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“One-pot” preparation of cadmium sulfide quantum dots doped silica nanomaterials and its properties

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A simple approach for the synthesis of large quantities of CdS quantum dots doped silica nanomaterials was developed via sol-gel process at room temperature. 3-Mercaptopropyltrimethoxysilane was used as a cadmium chelator, and cadmium acetate as cadmium source and sodium sulphide as sulphur precursor during the preparation process. The effect of preparation conditions on properties of synthesized materials was discussed in detail. The prepared CdS quantum dots doped silica particles were characterized using techniques such as scanning electron microscope (SEM), fluorescence spectroscopy, and UV–VIS absorption spectroscopy, respectively. The absorption peak is shifted towards shorter wavelengths compared with the bulk CdS. The synthesized quantum dots doped silica nanoparticles exhibited strong emission.

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1. Introduction

Semiconductor nanocrystals, also referred as quantum dots (QDs), have attracted a tremendous interest due to their unique physical and chemical properties, which are different from those of their corresponding bulks [1-3]. Substantial research efforts have been devoted to synthesizing semiconductor nanomaterials with different size, shape and polydispersity, and investigating applications in sensors [4-6], electroluminescent [7,8] nonlinear optical devices [9], photovoltaic devices [10-12], biological labeling and diagnostics [13]. Towards these applications, semiconductor nanocrystals often need to be coated with inert materials or assembled together to improve optical and electronic stabilities.

Silica gel is considered as an ideal supporting material for semiconductor nanocrystals, because it is inert, stable, biocompatible and optical transparent from the near UV region through the near infrared. Over the past several years, modifying or assembling semiconductor nanocrystals with silica has been widely investigated [14-23]. Liz-Marzán and co-workers [14] have coated aqueous CdS nanocrtstals by using the Stöber method and obtained core-shell structured CdS@SiO_2 particles. By using similar method, Alivisatos and co-workers [15] have coated organic-soluble semiconductor nanocrystals. Murase and co-workers reported an elegant method to synthesize silica coated CdTe particles using the reverse microemulsion method [16]. Gao and co-workers also reported the preparation of fluorescent SiO_2 particles with CdTe nanocrystals by the similar method [17]. Besides QDs coated with silica, a monolithic silica sol-gel material containging dispersed QDs have also been prepared by using simulstaneous ligand-exchange and shell formation method [18, 19]. In 2006, a low-density silica aerogels with covalently integrated CdSe-ZnS core/shell QDs was first fabricated by Sorensen and co-workers [20]. Recently, silica aerogels containing CdS QDs have also been fabricated by a novel laser-writing technique [21, 24]. In general, the preparation procedure described in these works involved in at least two stages: (a) preparation of QDs and (b) coating QDs. However，multi-step reactions are tedious and time-consuming those not only decrease the yield but also hamper large scale of production. In addition, surfactants are often employed to avoid QDs aggregation in the silica sol precursor medium, which usually impact the optical properties. Thus, there is still a need to develop a more simple method to incorporate QDs into silica without losing its original properties.

Cadmium sulphide (CdS), a direct band gap semiconductor with Eg of 2.42 eV at room temperature, has already shown promising applications in multiple technical fields including solar battery, laser light-emitting diodes, photoelectrocatalysis and sensor [25-27].

In the present work, we reported the preparation of novel silica materials containing CdS QDs via sol-gel technique at room temperature, in which cadmium acetate ($Cd(Ac)_2$) was used as cadmium precursors and 3-mercaptopropyltrimethoxysilane (MPTMS) as a chelator for cadmium. The CdS quantum dots doped silica nanomaterials were obtained by one-step method. The effect of preparation conditions on the morphology and property of materials were investigated. The novelty of the approach described in this research relies on its fundamental simplicity.

2. Experimental section

2.1 Instrumental and reagents

TEOS and $Cd(Ac)_2$ were obtained from Kemiou Chemical Reagent (Tianjin, China). Ethanol and sodium sulphide were purchased from North Medical Chemical Reagent (Tianjin, China). MPTMS was obtained from Alfa Aesar (Tianjin, China). All the reagents are at least of analytical grade and used as received without further purification. Ammonium solution (28–30% NH_4OH) was purchased from North Medical Chemical Reagent (Tianjin, China). Deionized water (>18.2 MΩ cm) was obtained from a Millipore Milli-Q purification system.

2.2 Preparation of CdS doped silica materials

In the present research, the materials were prepared in one step. The detail procedure was shown as following: $Cd(Ac)_2$ and MPTMS were added to 50.0 mL ethanol, and constantly stirred for 1h. TEOS (7.0 mL), water (5.0 mL) and ammonium solution (5.0 mL) were put into the mentioned mixtures, respectively. The mixtures were then stirred for 2 h at room temperature. At last, sodium sulfide was added into the solution and stirred for 2 h. The obtained yellow precipitates were subjected to centrifugation to collect the silica nanomaterials, which were washed three times with fresh alcohol and water, respectively, to remove residual NH_4OH, disodium sulphide, $Cd(Ac)_2$ and unreacted TEOS.

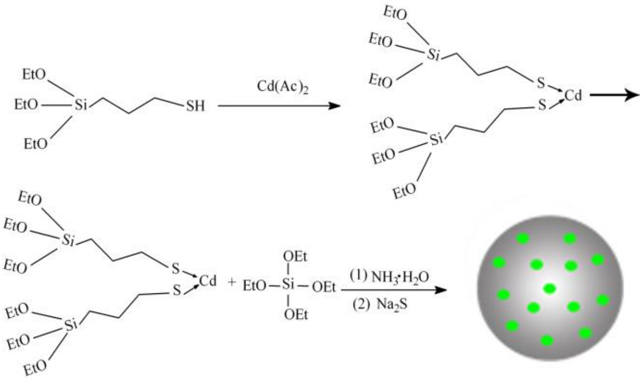
2.3 Characterization

Fluorescent emission spectra were recorded on an F-4600 spectrofluorometer (Shimadzu, Japan). Extinction spectra were investigated at TU-1901 (Beijing Purkinje General, China). Scanning electron microscopy (SEM) was performed using SU-1510 (HITACHI SU-1510, Japan). Transmission electron microscopy images（TEM）was performed using Tecnai F20 G^2 (FEI Company, Netherland.). Energy dispersive X-Ray spectroscopy (EDS) was performed using a system attached to the TEM. Fourier Transform Infrared (FTIR) spectra were obtained at a resolution of 1 cm^{-1} with a Bruker FT-IR spectrophotometer between 4,000 and 400 cm^{-1}. The FTIR measurements of the powder samples were performed in the form of KBr pellets.

3. Results and discussion

3.1 Preparation of CdS doped silica materials

In this research, CdS doped silica materials were prepared by one-step method. The present method is based on the fact that the thiol groups of MPTMS tend to interact with cadmium ions by the cleavage of an S-H bond and the spontaneous a complex. Cadmium ions are incorporated into silica by subsequent co-hydrolyzing and condensation of MPTMS with TEOS. Lastly, sodium sulphide is added into the mixed system, and CdS is formed by the coordination reaction of sulfur ions with cadmium ions. Preparation process is shown in scheme 1.



Scheme 1 a scheme diagram to illustrate preparation process of hybrid silica materials.

A series of hybrid silica materials were synthesized in order to investigate the effect of MPTMS on the morphology and property of the resulted silica materials (Table 1).

Table 1. Composition of the reactive system.

samples	MPTMS (mL)	Cadmium acetate(g)	TEOS (mL)	Ethanol (mL)
1		1.0	7.0	130
2	0.15	1.0	7.0	130
3	0.3	1.0	7.0	130
4	0.15		7.0	130

3.2 Morphology characterization

In order to investigate the role of the chelator, sample 1 was prepared in the absence of MPTMS. Different amount of MPTMS was adopted to produce sample 2 and sample 3. Sample 4 was produced in the absence of $Cd(Ac)_2$. All samples were first investigated by using SEM (Fig. 1). By compare of SEM images in Fig. 1, we can find that all materials that obtained in the presence of $Cd(Ac)_2$ showed irregular particles. However, sample 4 that prepared in the absence of $Cd(Ac)_2$ showed uniformed dispersed sphere particles. Thus we can conclude that the metal ion has a significant effect on the morphology of the materials.

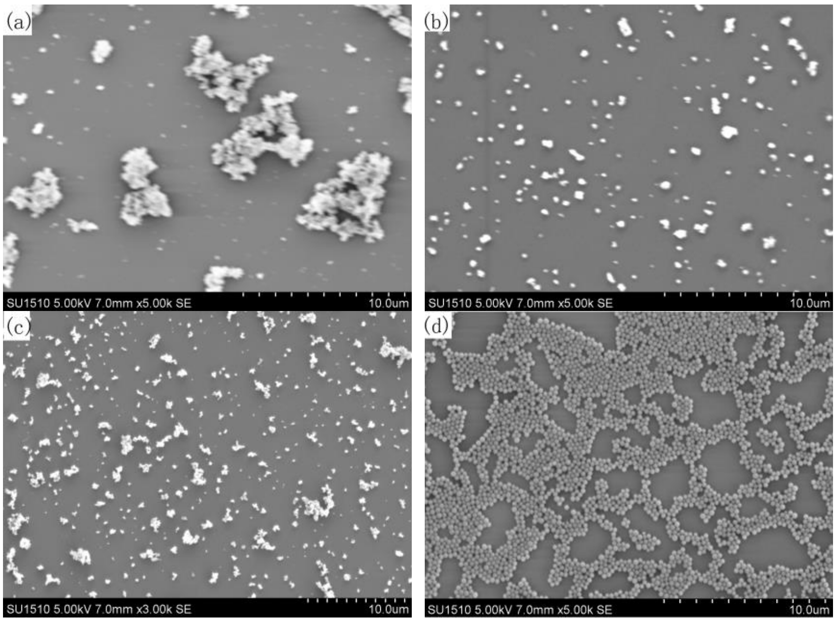


Fig. 1. SEM images: (a) sample 1; (b) sample 2; (c) sample 3; (d) sample 4.

In order to investigate the morphology of doped quantum dots in silica materials, these materials were further checked by TEM (Fig. 2). Larger CdS particles were formed and aggregated in sample 1, which was prepared in the absence of MPTMS. In sample 2 and sample 3, quantum dots were dispersed more uniform than that of sample 1 due to the addition of MPTMS in the preparation process. The resulted quantum dots were 3.5-4 nm and 3-3.5 nm in sample 2 and sample 3, respectively. However, more quantum dots were formed in sample 3 than that in sample 2. These results indicated that MPTMS had a pivotal role for the formation of CdS doped silica materials.

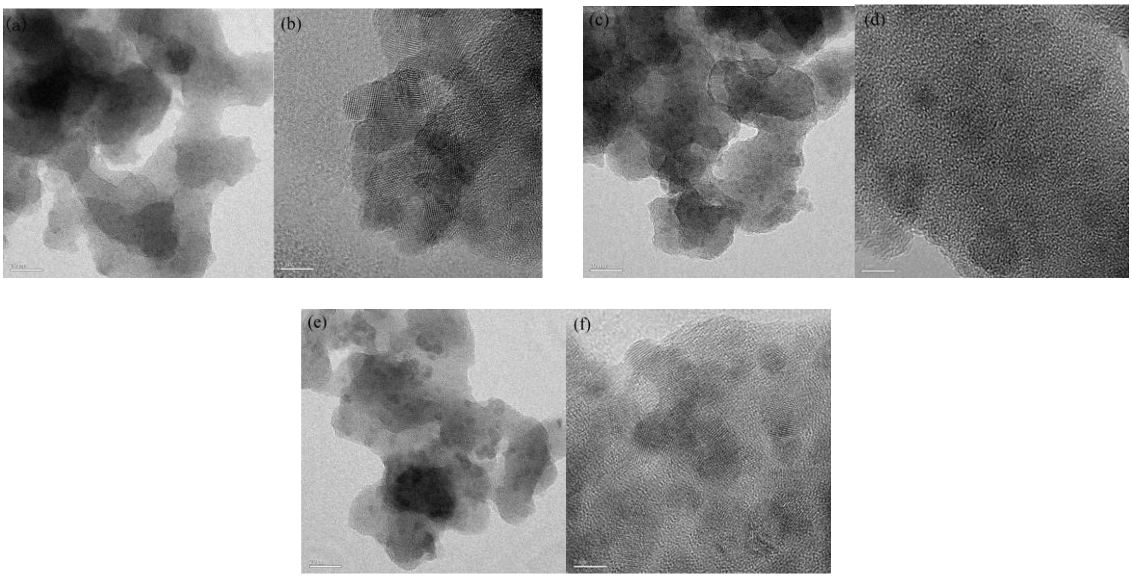


Fig. 2. TEM images: (a) sample 1; (b) and (c) sample 2 (with lower and higher magnification, respectively); (d) and (e) sample 3 (with lower and higher magnification, respectively).

3.3 Energy dispersive X-Ray spectroscopy analysis

The elemental composition of the quantum dots doped silica materials was performed using the EDS on the TEM. Fig. 3 showed the EDS spectrum of the quantum dots doped silica materials. The peaks around 3.20 keV corresponds to cadmium. The peak situated at binding energies of 0.25 KeV belongs to carbon of the propyl hydrocarbon chains of MPTMS. The peak of 2.3KeV is attributed to sulfur of CdS and the thiol groups of MPTMS. The peak around 1.74 KeV belonging to silicon of silica network is also detected. The copper peaks corresponding to TEM holding grid are observed at 8.06 and 8.94 KeV. The results indicated that CdS quantum dots have been successful doped in silica materials. The quantitative results on the chemical composition analyses of quantum dots doped silica materials were displayed in Table 2.

Table 2 presented the average mass values (%), obtained by EDS ananlysis, to the materials. In this case, the peaks of the copper from holding grid were excluded of the calculus.

Table 2. Percentage of elements presents in silica materials doped with CdS quantum dots.

Element	Weight % in silica materials		
	Sample1	Sample2	Sample3
C(K)	------	20.84	24.99
O(K)	56.53	31.43	16.72
Si(K)	37.98	27.11	25.09
S(K)	4.45	7.51	8.24
Cd(K)	1.92	13.12	24.94

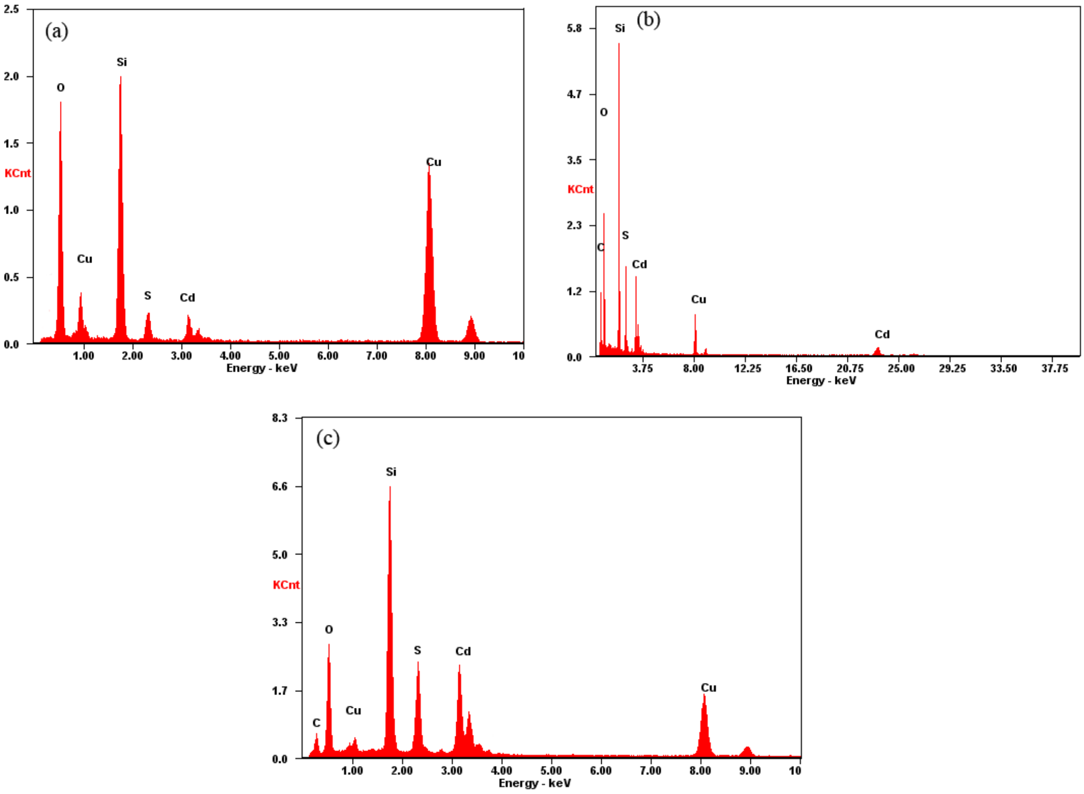


Fig. 3. EDS analysis of quantum dots doped silica material: (a) sample 1; (b) sample 2; (c) sample 3.

3.4 Fourier transform infrared spectroscopy analysis

In order to qualitative identification of the organic functional groups, sample 1, sample 2 and sample 3 were also been characterized by FTIR spectroscopy. Figure 4 illustrated the FTIR spectra of the CdS doped silica nanomaterials. The bands at 1220, 1070, 791, and 470cm^{-1} are assigned to the typical Si-O-Si bands of the condensed silica network. The weak frequency bands at 2928 and 2962 cm^{-1} are attributed to the methylene stretching vibrations of the propyl chains of MPTMS, which is invisible for sample 2 and sample 1. The broad band around 3428 cm^{-1} and the strong peak around 1633 cm^{-1} are due to the stretching and bending vibrations of adsorbed H_2O. Although the methylene stretching vibrations of the propyl chains of MPTMS was verified, the peak associated with the S-H bond could not been observed in its FTIR spectrum. That may be attributed to the low absorption coefficient of the S-H stretching [27].

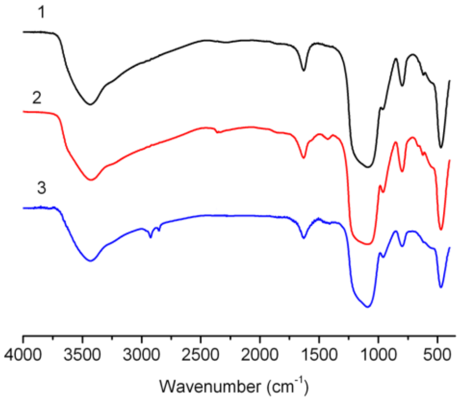


Fig. 4. FTIR spectra of silica nanomaterials: (1) sample 1; (2) sample 2; (3) sample 3.

3.5 Fluorescence spectroscopy analysis

To examine the optical property, the fluorescence spectra of all samples were recorded (Fig. 5). The results indicated that the different preparation conditions lead to significant difference in emission intensity and position. Sample 1, which was prepared without using MPTMS during the preparation process, showed hardly any emission. Sample 2 showed stronger emission than that of sample 1, and sample 3 showed the strongest emission among these samples. Thus it can be concluded that fluorescence emission intensity increased significantly with the increase amount of MPTMS in the preparation process. In addition, the maximum emission position shifted from 560 nm to 530 nm with increasing the amount of MPTMS in the preparation process. These results demonstrated that MPTMS affected not only emission intensity of the resulted materials but also emission position, did display an important role for controlling materials' optical property.

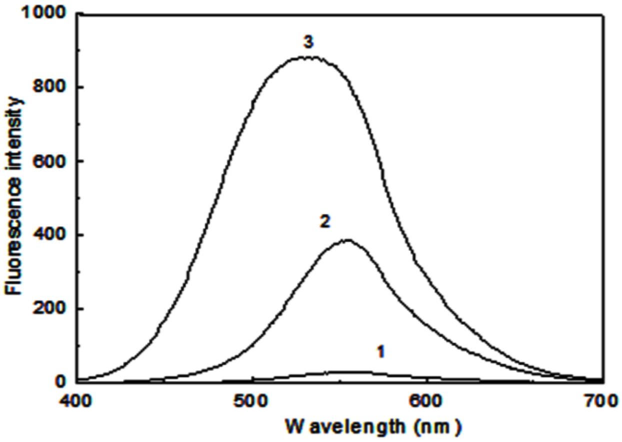


Fig. 5. Fluorescence emission spectra of CdS doped silica nanomaterials: (1) sample 1; (2) sample 2; (3) sample 3.

3.6 UV-Vis spectroscopy analysis

The CdS doped silica nanomaterials was also monitored using UV-Vis absorption spectroscopy. Figure 6 showed absorption spectra of sample 2 and sample 3. The absorption edge for the bulk hexagonal CdS is at 512 nm (2.42 eV). Comparing with the bulk CdS, it is believed that the blue shift in the absorption peak is obviously caused by the quantum confinement effect. Uv-Vis absorption of CdS nanorods (sulfur pre-cursor: Na2S) is shown in Fig. 3. The blue shift to 485 nm can be found compared with the band gap of the characteristic absorption of bulk CdS due to the size quantum confinement effect.

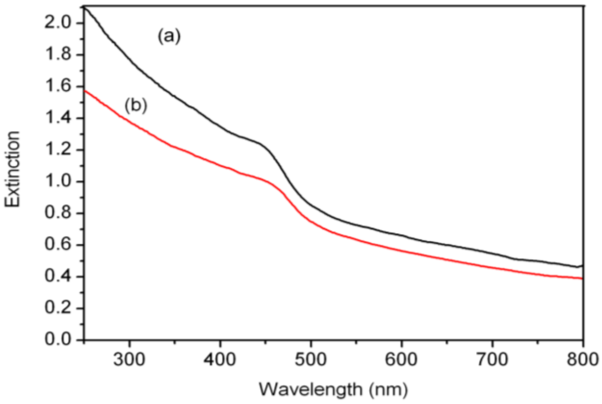


Fig. 6. UV-Vis extinction spectra of CdS doped silica nanomaterials (a) sample 2; (b) sample 3.

4. Conclusions

The strongly luminescent CdS doped silica materials have been obtained through a simple sol-gel process at room temperature, in which $Cd(Ac)_2$ has been employed as a cadmium precursor to guide the formation of quantum dots doped silica nanomaterials under the assistant of MPTMS. This synthetic strategy might be extended to synthesize other similar nanomaterials, which is potentially important for novel optoelectronic nanodevices. Further studies on the above system are underway and the results will be reported in near future.

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