One-step growth of high luminescence CdTe quantum dots with low cytotoxicity in ambient atmospheric conditions

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A simple, rapid, cost-efficient and convenient method has been developed for synthesis of water-soluble CdTe quantum dots (QDs) under ambient atmospheric conditions. Using this method, the preparation of Te precursor and growth of CdTe QDs were achieved with one-step synthetic route. Under the optimal conditions, the as-prepared CdTe QDs possessed a high photoluminescence quantum yield (84%), a narrow size distribution (full width at half maximum = 30 nm), small particle size (2.6 nm) and low cytotoxicity. The photoluminescence and electrogenerated chemiluminescence (ECL) behaviors of as-prepared CdTe QDs show their potential application in cell imaging and ECL biosensing with high sensitivity.

Introduction

Direct aqueous-phase synthesis of quantum dots (QDs) by employing short-chain thiols as ligands provides a cost-efficient and convenient alternative route as opposed to the commonly used organometallic synthesis method.[1] Since the first report on the synthesis of thiol-capped and water-soluble CdTe QDs in 1996, sufficient progress has been made in the preparation of high luminescence CdTe QDs in two steps, including the synthesis of Te precursor and the growth of CdTe QDs under the protection of inert gas (Fig. 1a).[2] Among them, the preparation methods of Te precursor, including chemical reduction (eqn (1)),[3] electrochemical reduction (eqn (2))[4] and chemical decomposition (eqn (3)),[5] were not convenient.

$$\mathrm{Te\ (powder)} + 2\mathrm{BH_4^-} \rightarrow \mathrm{Te^{2-}} \quad (1)$$

$$\mathrm{Te\ (electrode)} + 2\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{H_2Te} \quad (2)$$

$$\mathrm{Al_2Te_3\ (powder)} + 3\mathrm{H^+} \rightarrow 3\mathrm{H_2Te}\uparrow \quad (3)$$

Moreover, the as-prepared CdTe QDs with 40–60% photoluminescence quantum yield (PLQY) (increased to higher PLQY after further treatment, such as photochemical etching,[6] size-selective precipitation,[7] long-term illumination[8] and ultrasonic irradiation[9]) were generally obtained. Due to the release of Cd^{2+} in aqueous solution, CdTe QDs are highly toxic to biological systems, which limit their application in the field of nanomedicine.[10]

Herein, we report a one-step synthetic route for the preparation of high luminescence and water-soluble CdTe QDs under ambient atmospheric conditions (Fig. 1b). Reduced glutathione (GSH) was applied to improve the stability, PLQY and biocompatibility of CdTe QDs. The best PLQY of as-prepared CdTe QDs was 84% without any posttreatment. The proposed method is simple, rapid, efficient and low-cost. Moreover, the photoluminescence (PL) and electrogenerated chemiluminescence (ECL) behavior of the as-prepared CdTe QDs show their potential application in cell imaging and ECL biosensing with high sensitivity.

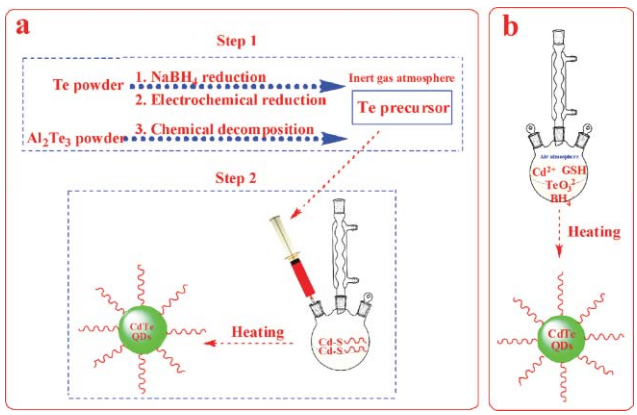

Fig. 1 Schematic of the formation of GSH-capped CdTe QDs with two-step (a) and one-step (b) synthetic route.

Experimental

Chemicals

$CdCl_2{\cdot}2.5H_2O$ (99.0%) and $NaBH_4$ (96.0%) were obtained from Tianjin Chemical Reagent Plant (Tianjin, China). Na_2TeO_3 and thioglycolic acid (TGA) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and GSH was obtained from Sanland-chem. International Inc. (Xiamen, China). 3-Mercaptopropionic acid (MPA, 99.0%) was purchased from Alfa Aesar. All other common solvents and salts were of analytical grade and used as received. Ultrapure water (18.25 MΩ cm) was used throughout the experiments.

Synthesis of GSH, TGA and MPA-capped CdTe QDs

In a typical synthesis, $CdCl_2{\cdot}2.5H_2O$, (2.5×10^{-4} mol) was dissolved in 25 mL ultrapure water in a three-necked flask, and GSH (3.0×10^{-4} mol), trisodium citrate dihydrate, Na_2TeO_3 and $NaBH_4$

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(2.4×10^{-4} mol) were added and the pH was adjusted to 10.5 with vigorous stirring. The molar ratio of Cd^{2+}, TeO_3^{2-} and GSH is 5 : 1 : 6. When the solution's color changed to pale green, the mixture was refluxed at 100 °C and GSH-capped CdTe QDs began to grow immediately. All reactions were carried out under ambient atmospheric conditions. A similar procedure using TGA or MPA instead of GSH was applied to synthesis of TGA or MPA capped CdTe QDs.

Characterization

The fluorescence spectra were recorded using LS-55 fluorescence spectrometer (Perkin-Elmer Company, USA). Ultraviolet-Visible (UV-Vis) absorption spectra were performed on evolution 300 UV-Vis absorption spectrometer (Thermo Niolet Corporation, USA). Transmission electron micrographs (TEM) and high resolution transmission electron micrographs (HRTEM) were obtained on a JEM2010FEF field-emission transmission electron microscope at an acceleration voltage of 200 kV (Japan). X-ray photoelectron spectroscopy (XPS) was carried out using a VG Multibab 2000 (Thermo electron corporation). Fluorescence imaging (at ×20) was carried out using an IS70 inverted optical microscope (Olympus, Japan) equipped with a charge-coupled device camera (TOTA 500II, Japan) and a 100 W Hg excitation lamp. The ECL emission was detected using a Model MPI-B ECL system (Xi'An Remax Electronic Science Technology Co. Ltd., Xi'An, China) with 800 V photomultiplier tube voltage. The lab-built electrochemical cell consisted of an Ag/AgCl reference electrode (saturated KCl), a platinum wire counter electrode and an ITO electrode as working electrode. The PLQY of as-prepared CdTe QDs was evaluated according to the procedure described in ref. 11 using a rhodamine 6G solution in anhydrous alcohol as a reference standard (PLQY = 95%).

MTT assay

PK15 cells were dispensed in 96-well plates (90 mL per well containing 3×10^4 cells). Serial dilutions of GSH and TGA capped CdTe QDs were prepared in Milli-Q water and added to each well (10 mL), respectively. Concentrations were calculated following a previously published method by Yu *et al.*[12] Cells were incubated at 37 °C in a humidified atmosphere with 0.5% CO_2 for 24 h, then the cytotoxicity of the CdTe QDs was evaluated using an MTT assay. The formazan concentration is finally quantified using a spectrophotometer by measuring the absorbance at 570 nm (Gene Company, USA). A linear relationship between cell number and optical density is established, thus allowing an accurate quantification of changes in the rate of cell proliferation.

Results and discussion

The synthetic process of water-soluble CdTe QDs was described in Fig. 1b. The Te precursor (Te^{2-}), generated from Na_2TeO_3 in the presence of $NaBH_4$ (eqn (4)), reacted rapidly with the Cd-GSH complex, to form GSH-capped CdTe QDs.

$$4TeO_3^{2-}\text{ (solution)} + 3BH_4^- \rightarrow 4Te^{2-} + 3BO_2^- + 6H_2O \qquad (4)$$

Compared with some Te sources such as Te powder, Te electrode and Al_2Te_3, Na_2TeO_3 was water soluble and low cost.[3–5] Moreover, it was easy to synthesis CdTe QDs with a one-step route. The reduced GSH was used as a capping ligand for the surface stabilization of CdTe QDs. It exists naturally in most organisms, and has lower toxicity and higher biocompatibility than TGA and MPA, which were generally used as ligands.[13–15] Moreover, the reduced GSH was more likely to be prone to thermal decomposition than other ligands, thus forming a layer of CdS shell on the surface of the CdTe QDs. This CdS shell could effectively passivate the surface trap states, and enhance the PLQY and stability of CdTe QDs.

To further understand the above results in our system, XPS, TEM and HRTEM were employed to characterize its structure and morphology. As shown in Fig. 2, the binding energy of S2p from as-prepared GSH-capped CdTe QDs was 161.5 eV, which was lower than the binding energy of Cd-SR chemical bond between Cd^{2+} and thiols on the surface of CdTe QDs (163.6 eV). The results showed that the coordination situation of S from GSH-capped CdTe QDs is different from that of Cd-SR. Therefore, the new S2p binding energy can be attributed to the sulfur from CdS, which acts as a shell encapsulating the CdTe core.[8,16] The TEM image confirmed that GSH-capped CdTe QDs were spherical particles (Fig. 3a). The average diameter was 2.6 nm. The existence of well resolved lattice planes on the HRTEM image further confirms the crystalline structure and high quality of as-prepared GSH-capped CdTe QDs (Fig. 3b). Moreover, the lattices stretch straight across the QDs with no evidence of an interface, which is consistent with a coherent epitaxial growth mechanism.[17]

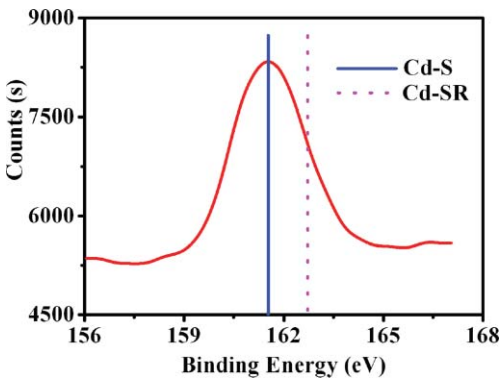

Fig. 2 XPS spectra of S2p recorded from GSH-capped CdTe QDs. The vertical lines are guides for positions of S2p from Cd-SR (163.6 eV) and Cd-S (161.5 eV), respectively.

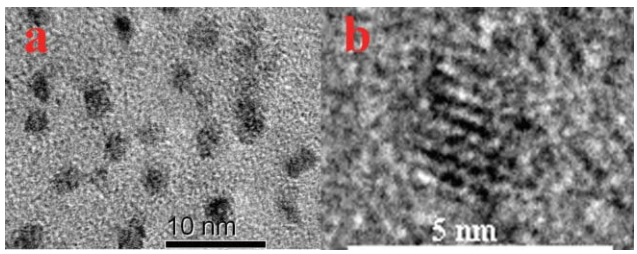

Fig. 3 The TEM (a) and HRTEM (b) of as-prepared GSH-capped CdTe QDs.

The morphology and structure of QDs are correlated with luminescent properties, which were recorded with UV-Vis adsorption and PL spectra. As shown in Fig. 4, as the reaction proceeds,

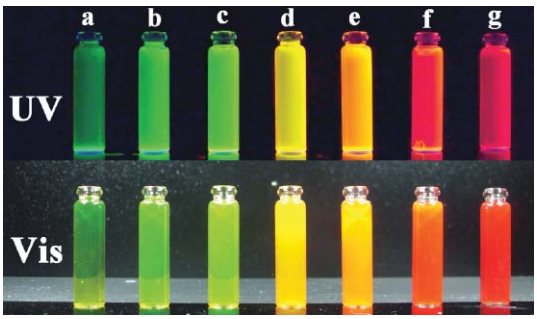

Fig. 4 Photograph of GSH-CdTe QDs aqueous solution without any post preparative treatment under irradiation with 365 nm ultraviolet and visible light. (Reaction time, a: 5 min; b: 10 min; c: 15 min; d: 25 min; e: 45 min; f: 60 min; g: 80 min).

the solution's color changed gradually from green to orange, red and finally to deep red, and the excitonic absorption peak in the absorption spectra and emission peak in the PL spectra shifted systematically to longer wavelengths due to the quantum confinement.[18] Therefore, the particle size of the CdTe QDs could be controlled by the duration of reflux and easily monitored by absorption and fluorescence spectra. During the 1.5 h reflux, the emission peaks of CdTe QDs shifted from 520 nm to 625 nm, and the full width at half maximum (FWHM) increased from 30 nm to 48 nm (Fig. 5). The PLQYs for all sizes shown in Fig. 5 were 20%, 57%, 84%, 62%, 48%, 37% and 16%, respectively. These findings suggest that, compared to other thiol ligands such as TGA and MPA for synthesis of CdTe QDs, GSH is an excellent surface stabiliser.

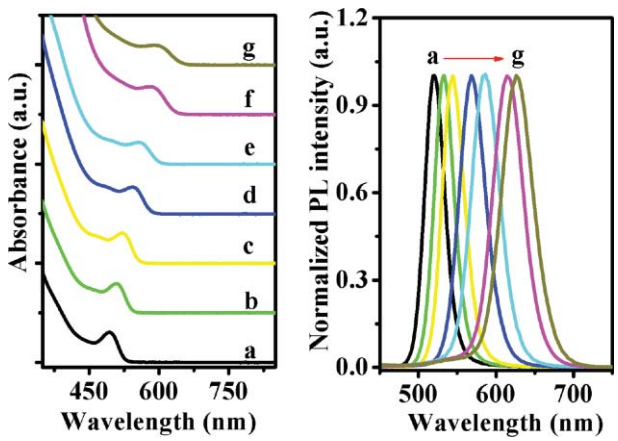

Fig. 5 Temporal evolution of absorption and corresponding PL spectra of GSH-CdTe QDs at different reaction times. (a: 5 min; b: 10 min; c: 15 min; d: 25 min; e: 45 min; f: 60 min; g: 80 min).

The biocompatibility of QDs is a critical characteristic for future biological applications, especially applications in cellular as well as *in vivo* imaging.[19] In this work, the cytotoxicity of GSH-capped CdTe QDs was evaluated by MTT viability assays. As shown in Fig. 6, the GSH-capped CdTe QDs were of low cytotoxicity to PK-15 cells in different concentrations after 24 h incubation. Compared with TGA-capped CdTe QDs, the as-prepared QDs showed lower cytotoxicity under the same conditions. CdTe QDs are highly toxic for cells due to the release of Cd^{2+}. However, epitaxial growth of a CdS layer and encapsulating the CdTe core

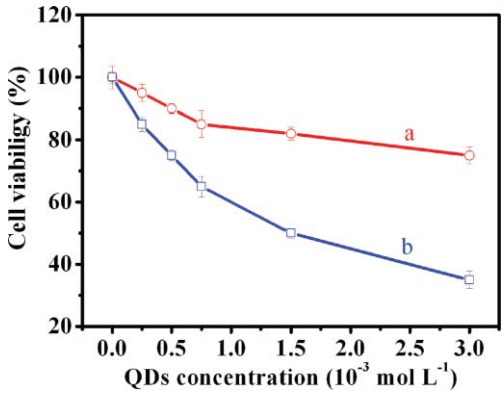

Fig. 6 Cytotoxicity of GSH (a) and TGA (b) capped CdTe QDs with different concentrations to PK-15 cells (Incubation time: 24 h).

with GSH reduce the cytotoxicity of QDs to a small extent. A reasonable interpretation is that the chemical bonds between Cd^{2+} and S^{2-} at the surface of CdTe/CdS QDs are more stable than that in CdTe QDs, leading to less released Cd^{2+}.[10c]

The as-prepared GSH-capped CdTe QDs have some benefits, especially in fixed-cell staining. At physiological pH, the negatively charged GSH-CdTe QDs (2.6 nm) might bind to positively charged basic proteins, such as histone, which are abundant in cell nuclei. As shown in Fig. 7a and 7b, the GSH-capped CdTe QDs (emission wavelength: 520 nm) could swiftly penetrate the cellular matrix and bind to cell nuclei, staining these regions green after 2 h incubation. Moreover, as a novel ECL reagent, GSH-capped CdTe QDs could be used to generate a strong ECL signal (Fig. 7c). The ECL behavior further confirms the potential ECL biosensing application of GSH-capped CdTe QDs.

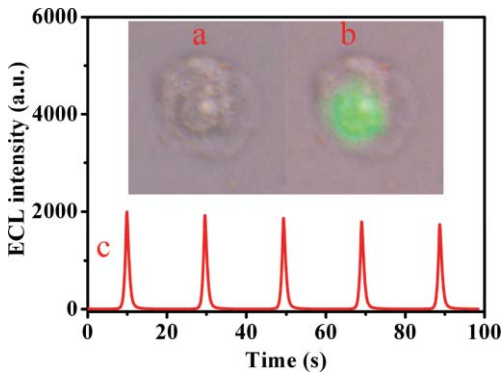

Fig. 7 Fluorescent microscope image of QD labeled PK-15 cells in the light field (a), the sum of the light field and UV irradiation (b), and anodic ECL of GSH-capped CdTe QDs (c).

In summary, a simple, rapid, cost-efficient and convenient synthesis of highly luminescent and water-soluble CdTe QDs is discussed in this paper. This method allows one-step growth of GSH-capped CdTe QDs under an air atmosphere. The as-prepared GSH-capped QDs without any post-preparative treatment possessed a high PLQY, a narrow size distribution (FWHM = 30 nm), small particle size (2.6 nm) and low cytotoxicity. More importantly, our investigations show that the proposed method is extremely suitable for growth of a CdS shell on the surface of the CdTe core, and the CdTe/CdS core/shell QDs have potential applications in

cell imaging and electrogenerated chemiluminescence biosensing with high sensitivity.

Acknowledgements

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