

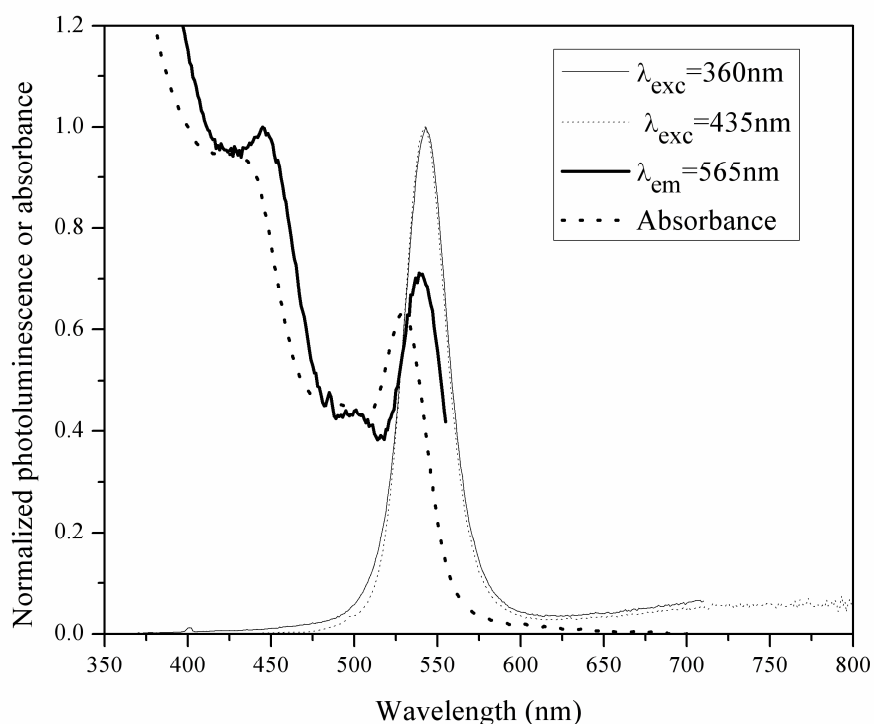
## CdSe/TiO<sub>2</sub> core-shell nanoparticles produced in AOT reverse micelles: applications in pollutant photodegradation using visible light

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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, Fe<sub>3</sub>O<sub>4</sub>, ...) 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.

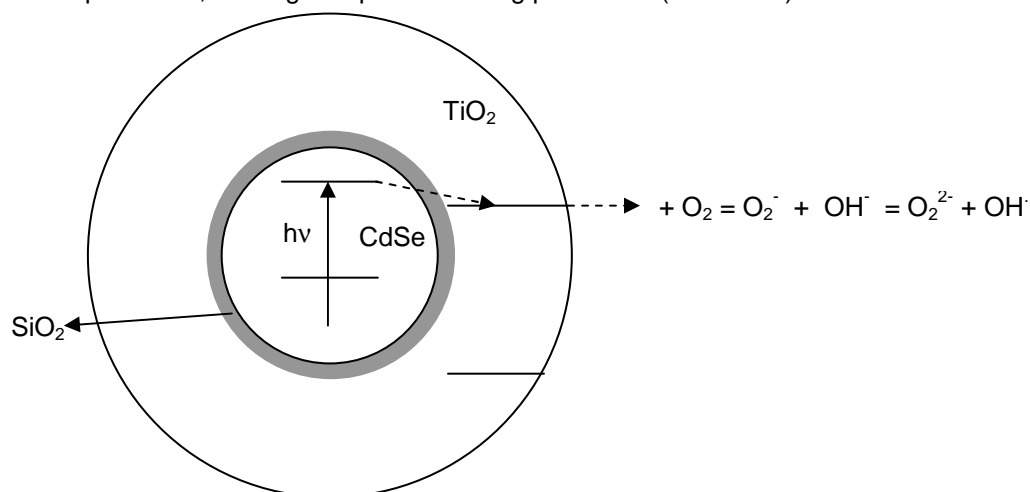
In this work we succeeded in the production of CdSe nanocrystals with ~2.7nm size emitting with high quantum yield at 545nm with a halfwidth of 30 nm (Figure 1).



**Figure 1.** Absorption and photoluminescence spectra of CdSe nanoparticles.

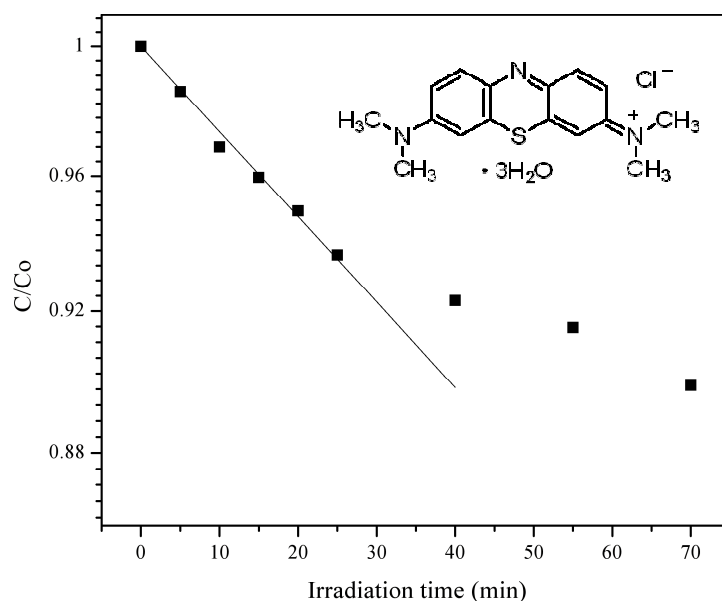
We have used AOT reverse micelles templating procedure and cadmium nitrate and polyselenide as precursors. The nucleation and growth processes proceed in the water pools and the resulting particles are probably stabilized by non-covalent surface covering with AOT surfactant molecules. The particles surface 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 other materials on it (core-shell nanoparticles). We have grown a titanium dioxide shell above the cadmium selenide core using a mercapto derivative of a silicon alkoxide as coupling agent followed by the addition of TBOT (titanium tetrabutoxide). The observed huge decrease of the photoluminescence quantum yield of the resulting particles indicates the formation of core-shell CdSe/TiO<sub>2</sub> nanoparticles as it was reported a photoinduced electron transfer from CdSe to TiO<sub>2</sub> in a linked arrangement [3]. This process can thus capacitate the TiO<sub>2</sub> outer layer for electron transfer reactions with adsorbed or

surrounding molecules. These can be oxygen generating superoxide or hydroxyl radicals, which can act as strong oxidants of pollutants, leading to a photocleaning procedure (scheme 1).



**Scheme 1.** Photodegradation mechanism using CdSe/TiO<sub>2</sub> core-shell nanoparticles (dashed line represents electron path).

TiO<sub>2</sub> can originate this photocatalytic process by itself but, due to a high band gap, UV radiation is needed with  $\lambda < 387$  nm. The advantage of the prepared nanoparticles is the possibility of efficiently using visible light for the same purpose. In Figure 2, our results show a significant photodegradation of the dye methylene blue (generally used as a standard) under 405nm irradiation with a 150W Xe arc source and a  $405 \pm 5$  nm interference filter. The light intensity in the irradiation cell was  $3.2 \times 10^{-8}$  Einstein  $\text{cm}^{-2} \text{s}^{-1}$  and the resulting initial first order kinetics constant for the photodegradation process was  $2.7 \times 10^{-3} \text{ min}^{-1}$ . As the initial methylene blue concentration was  $1.4 \times 10^{-5}$  M, we estimate a photodegradation quantum yield of 0.034%.



**Figure 2.** Photodegradation of methylene blue using CdSe/TiO<sub>2</sub> core-shell nanoparticles.

## References

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