GREEN SYNTHESIS OF STARCH-CAPPED CdSe QUANTUM DOTS IN AQUEOUS SOLUTION

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Abstract

A simple and eco-friendly method, also called the green synthesis, for preparation of starch-capped CdSe quantum dots in aqueous phase at room temperature has been reported in this work. The Se powder, cadmium chloride, and starch were used as the selenium precursors, cadmium precursors, and capping agent, respectively. The appearance of a red color in mixture is the indication of formation of CdSe particles in nanometer size. The physical and optical properties of as-synthesized starch-capped CdSe quantum dots were characterized by X-ray diffraction spectrometry, transmission electron microscopy, UV-visible spectroscopy, and fluorescent spectroscopy. The starch-capped CdSe quantum dots were found to be monodispersed and spherical particles with diameter about of 4.3 nm. The crystallinity with cubic phase is evidenced by clear diffraction peaks in the X-ray diffraction pattern corresponding to the (111), (220), and (311) planes. The emission maximum of the starch-capped CdSe quantum dots was 569 nm, green region, in water with excitation wavelength at 450 nm. It showed that the particles synthesized by this present method exhibited quantum confinement effect. This method may be therefore applied for preparation of other selenides semiconductor nanoparticles.

Keywords: CdSe, quantum dots, green synthesis, nanoparticles

Introduction

In recent years, quantum dots (QDs) or semiconductor nanoparticles with a diameter of 1-10 nm have been interested intensively from worldwide researchers due to their unique optical and electronic properties such as size-dependent band gap, broad excitation spectra and narrow, and tunable emission spectra [1-3]. Compared with corresponding bulk materials, QDs are consequently applied as fluorescent markers in molecular and cellular labeling and imaging, LED flat panel displays, solar cells, and photovoltaic cell [3-5]. Among all semiconductor nanoparticles, CdSe classified as a II-VI semiconductor of the n-type is mainly focused because of their tunable emission in the visible range [4].

Many synthetic methods have been developed for producing CdSe QDs such as electrochemical method, solid-state reaction, solid-state metathesis, and self-propagating high temperature synthesis [6]. Some processes require high temperature, high pressure, difficult and complicated steps, extended reaction time, expensive equipments, and using high toxic H_2Se as selenium source. Furthermore, many suitable capping agents to form uniform and monodisperse CdSe NPs are usually organic passivators such as thiolphenol, thiourea, mercaptoacetic acid, and so on, which are toxic [7]. In order to minimize hazard to synthesizer/user's health and pollution to environment, recently, much effort has been paid on green routes for synthesis of CdSe QDs [3-4, 7].

The green synthesis is based on low-toxic chemicals as precursors, nontoxic chemicals as capping agents, and environmentally benign solvents. Therefore, a simple,

economical and mild method to synthesize CdSe QDs at room temperature has been described in this work. Se powder and cadmium chloride, which are low-toxic, were used as the selenium and cadmium precursors, respectively. In addition, starch also known as biopolymer was chosen as the capping agent because it is a carbohydrate consisting of a large number of glucose units joined by glycosidic bonds and can be easily dissolved in water and transform into other products. Using a simple refluxing route in aqueous solution, the water soluble starch-capped CdSe QDs were produced and their optical and physical properties were characterized using UV-vis spectrophotometer, fluorescence spectrophotometer, X-ray diffraction (XRD) and transmission electron microscope (TEM).

Materials and Methods

Chemicals

Several commercial chemicals of selenium powder, Na_2SO_3, $CdCl_2 \cdot 2.5H_2O$ and soluble starch were purchased from Ajax Finechem. All the chemicals were of analytical grade and used as received without any further purification. Deionized water was used for prepared aqueous solutions. Prior to use, all glassware were cleaned with aqua regia and thoroughly rinsed with deionized water.

Preparation and Characterization of Starch-Capped CdSe NPs

The synthetic method proposed herein is simple and does not require any high-cost equipment. The method involves an addition of selenide ion solution to an aqueous solution of soluble starch and cadmium precursor. A stock solution of 0.5 M sodium selenosulfate (Na_2SeSO_3), selenium source, was prepared by refluxing the aqueous solution containing 1 M Na_2SO_3 and 0.5 M elemental Se under constant stirring at approximately 75 °C for 5 h until the black color disappeared. Then, the stock solution of Na_2SeSO_3 was filtered and collected for further step.

In a typical room temperature reaction, 1 ml of 0.1 M $CdCl_2$ solution was added to an aqueous solution of soluble starch (100 ml, 0.05 wt%) with constant stirring at 37 °C. After stirring for 30 min, 1 ml of as-prepared Na_2SeSO_3 colorless solution was slowly added into a mixture and stirred at 37 °C for 2 h to achieve a red transparent solution. The red transparent solution was taken to measure absorption spectrum and fluorescence emission spectrum by an Avantes AvaSpec fiber optic spectrometer and a F-2500 fluorescence spectrophotometer (Hitachi, Japan), respectively.

To determine the crystal structure and particle size of as-synthesized CdSe QDs, the red transparent solution was extracted with acetone to obtain a red precipitate of CdSe QDs. The precipitate was washed several times with acetone and dried in air at room temperature. The XRD measurement of the CdSe powders was performed using a Bruker D8 Advance X-ray diffractometer with CuK_α radiation (λ = 1.5406 Å) operated at 40 kV and 40 mA. A FEI Tecnai G2 20 TWIN TEM was used to carry out an average particle size of achieved starch-capped CdSe QDs colloid solution.

Results and Discussion

The chemical reactions involved in the production of CdSe QDs are shown by the following equations:

$$Na_2SO_3 + Se \longrightarrow Na_2SeSO_3 \quad (1)$$

and

$$Cd^{2+} + SeSO_3^{2-} + 2OH^- \longrightarrow CdSe + SO_4^{2-} + H_2O. \quad (2)$$

The color of mixture solution changed from colorless to red indicated the fabrication of CdSe QDs. In aqueous solution, the hydroxyl groups of the starch acts as the coordination site of cadmium ions and passivating centres for dispersion, stabilization, and solubility of the as-

synthesized CdSe QDs in water. Furthermore, the free aldehyde group on one end of the starch polymer could also act as conjugation site for other biomolecules [7].

The XRD pattern of as-synthesized CdSe was illustrated in Figure 1. It showed a good agreement with the JCPDF file No. 19-0191. Three clear diffraction peaks appeared at 2θ = 25.6°, 42.6°, and 49.8° that are corresponding to the (111), (220), and (311) planes of bulk cubic CdSe, respectively. The broad peaks imply that the particle size is nanometer size. TEM was employed to characterize the morphology and size of as-synthesized CdSe QDs. In Figure 2, TEM image showed that the CdSe QDs were spherical morphology and the diameters estimated from TEM image were approximately 4.3 nm which were in good agreement with XRD.

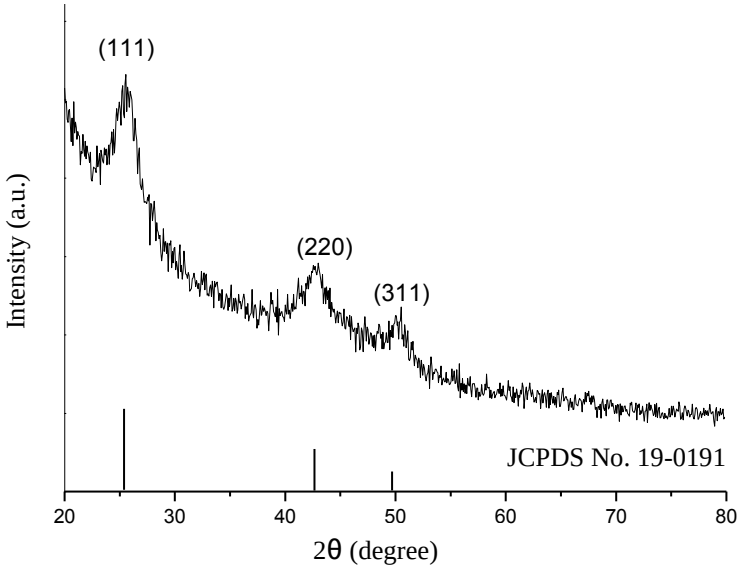

Figure 1. XRD pattern of as-synthesized CdSe QDs.

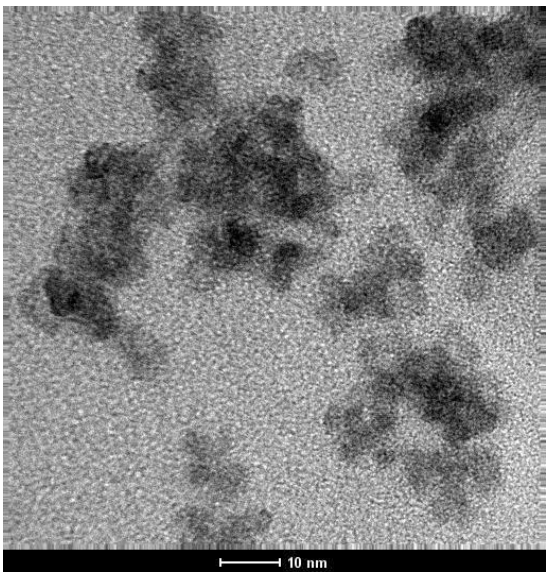

Figure 2. TEM image of starch-capped CdSe nanoparticles.

The optical properties of CdSE QDs were characterized using UV-vis absorption spectroscopy and fluorescent spectroscopy. Figure 3 exhibits the optical absorption edge at

about 568.2 nm (2.18 eV) that blue shifted from the absorption edge of bulk CdSe (730 nm, 1.70 eV) [8]. This clearly indicates the quantum confinement effect. The fluorescent spectrum of as-synthesized CdSe QDs was shown in Figure 4. A strong emission peak was observed at around 569 nm with the excitation wavelength 450 nm. In comparison with that of bulk CdSe at 730 nm [8], there is a blue shift in fluorescent spectrum of as-synthesized CdSe QDs. This effect might be also related to the quantum effects.

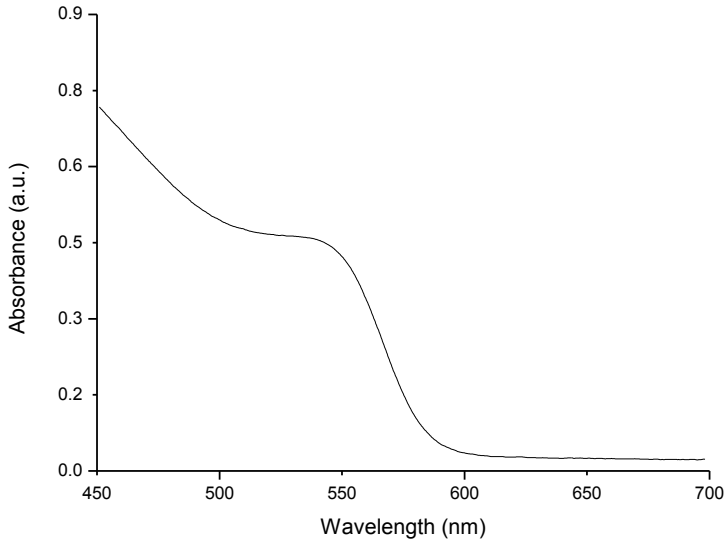

Figure 3. Absorption spectrum of the starch-capped CdSe QDs in aqueous solution.

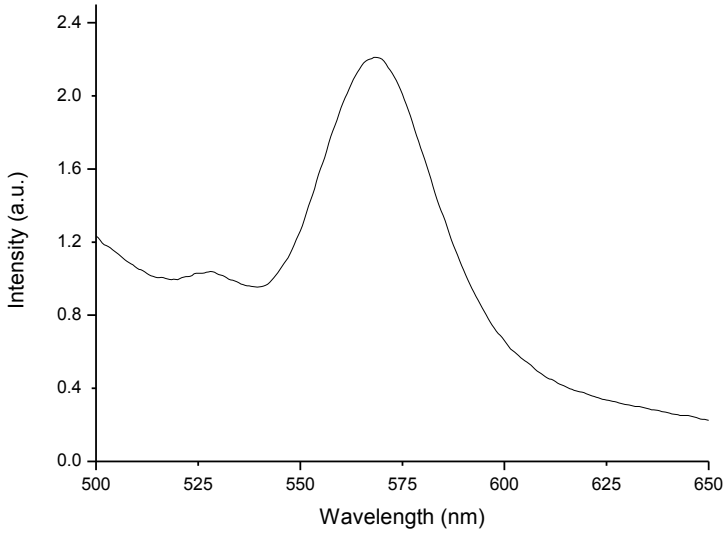

Figure 4. The florescent spectrum of the starch-capped CdSe QDs in aqueous solution. The excitation wavelength is 450 nm.

Conclusion

This work has shown the success in the preparation of monodispersed CdSe QDs using soluble starch as a capping agent at room temperature. The diameter of as-prepared spherical CdSe QDs was in the region of 4-5 nm. They emitted light in the green region. This proposed method is a simple, low-cost, environmentally benign solution growth method without additional another stabilizers. Thus, this method may be applicable to synthesize other selenide nanostructures and also large-scale productions. Additionally, the as-

synthesized CdSe NPs in aqueous phase were utilized in the field of forensic science as labeling agent in latent fingerprint (LFP) detection due to outstanding fluorescent property. However, the effects of pH solution and reaction time on the particle size should be investigated in the future work.

References

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