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Preparation and characterization of water-soluble CdS nanocrystals by surface modification of ethylene diamine

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Abstract

The water-soluble CdS nanoparticles were obtained by hydrogen bond between the cadmium-thiolate complex on the surface of CdS nanoparticles and ethylene diamine (anhydrous). The modified CdS nanoparticles enhanced its solubility in H_2O and alcohol. The ethylene diamine-capped CdS nanoparticles were characterized by Fourier Transform Infrared Spectroscopy (FTIR), photoluminescence (PL) and Ultraviolet–Visible absorption spectrum (UV–Vis spectrum). The absorption peak at 262 nm was observed, which belonged to ethylene diamine-modificated Cd-thiolate complex at the surface of as-grown CdS nanoparticles. The results of the PL spectra indicated that the modification of CdS nanoparticles reduced effectively the local surface-trap states. Based on the above results, a possible mechanism for the formation of the water-soluble CdS nanoparticles was discussed.

Keywords: CdS; Nanoparticles; Surface modification

1. Introduction

Over the past decade, the synthesis and functionalization of nanostructures have attracted great interest due to their significant potential application [1–3]. Due to the quantum confinement effect and the large surface to volume ratio, small nanocrystals show very special physical and chemical properties corresponding to their bulk materials, when their size is close to or smaller than that of the Bohr exciton. However, the aggregation of nanocrystals always decreases their original nano-effects. During the wet chemical synthesis of nanoparticles, organic stabilizers are usually used to prevent them from aggregating by capping their surfaces. Moreover, the introduction of stabilizers also influences on the chemical properties as well as to the physical properties of semiconductor materials, from stability to solubility and to light emission. Therefore, proper surface modification by stabilizers can remove the localized surface-trap states and significantly increases the quantum yield of the excitonic emission. Commonly used stabilizers are phosphine oxide [4], phosphates [5], various thiols [6–9], biomolecule [10,11], and organic dendrons [12,13], which becomes the hot topic of nanotechnology [14–17].

Cadmium sulfide, a direct band gap material with Eg of 2.42 eV at room temperature, can be used for photoelectronic devices. In recent years, CdS nanostructural materials have been widely investigated [18–23]. The synthesis of water-soluble CdS nanoparticles not only improves their properties, but also broadens their application such as uniformly doping. However, only few reports describe the preparation of water-soluble CdS nanoparticles with complex molecules [12,13]. Furthermore, it is difficult to synthesize those macromolecules. Herein, the water-soluble CdS nanoparticles were prepared by a simple reaction with ethylene diamine. The experimental results indicate that the modification of CdS nanoparticles prevents the nanoparticles from aggregating and improves the solubility of CdS nanoparticles in H_2O. It is considered that the modification of CdS nanoparticles reduces the local

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surface-trap states from the CdS nanoparticles. The modified CdS nanoparticles will help us to study exactly the special physical and chemical properties of the nanomaterials and broaden its application. A possible mechanism for the formation of water-soluble CdS nanoparticles has been discussed.

2. Experiment

All the used chemicals were analytic grade reagents without further purification. The CdS nanoparticles was synthesized by thioglycollic acid (TGA) assisted hydrothermal method [18]. The as-grown CdS nanoparticles and 20 ml ethylene diamine (anhydrous) were stirred at 105 °C for 12 h. Subsequently, the resulting yellow solid products were centrifugalized, dissolved in deionized water and re-precipitated with acetone. After re-centrifugalized, the products were finally dried at 60 °C in vacuum for 2 days.

The dried CdS nanoparticles mixed with KBr were characterized with FTIR. The modified powdery CdS nanoparticles were redispered into water, and then a clear colloidal solution was obtained. The solution can be stored at ambient conditions for 2 days without aggregating. The UV–Vis absorption spectrum of the above-obtained water-soluble CdS nanoparticles was recorded at room temperature with a Perkin-Elmer Lambda20 double beam Spectrometer in the wavelength range of 200–700 nm. The photoluminescence spectrum (PL) of the modified CdS colloidal solution was achieved on a Hitachi F-4500 fluorescence spectrophotometer using a 390 nm excitation line.

3. Results and discussion

In Fig. 1, FTIR spectra are shown for the pure CdS nanoparticles prepared by thioglycollic acid assisted hydrothermal method (a), ethylene diamine-capped CdS nanoparticles (b) and pure TGA (c). Pure TGA (Fig. 1(c)) showed an S–H stretching band at 2564 cm^{-1}. CdS nanoparticles before modification (Fig. 1(a)) exhibited an O–H stretching band at 3440 cm^{-1}, a COO-unsymmetrical stretching at 1390 cm^{-1} and a COO-symmetrical stretching at 1600 cm^{-1}, which were induced by the cadmium-thiolate complexes covalently bound to the CdS core [24]. Yet there was no S–H stretching in the CdS nanoparticles, which indicated that the H atom of the mercapto was replaced by Cd and formed the Cd–S–CH$_2$COOH (Cd-thiolate) complex at the surface of the as-grown CdS nanoparticles. After capped with ethylene diamine, CdS nanoparticles showed four stretching bands at 2877, 2921 and 3311, 3158 cm^{-1}, associating with C–H stretching and N–H stretching, respectively. And there were still bends related to the COO-unsymmetrical stretching at 1390 cm^{-1} and COO-symmetrical stretching at 1600 cm^{-1}. However, there were no bends related to the C=O stretching in –CONH– at 1640–1680 cm^{-1}. It must be noted that there were a broad bend at 2500–3500 cm^{-1}, which was due to the strong hydrogen bonding. So it can be considered that –COOH groups from the cadmium-thiolate complexes don't react with the –NH$_2$ groups in ethylene diamine but interact with hydrogen bond. Therefore, it is believed that the capped with thioglycollic acid CdS nanoparticles bonded to –NH$_2$ groups in ethylene diamine by hydrogen bond.

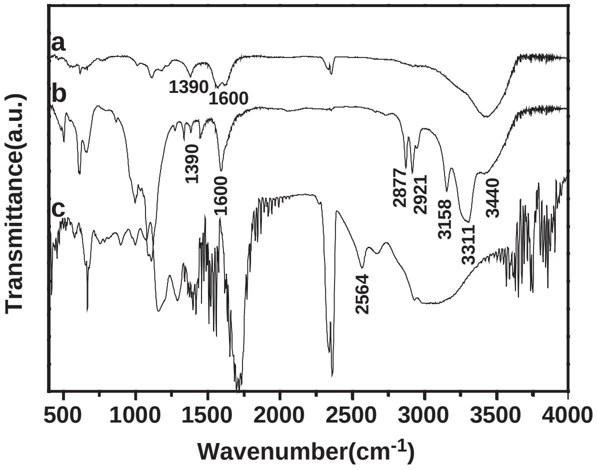

Fig. 1. FTIR spectra of (a) CdS nanoparticles before modification; (b) ethylene diamine capped CdS nanoparticles; (c) pure TGA.

Fig. 2 presents typical evolution of UV–Vis absorption spectra of the as-grown CdS nanoparticles, pure TGA and ethylene diamine-capped CdS nanoparticles dispersed in water, performed at room temprerature. It can be seen that pure TGA shows the absorption peak at 295 nm from Fig. 2. The as-grown CdS nanoparticles exhibits the absorption peak at 290 nm, which is assigned to the Cd^{2+}(SCH$_2$COOH)$_2^{2-}$ complexes[25]. And the absorption peak of 480 nm belongs to the CdS cores [24]. Thus it can be concluded that Cd-thiolate complex formed at the surface of the as-grown CdS nanoparticles, which accords with the result of FTIR. Fig. 2 also presents the absorption spectrum of the ethylene diamine-capped CdS nanoparticles. The absorption peak of CdS cores still exists (shown in the inset of Fig. 2), whereas, the intensity of the peak becomes weak. Yet the significant change occurs in the ultraviolet region. The absorption peak of Cd-thiolate complex blue shifts to 262 nm, which belongs to the ethylene diamine-modified CdS nanoparticles. Its rather narrow absorption peak indicates the size dispersion of the modified CdS nanoparticles are fairly monodiperse. In other words, the modification prevents effectively the aggregation of the nanoparticles. Thus the CdS nanoparticles can be stabilized by the simple method.

Fig. 3 shows photoluminescence spectra of the CdS nanoparticles before and after modification taken at room temperature. The powdery ethylene diamine-capped CdS and the unmodified CdS nanoparticles were dispersed into water. Then the photoluminescence spectra of the CdS