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Synthesis and characterization of water-soluble L-cysteine-modified ZnS nanocrystals doped with silver

Fenghua Huang · Yaling Lan · Peifeng Chen

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Abstract The water-soluble Ag^+-doped ZnS nanocrystals surface capped with cysteine (expressed as ZnS:Ag/Cys) were synthesized in aqueous solution by using L-cysteine as surface modifier. The crystal structure, size, shape, component, and spectral properties of ZnS:Ag/Cys nanocrystals were characterized by X-ray power diffraction, transmission electron microscope, energy dispersive X-ray analysis, inductively coupled plasma atomic emission spectrometry, infrared spectrum, UV–Vis absorption spectrum, and photoluminescence spectrum. The results show that the spherical ZnS:Ag/Cys nanocrystals with an average diameter of 2.6 nm have good fluorescent characteristics, their fluorescence intensity is enhanced greatly after doped with Ag^+. And the sulfur atoms in cysteine molecules are coordinated with metal ions on the surface of the nanocrystals, the cysteine modified on the surface of ZnS:Ag/Cys nanocrystals renders the nanocrystals water soluble and biocompatible. The ZnS:Ag/Cys nanocrystals have potential applications in molecular assembly and biological fluorescence analysis.

Introduction

The synthesis of high-quality fluorescent semiconductor nanocrystals has received wide attention in the past decade due to their unique physical and chemical properties and potential applications in optoelectronic and biotechnological fields [1–5]. The fluorescent properties of semiconductor nanocrystals can be tuned by changing the particle size or its composition. Doped nanocrystals exhibit unique photoelectric properties and novel optical characteristics, which is attributed to quantum size effect and the doped ingredient, respectively. The surface modification of nanocrystals not only enhanced the stability of the nanocrystals but also facilitated the control of size of the particles, resulting in the change of fluorescence property, and the groups of modifier on nanocrystals surface are also available for the molecular self-assembly of nanocrystals. Moreover, the suitable modifier may make the nanocrystals water soluble and biocompatible for their used as a fluorescence probe in biological analysis [5–10]. Therefore, the study of surface-modified doped nanocrystals will play an important role in developing a novel luminescent material and biological fluorescence probe.

The ZnS nanocrystals have been studied for a long time. It is a wide band gap material with unique optical properties, which has found important application in many fields [11, 12]. Based on the unique fluorescent characteristics of semiconductor ZnS nanocrystals, the photoelectric properties of ZnS nanocrystals can be improved by doping different metallic ions on them, this has received considerable attention [13–18]. In 1994, Bhargava et al. [3] reported the first observations of optical properties of Mn^{2+}-doped ZnS nanocrystals. Most researches are concerned about pure ZnS and ZnS nanocrystals activated by copper or manganese, there are only a few reports on Ag^+-doped ZnS nanocrystals [19, 20].

In this article, the water-soluble Ag^+-doped ZnS nanocrystals surface capped with L-cysteine (expressed as ZnS:Ag/Cys) are successfully synthesized in aqueous solution by using L-cysteine as a surface modifier.

F. Huang · Y. Lan · P. Chen
College of Chemistry and Material Science, Fujian Normal University, Fuzhou 350007, Fujian, People's Republic of China

F. Huang (✉)
Key Laboratory of Polymer Materials of Fujian Province, Fuzhou 350007, Fujian, People's Republic of China
e-mail: huangfenghua63@163.com

Compared with using mercaptoacetic acid [19] or 3-mercaptopropionic acid [20] as a surface modifier (or named as stabilizer) for the synthesis of ZnS:Ag, cysteine is more stable, inexpensive, and nontoxic. The novel ZnS:Ag/Cys nanocrystals are water soluble and biocompatible due to the use of cysteine as a surface modifier, which uses the mercapto groups to bind to the Zn^{2+} or Ag^{+} ions on the surface of ZnS:Ag nanocrystals. The polar carboxylic acid group of cysteine on the surface of ZnS:Ag/Cys nanocrystals renders the nanocrystals water soluble, and is also available for interaction with various biomacromolecular and applications in biosystem.

Chemicals and instruments

All the chemicals including silver nitrate, zinc acetate, sodium sulfide, L-cysteine, absolute ethanol, and other routine chemicals were purchased from Shanghai Chemical Co., China. All the reagents were of analytical reagent grade and were used without further purification. Double-deionized water was used throughout the experiment.

The X-ray power diffraction (XRD) pattern was obtained on an X'pert-MPD X-ray power diffractometer (Philips, USA). The morphologic images and energy dispersive X-ray analysis (EDX) of the nanocrystals were obtained on FEI TECNAI G2F20 high-resolution transmission electron microscope (TEM) (USA). The fluorescence spectra were performed on a CARY ECLIPSE spectrofluorometer (Varian, USA) with a quartz cell (1 × 1 cm). Infrared spectra were acquired on an AVATAR 360 FTIR spectrometer (Nicolet, USA). The UV/Vis absorption spectra were recorded on a CARY50 UV/Vis spectrophotometer (Varian, USA). The metal ions contents of the product were analyzed by ICAP6300 inductively coupled plasma atomic emission spectrometry system (Thermo, USA). The pH of solution was measured by Model pHS-3C pH meter (Shanghai, China). The temperature during the preparation of nanocrystals was controlled precisely by a Model DF-101B thermostat stirrer (Zhejiang, China) with a temperature sensor and a thermometer.

Experimental

Synthesis of L-cysteine-modified ZnS:Ag nanocrystals

Under a N_2 atmosphere, 0.6 mmol of L-cysteine, 0.295 mmol of zinc acetate, and 0.005 mmol of silver nitrate were added to 100 mL of pH 8.5 Na_2HPO_4–NaH_2PO_4 buffer solution in a three-necked flask with magnetic stirring. Seven milliliters of oxygen-free 3.0×10^{-2} mol/L Na_2S solution was then added dropwise into above reaction mixture followed by continuous stirring at 60 °C in a water bath with a slow N_2 flow for 1.0 h. Subsequently, a transparent and stable nano-ZnS:Ag modified with L-cysteine (expressed as ZnS:Ag/Cys) colloidal solution was obtained. The purified ZnS:Ag/Cys nanocrystals powder was obtained through the ethanol precipitation procedure [21, 22]. Colloidal solution of cysteine-modified ZnS nanocrystals (expressed as ZnS/Cys) of the same concentration was prepared in the same manner described above without the addition of silver nitrate. Colloidal solution of ZnS of the same concentration was also prepared in the same manner described above without the addition of silver nitrate and cysteine.

Results and discussion

Effect of cysteine on the stability of the as-prepared nanocrystals

From the experiments carried out by the authors of this study, it can be found that the ZnS:Ag/Cys nanocrystals and ZnS/Cys nanocrystals colloidal solution can remain stable without congregating and depositing for more than 3 month at room temperature. But the colloidal solution of ZnS or ZnS:Ag whose surface was not modified with cysteine can remain stable for only 2 days, and a floccule was found at the bottom of the beaker after aging for more than 2 days. The effects of cysteine on the stability of colloidal solution of ZnS:Ag/Cys and ZnS/Cys are obvious, cysteine is used both as a stabilizer and a modifier in the synthetic process to avoid flocculation and further growth of the particles.

XRD analysis

The XRD pattern of ZnS:Ag/Cys nanocrystals is shown in Fig. 1. In the pattern, the position of the diffraction peaks of ZnS:Ag/Cys nanocrystals almost matched with those of the standard β-ZnS (JCPDS No. 01-0792), the three diffraction peaks corresponded to (111), (220), and (311) planes of the cubic crystalline ZnS, respectively, which indicates that the as-prepared nanocrystals belong to the cubic zinc blende structure. The concentration of Ag^{+} is so low that its affect on the nanocrystals pattern can be neglected, therefore the values of 2θ in the pattern almost matched with those of the standard β-ZnS. The broadening in the diffraction peaks of the nanocrystals due to the small size effect of nanostructure can also be observed from this pattern. The average size of the ZnS:Ag/Cys nanocrystals was estimated at 2.4 nm from the Debye–scherrer formula [23].

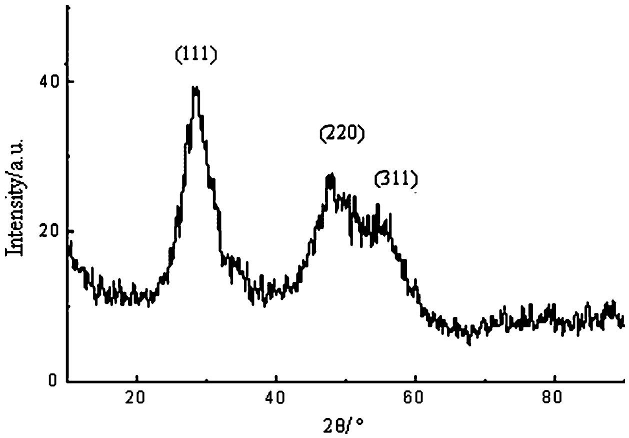

Fig. 1 XRD pattern of ZnS:Ag/Cys nanocrystals

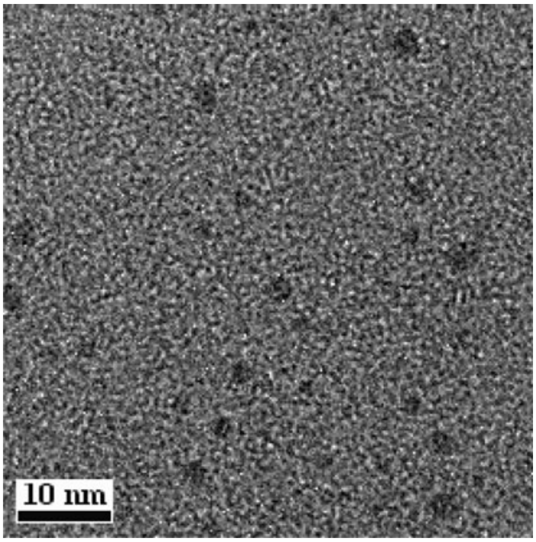

Fig. 2 TEM image of ZnS:Ag/Cys nanocrystals

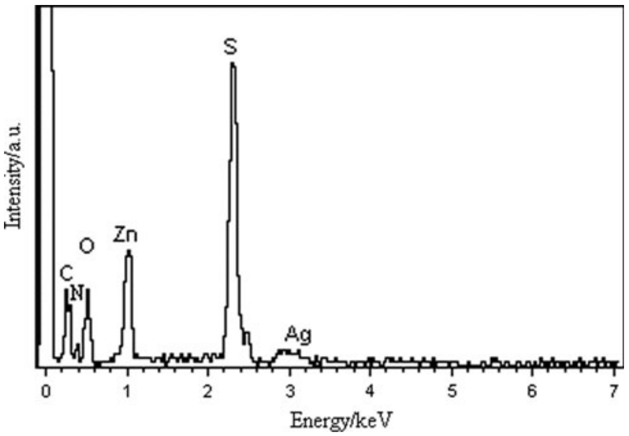

Fig. 3 EDX spectrum of ZnS:Ag/Cys nanocrystals

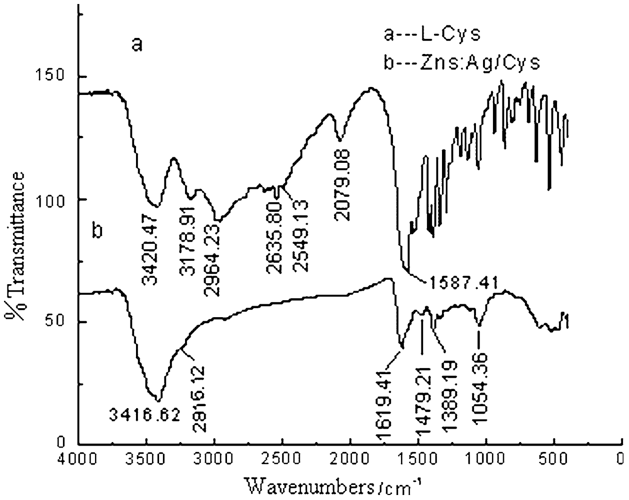

Fig. 4 IR spectra of cysteine (**a**) and ZnS:Ag/Cys nanocrystals (**b**)

TEM and EDX analysis

The TEM images of ZnS:Ag/Cys nanocrystals are shown in Fig. 2. It is clearly shown that the average diameter of the spherical ZnS:Ag/Cys nanocrystals is about 2.6 nm, which is in agreement with the result of XRD analysis. The size distribution of the nanocrystals is uniform, which indicates that the as-prepared nanocrystals have good monodispersity. Figure 3 shows the EDX of the ZnS:Ag/Cys nanocrystals. Every examined particle shows EDX signals of Zn, S, and Ag, which indicates Ag impurity has doped into the nanocrystals.

Infrared absorption spectrum analysis

The infrared (IR) spectra of L-cysteine molecule and ZnS:Ag/Cys nanocrystals are shown in Fig. 4, IR (KBr) ν: 1550–1650 cm^{-1} (s$\nu_{C=O}$), 1389 cm^{-1} (m$\nu_{C=O}$), 1200–1250 cm^{-1} (w$\nu_{C–O}$), 3500–3000 cm^{-1} (m$\nu_{O–H}$), 2900–3420 cm^{-1} (m$\nu_{N–H}$), 1054 cm^{-1} (mν_{C-NH_2}), and 600–800 cm^{-1} (w$\nu_{C–S}$) are found, while the 2550–2650 cm^{-1} ($\nu_{S–H}$) for L-cysteine [24] disappears in Fig. 4b, which indicates that the sulfur atom in mercapto group of L-cysteine is coordinated with Zn^{2+} or Ag^{+} ion on the surface of the nanocrystals, resulting in the formation of ZnS:Ag/Cys nanocrystals.

UV–Vis absorption spectrum analysis

Figure 5 shows the UV–Vis absorption spectra of ZnS:Ag/Cys and ZnS/Cys nanocrystals. The absorption edge of ZnS:Ag/Cys shows a red shift compared with that of ZnS/Cys nanocrystals, which implies the introduction of the Ag^{+} ions into the ZnS:Ag/Cys nanocrystals. The well-known absorption of the bulk ZnS locates at 340 nm. Compared with the bulk ZnS material, the as-prepared nanocrystals exhibit an obvious quantum size effect.

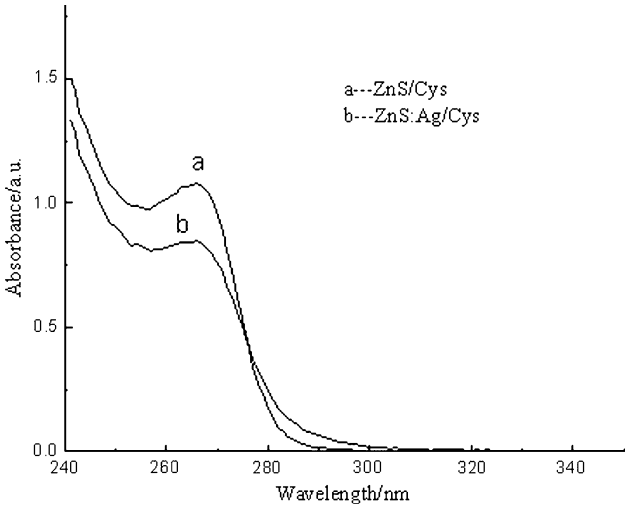

Fig. 5 UV–Vis absorption spectra of ZnS/Cys (**a**) and ZnS:Ag/Cys nanocrystals (**b**)

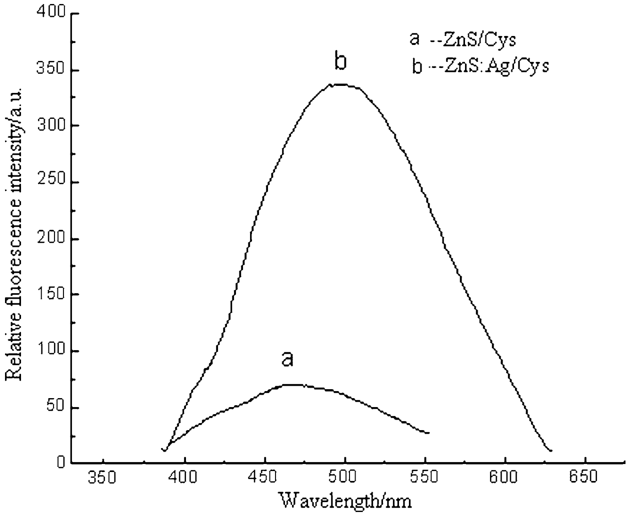

Fig. 6 Fluorescence spectra of ZnS/Cys (**a**) and ZnS:Ag/Cys nanocrystals (**b**)

Fluorescent spectrum analysis and inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis

The fluorescent spectra of ZnS/Cys and ZnS:Ag/Cys nanocrystals are shown in Fig. 6, with excitation at 290 nm. It is found that the maximum fluorescence emission peak of the ZnS:Ag/Cys nanocrystals is located at 490 nm, which shows a red shift compared with that of ZnS/Cys nanocrystals at 468 nm, and the emission intensity of ZnS:Ag/Cys nanocrystals is stronger than that of the ZnS/Cys nanocrystals. The quantum yields of ZnS/Cys and ZnS:Ag/Cys nanocrystals were measured in aqueous solution. Compared with that of ZnS/Cys nanocrystals, the quantum yield of the ZnS:Ag/Cys nanocrystals increased. The quantum yield of the ZnS/Cys nanocrystals increased from 2.3 to 7.2% after doped with Ag^+. Based on the research on photoluminescent mechanism of metallic ion-doped ZnS nanocrystals [25], it has been assumed that the change of fluorescence emission peak of the ZnS:Ag/Cys nanocrystals may be attributed to the effective radiative recombination of captured electrons at the conduction band or at the shallow trap energy level just below the conduction band with holes trapped at the energy level of Ag^+ impurities above the valence band. The result described above indicates that the Ag^+ ions were doped into the ZnS:Ag/Cys nanocrystals.

The result of ICP-AES analysis showed that the molar ratio of $n(Ag^+)$:$n(Zn^{2+})$ in the nanocrystals was 1:56. Due to the solubility product constant of Ag_2S ($Ksp = 6.0 \times 10^{-50}$) is much lower than that of ZnS ($Ksp = 2.2 \times 10^{-22}$), Ag_2S may be easier to precipitate than ZnS. On the other hand, the ion radius of Ag^+ and Zn^{2+} is 0.67 and 0.74 Å, respectively, so it is possible for Ag^+ ions to substitute the Zn^{2+} sites in ZnS lattice. Hence, it can be guessed that the doped silver may exist in three forms: (1) a small part of Ag^+ ions substitute the Zn^{2+} sites in ZnS lattice; (2) a small part of Ag^+ ions are adsorbed on the surface of ZnS nanoparticles, and (3) another part of the Ag^+ ions are presented in the form of an Ag_2S phase. The small part of the silver incorporated into ZnS lattice as Ag^+ impurities centers could give rise to localized energy levels above the valence bands [19]. From the red shift of maximum fluorescence emission peak of the ZnS:Ag/Cys nanocrystals compared with that of ZnS/Cys nanocrystals, it can be confirmed that a small part of Ag^+ ions substitute the Zn^{2+} sites in ZnS lattice.

Conclusion

A simple, green, and lower cost synthetic method for the preparation of ZnS:Ag/Cys nanocrystals in aqueous solution with L-cysteine as a surface modifier has been proposed in this article. The spherical ZnS:Ag/Cys nanocrystals with the average diameter of 2.6 nm have good monodispersity and favorable fluorescent properties, their fluorescence intensity is enhanced greatly after doped with Ag^+. The fluorescent emission is ascribed to a transition from a donor energy level to the energy level of the Ag^+ impurities. The cysteine modified on the surface of ZnS:Ag/Cys nanocrystals renders the nanocrystals water soluble and biocompatible, and provides the possibility of $-NH_2$ and –COOH groups of cysteine modified on the surface of nanocrystals for the molecular assembly or connecting with various biomacromolecular. This study will facilitate the further studies on ZnS:Ag/Cys nanocrystals in molecular assembly and biological fluorescence analysis.

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