Sonication treatment of CdTe/CdS semiconductor nanocrystals and their bio-application†

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Ultrasonic irradiation of core/shell structures was shown to lead to low toxicity and high quantum yields relative to thermal methods for bio-application.

Fluorescent semiconductor nanocrystals (NCs) are of great interest, in part because of their size-dependent emissions due to a quantum size effect, advantages related to various surface modifications with organic or inorganic materials, and due to their photochemical stability in comparison with organic dyes. A particular characteristic of semiconductor NCs concerns their applications in biological imaging, optoelectronic devices (LEDs, lasers), multicolor optical coding, and bio-therapy. Thus far, many research groups have made great efforts to synthesize semiconductor NCs with a core or a core/shell structures, such as CdSe, CdTe, CdS, ZnSe, PbSe, InP, CdSe/CdS, CdSe/ZnS, CdS/ZnS, CdTe/ZnS, CdTe/CdS, CdTe/CdSe, ZnSe/ZnS, or InP/ZnS. Investigators have studied the effects of different shell materials and thicknesses on the optical properties of semiconductor NCs.[1–11] Particularly, much interest in nanocrystals has focused on core/shell structures. The reason for this interest is that overcoating nanocrystals (core) with inorganic materials with a higher band gap has been shown to improve the photoluminescence quantum yields by passivating surface nonradiative recombination sites. Optimum shell-capping is typically believed to increase the PL quantum yields of nanocrystals to a large extent.[12]

For biological imaging or therapy modification of semiconductor NCs surfaces with organic materials to make them water soluble is required. At the present time, the number of treatment methods and the types and amounts of usable materials to prepare water-soluble semiconductor NCs are limited.

The most common method involves use of an organic reagent with a thiol group. Synthesized semiconductor NCs in an organic solvent were successfully transferred into aqueous media by capping water-soluble ligands onto thioglycolic acid, a hydrophilic ligand. Water-soluble NCs with thioglycolic acid have shown increased PL intensities and quantum yields.

The present study focuses on the synthesis of core/shell structures ranging from blue to red in colour. The preparation of NCs with various colors requires much time due to the drawn out repetitions of the same process. Therefore, a sonochemical approach was attempted as this is associated with a rapid reaction time, and milder operating conditions (*e.g.*, lower temperatures and pressures). Moreover, a sonochemical approach can reduce the number of synthesis steps while simultaneously increasing the end yields. The sonochemical approach has been in used for a number of years. It was discovered in 1934 that the application of ultrasonic energy can increase the rate of electrolytic water cleavage.[13,14] The sonochemical approach has been widely used in the preparation of various nano-sized materials such as oxides, sulfides, carbides and synthetic nanoparticles.[12] The effect of ultrasonic radiation on chemical reactions are due to acoustic cavitation within collapsing bubbles, which generates localized hot spots with very high temperatures (5000 K), pressures (1800 atm), and cooling rates (10^{10} K s^{-1}). In extreme environments, chemical reactions such as oxidation, reduction, dissociation and decomposition can occur.[14,15] Unfortunately, synthetic nanoparticles prepared by ultrasonic irradiation generally have a wide variety of shapes and wide size distribution. To solve these problems, surfactants are usually used in the sonochemical process to control the particle size and shape.

CdTe cores were synthesized in an organic solvent by injecting Te powder into a solution containing $Cd(NO_3)_2 \cdot 4H_2O$, dodecylamine and trioctylphosphine.[16] The resulting CdTe cores showed emission at a wavelength of 540 nm. After the synthesized cores were abstracted and precipitated in chloroform and methanol, they were dispersed in chloroform for use in the shell completion synthesis process. For the shell syntheses, two solutions were formulated using $Cd(NO_3)_2 \cdot 4H_2O$ and S powder/trioctylphosphine. These two solutions were injected into a solution containing synthesized CdTe cores in chloroform and dodecylamine at 100 °C many times until the shell was completed. Variation of the photoluminescence emission peak was not observed in the synthesized CdTe/CdS core/shell nanocrystals. The synthesized core/shell NCs were dispersed in chloroform for the next treatment step and were divided into 5 ml sample sizes and placed in sample tubes. The synthesized CdTe/CdS NCs in chloroform were ultrasonically irradiated at 20-s intervals. After ultrasonic irradiation, water-soluble nanocrystals were prepared by using the synthesized CdTe/CdS NCs in chloroform, thioglycolic acid (TGA) and distilled water.

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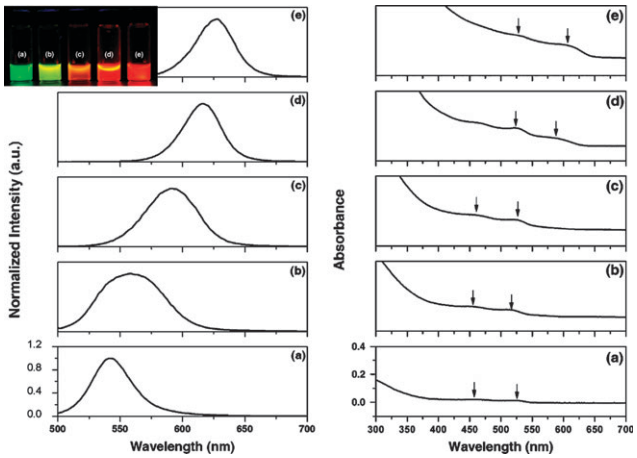

Fig. 1 Fluorescence (left) and absorbance (right) spectra of water-soluble TGA-capped CdTe/CdS NCs using TGA after ultrasonic irradiation: sample A: 0 s, B: 20 s, C: 40 s, D: 60 s, E: 80 s.

The synthesized water-soluble TGA-capped CdTe/CdS NCs using TGA after ultrasonic irradiation showed a dramatic red shift emission of 86 nm (from 542 to 628 nm) (left of Fig. 1). During ultrasonic irradiation, the color of the CdTe/CdS solution gradually changed from green to red. The shells in the CdTe/CdS grew to a much larger size compared to the size as a result of the dissociation of organic-coordinated S sources and other unknown impacts. The photoluminescence (PL) quantum yields (QYs) of the core/shell NCs increased by values similar to those for the original core/shell NCs. The CdTe/CdS showed a large increase in terms of the PL quantum yields (from ~3% for the initial core/shell NCs to 60% for the sonicated core/shell NCs irradiated at intervals of 20 s). The absorption spectra are shown on the right side of Fig 1. Weller *et al*. reported a correlation between the absorption spectrum and the size distribution of NCs.[17] The absorption width is a function of the particle distribution and the absorption edge corresponds to the largest particle diameter. The size distribution of CdTe/CdS increased due to decomposition after the dissociation of organic-coordinated S sources as caused by the ultrasonic irradiation. Thus, a difference in the peak position was clearly observable in the absorption spectra. While samples B and C did not show much change relative to the unirradiated sample A, a clear difference of peaks was observed for samples D and E irradiated for a longer time.

To characterize the core/shell nanostructures, CdTe and CdTe/CdS were examined by powder XRD. After passivating the CdS shells, the diffraction pattern of CdTe core moved toward higher angles. Fig. 2 shows TEM images and the diffraction patterns of CdTe core and CdTe/CdS core/shell structures. The CdTe cores correspond to cubic CdTe (JCPDS card No. 150770) with zinc blende type peaks with the three main peaks corresponding to the {111}, {220} and {311} lattice planes. Upon the growth of the CdS shell, diffraction peak positions shift to higher scattering angle, the main peak being towards the position of the cubic CdS (JCPDS card No. 210829) peak. The TEM image of the CdTe/CdS core/shell structure after ultrasonic irradiation show CdTe/CdS structures with size of 5–6 nm (60 s irradiation) relative to 4–5 nm prior to irradiation. EDS analysis gave Te : Cd : S atomic

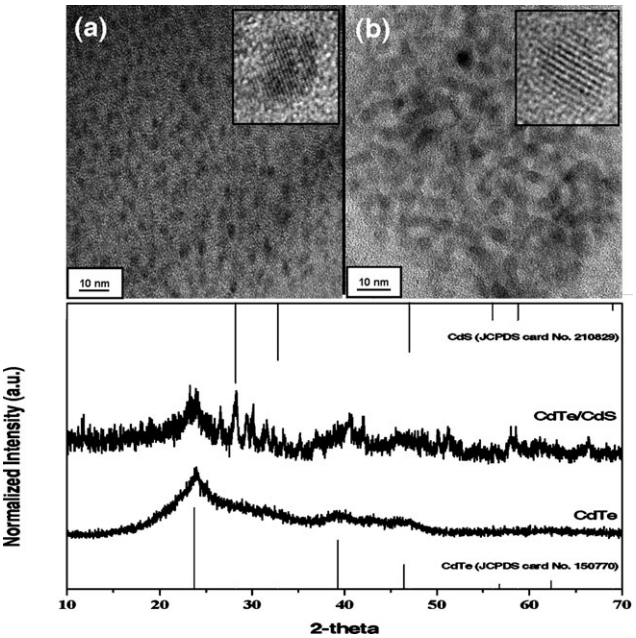

Fig. 2 XRD diffraction patterns and TEM image of water-soluble TGA-capped CdTe/CdS NCs using TGA after ultrasonic irradiation: (a) 0 s and (b) 60 s.

values of 54.4% Cd, 36.2% S and 9.4% Te (Te : S ratio of 1 : 3.85). This result is explained by formation of CdS shells on CdTe nanocrystals (Fig. S1, ESI†).[8,11] The ultrasonic irradiation influence growth and thus CdS shell thickness.

A cell cytotoxicity assay was conducted in order to ascertain damage to the cells by the NCs. The level of cytotoxicity of the prepared samples was investigated in HeLa cells and Vero cells in a 24 h test. A 50% cytotoxic concentration (CC_{50}) was defined as a concentration of a compound that reduced the absorbance of the control samples by 50%. The cytotoxicity of the prepared sample for HeLa and Vero cells at 24 h was lower compared to a reference sample (labeled QD in Fig. 3). Sample A had the lowest level of cytotoxicity in HeLa cells while sample E had the lowest level of cytotoxicity in Vero cells. When compared to CdSe/ZnS-SSA, CdTe, or CdSe/ZnS-MUA,[18] samples using ultrasonic irradiation were less cytotoxic and thus superior for bio-applications.

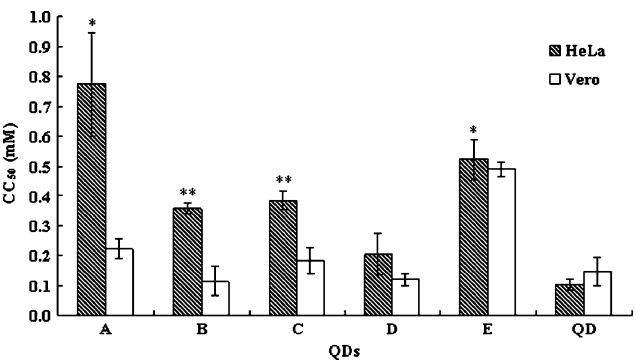

Fig. 3 Cytotoxicity tests of TGA-capped CdTe/CdS NCs with HeLa cells and Vero cells and MTT reduction assay. $*P < 0.001$ and $**P < 0.01$ compared with QD samples in HeLa cells.

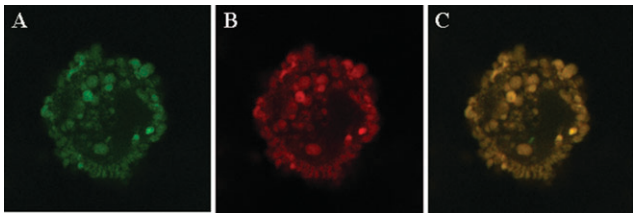

Fig. 4 Luminescence images of cultured HeLa cells that were incubated with sample A (non-irradiated). The QDs and the propiodium iodide-stained nuclei were recorded with confocal microscopy: QD clusters (green light) (A), propiodium iodide-stained nuclei (red light) (B), and merged image (C): (A–C), ×40 objective.

Fluorescence has long been used to visualize cell biology at many levels, from molecules to complete organisms. Fluorescence is mainly observed from small organic dyes attached by means of antibodies to a protein of interest. Fluorescent semiconductor NCs are an interesting alternative to organic fluorophores in some biotechnological and biomedical applications.[19,20] For biological application, the intracellular localization of protein (HSV-1 strain F Thymidine kinase (TK)) with NC-conjugated antibody was measured *via* confocal microscopy (Fig. 4).

When NCs are incubated in a solution of laboratory-derived rabbit anti-HSV-1 TK antibody, the antibodies will covalently attach to carboxylated NCs (NC-Ab). The fluorescence of the NCs was visible in the HeLa cells throughout the cytoplasm and nucleus. The mock-infected HeLa cells showed little fluorescence signals with or without NC-Ab clusters. The nuclei of the cells were stained with propiodium iodide.

In conclusion, in this study CdTe/CdS nanoparticles synthesis was conducted using a sonochemical approach on the initial CdTe/CdS NCs. The ultrasonic irradiation of synthesized NCs is a novel and rapid method for producing NCs of various colors with wavelength maxima from 542 to 628 nm.

The synthesized NCs were obtained from water-soluble TGA-capped CdTe/CdS with high luminescent and high quantum yields (>60%) using thioglycolic acid. These samples were investigated in terms of cell cytotoxicity towards HeLa and Vero cells in 24 h tests. The levels of cell cytotoxicity were found to be lower compared to a reference sample. A clear biological image of a HeLa cell with synthesized NCs was obtained. The prepared NCs are attractive for various biological applications due to favourable cytotoxicity and photostability characteristics.

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