

Simple green synthesis of amino acid functionalized CdTe/CdSe/ZnSe core-multi shell with improved cell viability for cellular imaging

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Abstract

We herein report a simple, economical and green synthesis of highly fluorescent, water soluble and stable arginine functionalized CdTe/CdSe/ZnSe multi core-shell nanoparticles (NPs) with enhanced cell viability for cellular imaging. The synthesis of the CdTe/CdSe/ZnSe NPs was carried out under ambient conditions in the absence of an inert environment. The as-prepared NPs were characterized using UV-Vis absorption and photoluminescence (PL) spectroscopy, energy dispersive spectroscopy (EDS) and high resolution transmission electron microscopy (HRTEM). The optical analyses showed an enhancement in the fluorescent intensity after the functionalization with improved optical properties. The functionalized NPs (F-NPs) displayed higher cell viability compared to the bare NPs when investigated on KM-Luc/GFP cell line at different concentrations. The fluorescent image indicated that the as-synthesized functionalized NPs were taken up by the cells. Recommendations are made for treatment centers to become trauma-informed that would help this recognition. Semiconductor core shell nanostructures have generated a lot of interest in various areas such as optics, electronics, and bio-medical applications due to their tunable chemical and physical properties across the visible spectrum. These properties are highly dependent on the size, shape and the composition of nanomaterial [1-7]. The composition of NPs plays a critical role in the stability, toxicity and solubility of the nanomaterial in biological fluid. Furthermore, studies have shown that apart from composition, surface functionalization of QDs plays an important role in the endocytosis process and has been reported to further reduce cytotoxicity [8-12]. Thus, functionalization and cytotoxicity assessment of nanomaterials have been an exciting research direction in bioimaging applications [12-18]. We have previously reported on the cytotoxicity as well as stability of thiol-stabilised CdTe and CdTe/CdSe core-shell QDs [12]. The results showed that the shell increased the stability but the cell viability against the mouse-bioclone histiocytoma cells was very poor. In this communication, we improve the stability as well as the cell viability of the as-synthesised CdTe/CdSe QDs by growing ZnSe shell to produce multi-core-shell structure. Furthermore, by functionalizing the surface of the as-synthesised CdTe/CdSe/ZnSe core-multi shell QDs with amino-acid, the cell viability was significantly enhanced. This makes the as-synthesised core-multi-shell QDs a good candidate for optical imaging and drug delivery applications. The synthesis was carried according to our reported method with slight modifications [12]. The molar ratio of Cd/Te/MPA/NaBH₄ was fixed at 1:0.2:1:10. After 5 mins of reaction, the solution was reduced at 98°C. This was followed by addition of 0.5 mL (0.02 M)

of Na₂SeO₃ after an hour under refluxing. Aliquots were taken at different intervals to monitor the growth and luminescence of the CdTe and CdTe/CdSe core shell NPs. After the reaction had reached the desired growth, MPA-Zn solution and selenium solution were added to the CdTe/CdSe NPs solution followed by further refluxing for 7 h. Aliquots were taken at different intervals to monitor the formation and the growth of CdTe/CdSe/ZnSe NPs. The as-synthesised QDs in 10 mL of DMSO were functionalized with arginine using N, N-Dicyclohexylcarbodiimide (DCC) as the conjugating agent under vigorous stirring for 2.5 h. The resultant precipitate was dispersed in 10 mL HPLC water followed by pH adjustment and sonication. The optical and structural properties were monitored using UV-visible (UV vis) and photoluminescence (PL) spectrophotometer, energy dispersive spectroscopy (EDS) and high resolution transmission electron microscopy (HRTEM). The colorimetric MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium Bromide) assay was used to study the cell viability of the as-synthesised CdTe/CdSe and CdTe/CdSe/ZnSe NPs while the transfection was performed according to manufacturer's instructions using lipofectamine a cationic liposome as transfecting agent. The transfected cells were viewed under the confocal fluorescence microscope with an argon laser excited at the wavelength of 580 nm. The optical properties of the synthesized CdTe/CdSe/ZnSe core multi-shell nanoparticles are shown in Fig.1. All the particles emit from green to red region under the UV light with average particle size diameter ranging from 2.2 to 4.1 nm as calculated using the Yu et al. method [19]. The absorption band gap is redshifted from visible region (550 nm) to the red region (650 nm) the reaction time increases. The absorption spectra show sharp excitonic peak indicating particles with focused size distribution. This is attributed to the proper passivation of the surface by MPA at the beginning of the reaction and later by CdSe and ZnSe shell formation as the reaction progressed. The absorption as well as the emission spectra reveals three growth stages indicating the formation of the three layers CdTe, CdTe/CdSe, CdTe/CdSe/ZnSe NPs. The typical representative microscopic image of the as-synthesised MPA capped-CdTe/CdSe/ZnSe NPs at 7 h reaction time is shown in Fig. 2. The HRTEM image (Fig. 2A) shows that the particles are small, spherical and highly crystalline while the particle size distribution curve (Fig. 2B) shows that, the particles are in the range of 2.5-6.5 nm with average particle diameter size of 3.7 nm. The presence of the lattice fringe (Fig. 2A inset) confirm the high crystallinity of the material while the selected area diffraction electron diffraction (SAED) pattern (Fig. 2D) consist of distinct rings which show that, the material are single crystal and highly crystalline. The

presence of Zn and increase in the amount of selenium in the EDS spectrum (Fig. 2D) compare to the EDS spectrum of the core-shell (not shown here) further indicate the formation of the CdTe/CdSe/ZnSe NPs. Fig. 3 shows the effect of the amino acid functionalization on the as-synthesised CdTe/CdSe/ZnSe NPs. The emission spectra showed narrow emission width for both MPA and arginine capped CdTe/CdSe/ZnSe NPs with band edge luminescence at the excitation wavelength of 400 nm. There was no change in the emission position after functionalization; however, the arginine capped CdTe/CdSe/ZnSe NPs showed significant increase in the emission intensity compared to MPA- capped CdTe/CdSe/ZnSe NPs. The increase in the emission intensity indicates proper passivation

of the NPs surface defect by arginine. The effect of shell and functionalization on the cell viability of CdTe/CdSe/ZnSe NPs is shown in Fig. 4. Fig. 4A shows the decrease in the mortality rate when the cells were exposed to CdTe/CdSe/ZnSe NPs compared to CdTe/CdSe NPs confirming the proper passivation by the ZnSe shell. The functionalization with arginine (Fig. 4B) showed an increase in cell viability with maximum of 95% at lower concentration of 0.1 mg/mL and 66% at 6 mg/mL for CdTe/CdSe/ZnSe NPs. This indicates that the addition of the shell and functionalization enhanced the surface properties of the as-synthesized cadmium based NPs. The confocal fluorescence image (Fig. 4C and D) confirms the cellular uptake of the NPs by the cell.