the lamp with a spot of 8mm. The cuvette was filled with a 0.1g/l dispersion of either TiO₂ from Degussa or the prepared CdSe/TiO₂ core/shell nanoparticles in a 1.4×10⁻⁵M methylene blue (MB) aqueous solution. The light intensity at the cuvette holder was measured by a handheld power meter model 3803 from New Focus. A value of 2.4mW was obtained at 405nm using an interference filter from Edmund Optics (20% peak transmission). From the known profile of the arc Xenon lamp and the transmission of a 340nm interference filter we can calculate the intensity of the lamp as 3.2×10⁻⁸Einstein cm⁻²s⁻¹ at 405nm and 6.9×10⁻⁹Einstein cm⁻²s⁻¹ at 340nm.

Results and Discussion

CdSe quantum dots

For the preparation of CdSe QDs we have used AOT reverse micelles templating procedure and cadmium nitrate and polyselenide as precursors. The nucleation and growth processes proceed in the water pools and the resulting particles are probably stabilized by non-covalent surface covering with AOT surfactant molecules. The particles surface can thus be easily changed, either by adding other molecules that covalently bind to the particles surface displacing the surfactant (capping/functionalization agents), or by growing layers of other materials above the CdSe nanoparticles that can

function as nucleation seeds. A more detailed study of the factors that determine the size distribution and quality of the CdSe QDs prepared via polyselenide precursors ~~and~~ will be published

elsewhere [5]. In figure 1 the absorption, photoluminescence (PL) and photoluminescence excitation (PLE) spectra of CdSe QDs are shown.

Using an empirical relation [6] we can estimate from the first excitonic absorption peak a 2.7nm particle size. The halfwidth of the photoluminescence is about 30nm, which indicates that the particles are fairly monodisperse although a small red shift of the excitation spectra in relation to the absorption is observed. This comes from the fact that PLE gives the absorption of the subpopulation of particles that contribute more to the emission at the select wavelength. In order to obtain the full range of the absorption spectra the selected emission wavelength is usually at the red-edge of the PL spectrum. This favours larger particles for which the absorption and photoluminescence occur at lower energies (quantum size effect). We thus conclude that the prepared CdSe QDs are not monodisperse but their size distribution is not large on account of the observed small halfwidth of the PL spectrum.

CdSe/TiO₂ core-shell nanoparticles

After the addition of the mixture of silicon and titanium alkoxides to the solution of CdSe QDs the photoluminescence disappeared. This is an indication that, upon hydrolysis of the alkoxides and covalent coupling through the SH group of MTMS, a mixed layer of SiO₂ and TiO₂ is formed above the CdSe nanoparticles. The observed strong quenching effect can be explained by an already reported efficient electron transfer from excited CdSe to TiO₂ conduction band [3]. The resulting solution was turbid so that the absorption spectra did not reveal the typical absorption peaks of CdSe. But by using reflection measurements of the particles in a capillary it was possible to obtain the spectrum in figure 3 that confirms the presence of CdSe nanoparticles with approximately the same size.

Photodegradation of methylene blue

In figure 4 the photodegradation of MB by the prepared CdSe/TiO₂ core shell nanoparticles is shown. The fraction of remaining MB in each irradiation time is obtained by subtracting the background from dispersion and comparing the 665nm absorption peak with the spectrum of pure MB in aqueous solution. The results are shown in figure 5 for the CdSe/TiO₂ nanoparticles and for commercial TiO₂ Degussa (25nm TiO₂ nanoparticles) at 340nm and 405nm. The lines represent an exponential decay of MB concentration corresponding to a first order kinetics. As expected, plain TiO₂ shows a very inefficient photodegradation rate at 405nm irradiation. But at 340nm, a wavelength well below TiO₂ band gap, the photodegradation occurs at a rate of $7.0 \times 10^{-3} \text{ min}^{-1}$. CdSe/TiO₂ shows a photodegradation rate of $2.7 \times 10^{-3} \text{ min}^{-1}$ at 405nm. At 340nm a biphasic behaviour occurs with a very fast initial photodegradation rate of $4.0 \times 10^{-2} \text{ min}^{-1}$ followed by slower process with a rate of $3.9 \times 10^{-3} \text{ min}^{-1}$. As the TiO₂ shell cannot absorb blue light, the observed photodegradation process at 405nm must originate from absorption by the CdSe core. This process

could be occurring in remaining CdSe QDs that did not couple with TiO₂ by the sol-gel process [7]. But the lack of photoluminescence argues against this possibility. On the other hand, if only plain TiO₂ particles were responsible for the photocatalytic effect, the dependence of the remaining methylene blue fraction on irradiation time at 340nm, should be similar for Degussa TiO₂ and CdSe/TiO₂. This was not observed as reported in figure 5 with the photodegradation efficiency of the core-shell nanoparticles being higher than that of Degussa TiO₂. Thus, we have strong indications that a synergistic effect exists between CdSe and TiO₂ in the prepared nanoparticles. This effect has been reported in the photoreduction of methyl viologen by CdSe and TiO₂ nanoparticles confined in the aqueous pools of AOT reversed micelles [8]. A possible mechanism for the photodegradation of MB mediated by CdSe in core-shell CdSe/TiO₂ involves an electron transfer step from the conduction band of excited CdSe to the conduction band of TiO₂. This electron can reduce oxygen and generating superoxide anion radical (O₂^{•-}) that in turn can originate OH[•] radicals. These highly reactive oxygen species can then oxidize MB resulting in its decomposition. The resulting hole in CdSe must be filled in order to regenerate the catalyst. This can also be accomplished by superoxide radical acting as a reductant and regenerating O₂.

Acknowledgements

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References

1. W. Zhong, Anal. Bioanal. Chem. **394**, 47 (2009)
2. A. R. Kortan, R. Hull, R. L. Opila, M. G. Bawendi, M. L. Steigerwald, P. J. Carroll, Louis E. Brus, J. Am. Chem. Soc. **112**, 1327 (1990)
3. I. Robel, M. Kuno, P. V. Kamat, J. Am. Chem. Soc. **129**, 4136 (2007)
4. H. Eggert, O. Nielsen, L. Henriksen, J. Am. Chem. Soc. **108**, 1725 (1986)
5. A. M. Fontes Garcia, P. J. G. Coutinho, submitted
6. W. W. Yu, L. Qu, W. Guo, X. Peng, Chem. Mat. **15(14)**, 2854 (2003)
7. Shih-Chen Lo, Cheng-Fang Lin, Chung-Hsin Wu, Pin-Hung Hsi, Nano Lett. **8(2)**, 637 (2008)
8. C. Harris, P. V. Kamat, ACS Nano **3 (3)**, 682 (2009)

Figure Captions

Figure 1. Photoluminescence of CdSe quantum dots under an UV lamp.

Figure 2. Absorption and photoluminescence spectra of CdSe quantum dots.

Figure 3. Absorption spectrum of CdSe quantum dots and CdSe/TiO₂ core shell nanoparticles.

Figure 4. Photodegradation of methylene blue by CdSe/TiO₂ core shell nanoparticles at 405nm.

Figure 5. Photodegradation kinetics of methylene blue using either Degussa TiO₂ at 340nm (○) and 405nm (●) or CdSe/TiO₂ core shell nanoparticles at 340nm (□) and 405nm (■). The lines

represent first order exponential kinetics. Control experiments without any photocatalyst at 340nm (Δ) and 405nm (\blacktriangle) are also shown.

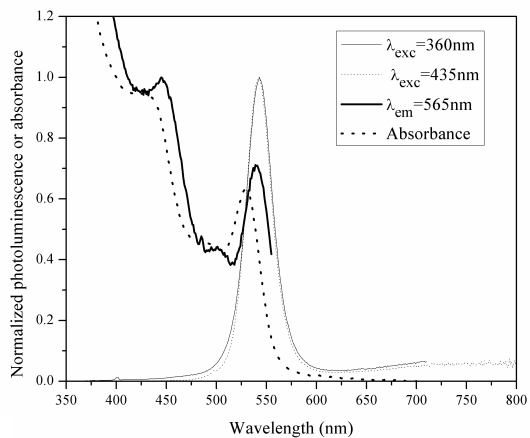
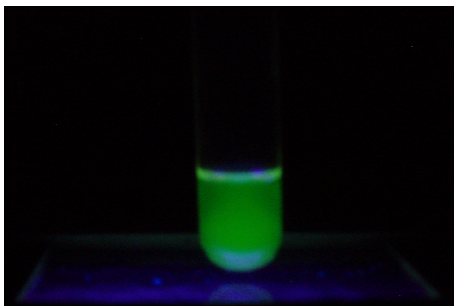


Figure 2

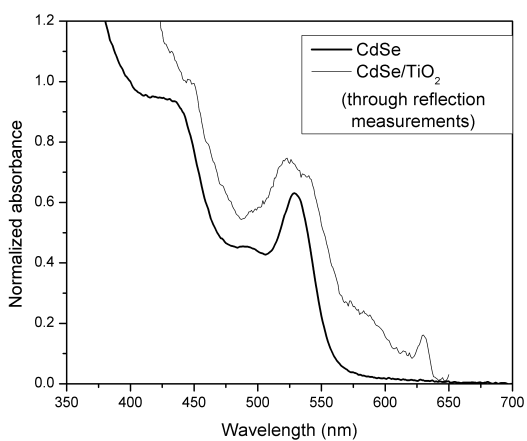


Figure 3

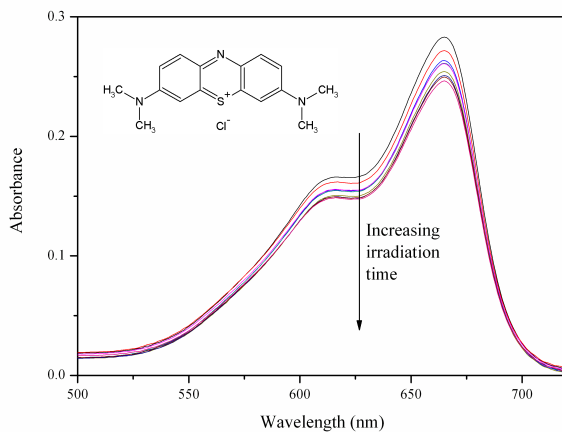


Figure 4

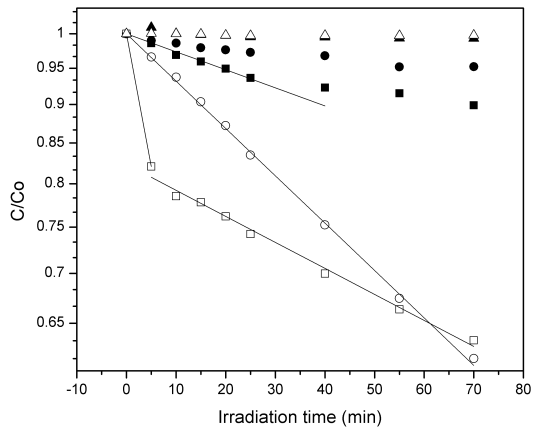


Figure 5