



Sonoelectrochemical synthesis of water-soluble CdTe quantum dots



Jian-Jun Shi^{a,b}, Sheng Wang^a, Ting-Ting He^a, E.S. Abdel-Halim^c, Jun-Jie Zhu^{b,*}

^a School of Chemical Engineering, Anhui University of Science and Technology, Huainan 232001, China

^b State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

^c Chemistry Department, College of Science, King Saud University, Riyadh 11451, P.O. Box 2455, Saudi Arabia

ARTICLE INFO

Article history:

Received 2 April 2013

Received in revised form 27 May 2013

Accepted 6 June 2013

Available online 15 June 2013

Keywords:

CdTe
Quantum dots
Sonoelectrochemistry
Synthesis
Water-soluble
Photoluminescence

ABSTRACT

A facile and fast one-pot method has been developed for the synthesis of CdTe quantum dots (QDs) in aqueous phase by a sonoelectrochemical route without the protection of N₂. The morphology, structure and composition of the as-prepared products were investigated by high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and energy dispersive X-ray spectrometer (EDS). The influences of current intensity, current pulse width, and reaction temperature on the photoluminescence (PL) and quantum yield (QY) of the products were studied. The experimental results showed that the water-soluble CdTe QDs with high PL qualities can be conveniently synthesized without precursor preparation and N₂ protection, and the PL emission wavelength and QY can be effectively controlled by adjusting some parameters. This method can be expected to prepare other QDs as promising building blocks in solar cell, photocatalysis and sensors.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Semiconductor nanocrystals and their clustered states present remarkable optical and electronical properties [1–3]. CdTe quantum dots (QDs), as one of the most important semiconductors, are envisaged as fundamental building blocks to fabricate nanostructures and nanodevices in photoelectric conversion [4,5], photocatalysis [6] and sensors [7–11]. General construction strategy is assembly of several functional components by taking advantage of the physiochemical interactions [12,13]. Obviously, it is critical to synthesize monodisperse QDs with tunable size and high QYs. Various synthetic methods of CdTe QDs with desired size, shape and surface have been developed in the past two decades. Among these, colloid chemical protocols, involving organometallic and aqueous phase routes, exhibited significant progress in QDs synthesis, while the procedure is still not facile as expected. For high temperature, it is indispensable for generating nucleus and maintaining QDs growth in organometallic routes [14,15]. Although the CdTe QDs with high PL QY can be obtained by organometallic route, the applications were limited because of hydrophobic and incompatible with the aqueous biological environment [16]. Thus, the preparation in aqueous phase has been widely studied. In brief, the water-soluble CdTe QDs were synthesized in an aqueous system by mixing tellurium and cadmium precursors in the presence of a thiolated capping agent under the protection of N₂. The most

popular tellurium precursor was prepared from Te powders by using NaBH₄ as reducing agent. It is a time-consuming process due to the inert of the Te powder. Cathodic stripping Te electrode could also be used as the Te precursor in aqueous phase, where the generation of CdTe precursor should be heated at a water bath at 80 °C more than 6 h [17]. Na₂TeO₃ was used as tellurium precursor for CdTe QDs by electrodeposition for its water-soluble property. Until now, only CdTe film [18] and nanowire [19] have been obtained by electrochemical method. All above methods required the protection of N₂ during the reaction to avoid oxidation of the precursors and products.

Traditionally, the properties of QDs were adjusted by changing the reaction temperatures and times on the basis of optimization of the mole ratio of S to Cd. By contrast, sonoelectrochemical technique [20,21] has been successfully used as a new strategy for the controllable synthesis of nanomaterials [22–26]. As described in our previous report [27], a sonoelectrode produced an ultrasonic pulse that was triggered immediately following a current pulse in the synthetic processes repeatedly, which were more convenient to control the shape and size by simply adjusting the ultrasonic and electrochemical parameters. Despite several semiconductors nanomaterials such as PbTe [28], CdSe [29], PbSe [30] have been synthesized by this technique, to the best of our knowledge, sonoelectrochemical synthesis of QDs has not been reported, not to mention the adjusting of QYs precisely.

Herein, we report a one-pot facile and controllable method to synthesize water-soluble CdTe QDs by sonoelectrochemistry without precursor preparation and N₂ protection. The morphology and

* Corresponding author. Tel./fax.: +86 25 83597204.

E-mail address: jjzhu@nju.edu.cn (J.-J. Zhu).

structure of the products were characterized by HRTEM, EDS and XRD. The influences of current intensity, current pulse width, and reaction temperature on the PL properties of products were studied.

2. Experimental section

2.1. Materials

3-mercaptopropionic acid (MPA) was purchased from Sigma Aldrich. Sodium tellurite (Na_2TeO_3), Cadmium Chloride (CdCl_2) and sodium hydroxide (NaOH) were purchased from Chinese Shanghai Regent Co. All the chemicals were used as received without further purifications. All solutions were prepared with Millipore water.

2.2. Apparatus

The sonoelectrochemical reactor was described previously [31,32]. The titanium horn (ultrasonic liquid processor VC-750, Sonic & Materials) acts both as the cathode and the ultrasound emitter. The electroactive part of sonoelectrode is the planar circular surface with an effective area of 1.23 cm^2 at the bottom of the horn. A CHI 6301B electrochemical workstation (CH Instruments Co., USA) was employed in the pulse current regime without reference electrode. A platinum sheet ($1.0 \times 1.0 \text{ cm}$) was used as a counter electrode. The ultrasonic system worked at an emission frequency of 20 kHz. The characterization of the ultrasonic power was performed using a standard calorimetric method [33]. Unless otherwise indicated, the experiments were performed at 30% the maximum power.

2.3. Synthesis of CdTe QDs

In a typical synthesis, 2 mL CdCl_2 (50 mM), 17.6 μL 3-mercaptopropionic acid (MPA) and 1 mL Na_2TeO_3 (50 mM) were added into 47 mL water in turn under stirring, followed by adjusting the pH to 11.0 by dropwise adding NaOH solution (1 M). The molar ratio of $\text{Cd}^{2+}/\text{MPA}/\text{TeO}_3^{2-}$ was 2:4:1. The CdTe QDs were produced in a sonoelectrochemical reactor with the current density of 81.3 mA cm^{-2} , ultrasound pulse intensity of approximately 20 W and reaction time of 3000 s. The pulse-on time of the current was 0.5 s, the pulse-off time of the current was 1.5 s, and the duration of the ultrasonic pulse was 0.3 s. Various reactions were also carried out with different current densities, temperatures and pH values.

2.4. Characterization

Characterization was performed via X-ray powder diffraction (XRD, Shimadzu XD-3A, with Cu $K\alpha$ radiation, $\lambda = 0.15418 \text{ nm}$) and high resolution transmission electron microscopy (HRTEM, JEOL 2100, with a 200 kV accelerating voltage) equipped with an energy dispersive X-ray spectrometer (EDS). The UV-vis spectra of CdTe QDs were recorded by a Shimadzu UV-3600 spectrophotometer. Photoluminescence (PL) spectra were measured on a Shimadzu RF-5301PC fluorescence spectrometer at room temperature. The PL QYs were estimated by comparing the area of the fluorescence spectrum from Rhodamine 6G ($\lambda_{\text{ex}} = 475 \text{ nm}$, QY: 0.95) in ethanol. To investigate the electrochemical process, cyclic voltammogram (CV) measurements were carried out in the reaction precursor solution on a CHI 6301B electrochemical workstation with Pt-sheet as working electrode, Pt-wire as counter electrode, saturated calomel electrode (SCE) as reference electrode, and the scan rate was 100 mV s^{-1} .

3. Results and discussion

3.1. Characterization of CdTe QDs

The HRTEM of the CdTe QDs in typical synthesis was shown in Fig. 1A. The clear lattice fringes of the particles indicated a highly crystalline structure of CdTe. The average size of 3.5 nm was consistent with the result obtained from the UV-vis absorption. The insert of Fig. 1A shows interplanar distances of 2.41 Å corresponding to the (220) planes of cubic zinc blende structure (JCPDS 15-0770). As observed in Fig. 1B, the three major peaks in the powder X-ray diffraction (XRD) spectrum can be indexed to the (111), (220) and (311) planes of the cubic zinc blende lattice of CdTe (JCPDS 15-0770). For comparison, the typical CdTe reflections (black) and cubic CdS reflections (red) are given as line-pattern below the recorded diffraction pattern. Noticeably, all of the three peaks are close to the peaks of CdS (JCPDS 89-0440). Such a consistent shift indicated the formation of CdS on the surface of CdTe, which has been observed in previous report of mercapto-capped QDs [17]. In addition, the average size of the CdTe QDs is about 3.7 nm calculated by Debye–Scherrer equation, which is consistent with the result of HRTEM. As shown in Fig. 1C, the EDS results further confirmed that the products were composed of Cd, Te and S.

The typical optical properties of CdTe QDs synthesized at 70 °C in the presence of MPA ligands are shown in Fig. 1D and E. With the increase of reaction time, the solution color gradually changed from yellow to orange under visible light, and the fluorescence were observed from green to bright orange under an UV lamp with 365 nm excitation. The red-shift of PL peak and UV-vis absorbance spectra indicated the increasing particle size. The average size of CdTe QDs was estimated by UV-vis spectrometry based on the Peng's empirical equation [34], which is consistent with the result of HRTEM and XRD. The average concentration of the obtained CdTe QDs in typical synthesis is $1.95 \times 10^{-6} \text{ mol L}^{-1}$, which was calculated by previous reported formula [34]. The average yield of product is 30.83%, which was determined by using gravimetric analysis method.

3.2. Mechanism of the formation of CdTe QDs

Scheme 1 shows the sonoelectrochemical formation reaction for CdTe QDs as follows: Firstly, the Cd^{2+} and TeO_3^{2-} diffused toward the surface of the sonoelectrode; Secondly, the TeO_3^{2-} ions were reduced to Te^{2-} by a controlled electric pulse; The Te^{2-} combined with Cd^{2+} to form CdTe nanoparticles immediately on the electrode nearby; Then the CdTe nanoparticles were removed from the electrode surface by ultrasonic pulse. With the amount of primary CdTe nanoparticles increasing in the electrolyte, the Ostwald ripening exhibited as the dominant mechanism. Namely, the CdTe nanoparticles were recrystallized and the surface defects were gradually reduced [35]. Finally, the well dispersed water-soluble CdTe QDs could be obtained by repeating above procedures.

The electrochemical reduction process was further investigated by CV method. The result was shown in Fig. S1. According to the previous report [28], the peak at -1.1 V corresponds to the reduction of TeO_3^{2-} to Te^{2-} , while the peak at -0.8 V , which corresponds to the reduction of TeO_3^{2-} to Te^0 , was not observed. The results demonstrate that the TeO_3^{2-} was reduced to Te^{2-} under the employed experimental conditions.

3.3. Influence of the reaction temperature

The evolution for the synthesis of the CdTe QDs was performed at different temperatures. The fluorescence of CdTe QDs during the reaction at 60, 70 and 80 °C are shown in Fig. 2A–C, respectively.

Download English Version:

<https://daneshyari.com/en/article/1265122>

Download Persian Version:

<https://daneshyari.com/article/1265122>

[Daneshyari.com](https://daneshyari.com)