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Ligand exchange on the surface of cadmium telluride quantum dots with fluorosurfactant-capped gold nanoparticles: Synthesis, characterization and toxicity evaluation

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ABSTRACT

CdTe quantum dots (QDs) can provide high-intensity and photostable luminescent signals when they are used as labeling materials for sensing trace amounts of bioanalytes. However, a major concern is whether the capping ligands of CdTe QDs cause toxic effects in living systems. In the current study, we address this problem through the complete ligand transformation of CdTe QDs from toxic thiolglycolic acid (TGA) to green citrate, which is attributed to the Cd—S bond breaking and the Au—S bond formation. The highly efficient depletion of S atom from the surface of the CdTe QDs occurs after the addition of fluorosurfactant (FSN)-capped gold nanoparticles into TGA-capped CdTe QDs, accompanying with the rapid aggregation of FSN-capped gold nanoparticles via noncrosslinking mechanism in the presence of high salt. After the ligand transformation, negligible differences are observed on both photoluminescence spectra and luminescent quantum yield. In addition, the cytotoxicity of the original and new-born CdTe QDs is detected by measuring cell viability after the nanoparticle treatment. In comparison with the original TGA-capped QDs, the new-born CdTe QDs can induce minimal cytotoxicity against human hepatocellular liver carcinoma (HepG2) cells even at high dosages. Our study indicates that the extremely simple method herein opens up novel pathways for the synthesis of green CdTe QDs, and the as-prepared citrate-capped CdTe QDs might have great potential for biological labeling and imaging applications.

1. Introduction

CdTe quantum dots (QDs) have received great attention for both fundamental research and potential applications due to narrow emission band, broad absorption, and high fluorescence quantum yields [1–3]. CdTe QDs can be synthesized by a non-aqueous organometallic route at high temperature (e.g., 300 °C) or an aqueous method at 100 °C [4–6]. The synthesized QDs through non-aqueous organometallic routes usually need to undergo surface exchange with hydrophilic ligands in aqueous solution for biological applications. Over the last decade, the ligand exchange procedures of quantum dots have been significantly improved [7]. On the other hand, the preparation of water soluble QDs with long-term colloidal stability and high quantum yields has been well demonstrated using thiol as capping ligands, such as 3-mercaptopropionic acid (MPA) and thiolglycolic acid (TGA) [5]. However, it is noteworthy that these thiol ligands are volatile liquid with an awful odor and their carcinogenic property further deters their use from laboratories under stringent safety requirements. Furthermore, it recognizes that the cytotoxicity of CdTe QDs is dependent on the surface ligands rather than on the core material, and thus surface modification of CdTe QDs have an important effect on cytotoxicity [8,9]. In conclusion, it still remains with primary importance to explore environment-friendly synthetic routes for high-quality aqueous CdTe nanocrystals.

Recently, it has been reported that citrate can act as a green capping agent to substitute TGA or MPA for the synthesis of water-soluble QDs [10–13]. However, citrate is a relatively weak stabilizer bound to the surface of colloidal QDs, which may suffer from a decrease in quantum yield to a certain degree. In addition, the colloidal stability of citrate-capped QDs would be sensitive to pH and salt concentration. Therefore, the citrate-capped QDs might have little potential for biological labeling and imaging applications. On the other hand, there have been several researches reported on the great improvement of the ligand exchange procedures [14–16]. In this study, we are motivated to explore the possibility of TGA ligand transformation of CdTe QDs without affecting luminescent characteristics of the QDs to meet the future's demand for nanotoxicity studies and bioapplications.

It is now well-known that thiol ligands are considered to show a high affinity to noble metal surfaces via an Au—S bond. In recent

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years, thiol compounds have been used to modify gold nanoparticles to improve their stability, dispersibility, and biocompatibility, triggered by potential applications in different branches of nanotechnology such as sensing, electronic devices, catalysis and biomedical applications [17–20]. On the other hand, thiol compounds (e.g., cysteine and homocysteine) can induce the aggregation of gold nanoparticles via interparticle crosslinking mechanism or noncrosslinking mechanism, which could be used for colorimetric sensing of thiol compounds [21]. Nonionic fluorosurfactants (Zonyl FSN) are commercially available with a polyoxyethylene chain in their hydrophilic part and a fluorocarbon chain at the hydrophobic part. FSN ligands can be attached to the surface of gold nanoparticles via physical interaction between its hydroxyl group at the end of the hydrophilic part and gold [22]. In 2007, Zu group pioneered in the use of the distance-dependent optical properties of FSN-capped gold nanoparticles for selective colorimetric detection of aminothiols (cysteine and homocysteine) via noncrosslinking mechanism in the presence of high salt [23]. Subsequently, the FSN-capped gold nanoparticles have been extensively used as colorimetric probes for a variety of aminothiols and DNA [24–27]. These interesting reports inspire us to extend the application of FSN-capped gold nanoparticles in the field involving in thiol compounds.

In this study, we reported a simple method to transform capping ligands of CdTe QDs from toxic TGA to green citrate, allowing to retain sufficiently strong luminescence of CdTe nanocrystals. The procedure was schematically described in Fig. 1: a certain amount of TGA-capped CdTe QD was mixed with an appropriate volume of the FSN-capped gold nanoparticles in the presence of phosphate buffer solution (PBS). TGA ligands were removed from the surface of CdTe QDs attributing to the Cd—S bond breaking and the Au—S bond formation. As a result, the aggregation of the FSN-capped gold nanoparticles occurred via noncrosslinking mechanism in the presence of high salt. The ligand transformation mechanism was demonstrated by UV–visible spectroscopy, powder X-ray diffraction (XRD) measurements, transmission electron microscopy (TEM) images, energy dispersive X-ray spectroscopy (EDX) and Fourier transform infrared (FT-IR) spectrum. In addition, the cytotoxicity of the as-prepared citrate-capped CdTe QDs on HepG2 cells was compared to that of the TGA-capped CdTe QDs. The results showed the as-prepared citrate-capped CdTe QDs can induce minimal cytotoxicity even at high dosages, which might be of interest for biological labeling and imaging applications.

2. Experimental

2.1. Reagents

All reagents were of analytical grade and used without further purification. All solutions were prepared with deionized water (Milli Q, Millipore, Barnstead, CA, USA). Zonyl FSN-100 ($F(CF_2CF_2)_{1-7}CH_2CH_2O(CH_2CH_2O)_{0-15}H$) and MTT(3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) were supplied by Sigma–Aldrich (St. Louis, USA). Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4{\cdot}3H_2O$), MPA and trisodium citrate were purchased from Acros (Geel, Belgium). The pH of PBS was adjusted with NaOH or HCl. Ethanol, Dimethyl sulfoxide (DMSO), NaOH, $Na_2HPO_4{\cdot}12H_2O$ and $Pb(NO_3)_2$ were obtained from Beijing Chemical Reagent Company. Tellurium powder (Te, 99.999%), TGA, $CdCl_2$, NaH_2PO_4 and $NaBH_4$ were obtained from Tianjin Chemical Reagent Company. Human hepatocellular liver carcinoma (HepG2) cells were provided by the Institute of Basic Medical Sciences Chinese Academy of Medical. Dulbecco's modified Eagle's medium (DMEM, Gibco, NY, USA) was purchased from Gibco (Invitrogen, USA) supplemented with 10% fetal bovine serum (FBS, Hyclone) and 1% penicillin/streptomycin (Hyclone).

2.2. Apparatus

The UV–visible spectra of the FSN-capped gold nanoparticles were acquired on a Shimadzu UV-3600 spectrophotometer (Tokyo, Japan). Fluorescence (FL) spectra were collected with a Hitachi F-7000 fluorescence spectrophotometer (Tokyo, Japan). The excitation slit and the emission slit were maintained at 5.0 nm and 10.0 nm, respectively. The scan rate of the monochromators was maintained at 2400 nm/min. The excitation wavelength was set at 390 nm. The EDX data and the sizes of CdTe QDs were confirmed through TEM measurements using Tecnai $G^2$20 TEM (FEI, USA) at an accelerating voltage of 200 kV. TEM specimens were prepared by depositing an appropriate amount of CdTe QDs onto the carbon-coated copper grid, and the excess solution was wicked away by a filter paper. The grid was subsequently dried in air before measure. Thermo Electron Nicolet 6700 FT-IR spectrometer (Madison, WI, USA) was used to record the spectrum of CdTe QDs. XRD patterns of the CdTe QDs were performed on a Bruker (Germany) D8 ADVANCE X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation

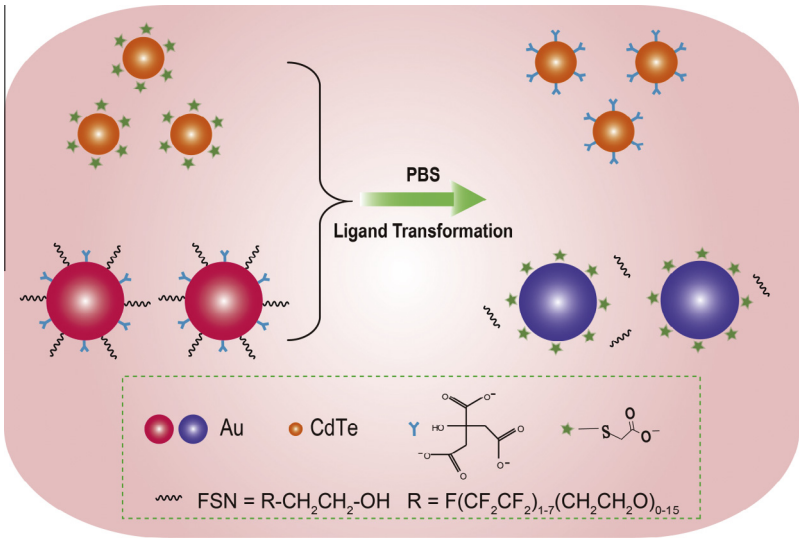

Fig. 1. Schematic illustration of ligand transformation mechanism between FSN-capped gold nanoparticles and TGA-capped CdTe QDs.