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Fabrication of silk fibroin coated ZnSe:Mn^{2+} quantum dots under γ-radiation and their magnetic properties

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ABSTRACT

Silk fibroin coated Mn^{2+}-doped ZnSe quantum dots (SF-ZnSe:Mn^{2+} QDs) were successfully synthesized via a one-step γ-radiation route in an aqueous system at room temperature. The prepared QDs were characterized by transmission electron microscopy (TEM) images, energy dispersion spectroscopy (EDS), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), ultraviolet–visible (UV–vis) spectroscopy, photoluminescence (PL) spectroscopy and superconducting quantum interference device (SQUID) magnetometry. The synthesized QDs were about 5 nm in diameter and had excellent water solubility. These QDs showed strong visible orange luminescence under UV excitation and were shown to have a strong emission peak at around 586 nm and a weak emission peak at around 425 nm. Moreover, the products exhibited excellent superparamagnetic behavior when the temperature was above 10 K. These QDs might afford many potential applications in biomedical and other areas. This method could be conveniently extended to fabricate other nanoparticles coated with silk fibroin.

1. Introduction

Nanometer-scaled semiconductor crystallites, also known as quantum dots (QDs), have been gaining popularity due to their unique optical properties and wide potential applications in optoelectronics, catalysis, fluorescence imaging and tumor therapy [1–4]. In the past few years, tremendous progress has been made in preparing various high-quality QDs [5–7]. QDs that are intentionally doped with impurities have also attracted increasing attention due to their unique photoluminescence and magnetic properties [8–10]. Many efforts have been made on II–IV QDs, such as ZnS, CdS, ZnSe, CdSe, which were doped with Mn^{2+} [11–15]. A variety of physical or chemical methods have been used to fabricate doped QDs [11,13]. However, many of the synthesis systems used an environmentally hazardous organic-solvent route, which were not suitable for biological and other environmentally friendly applications. So far, the γ-radiation route has been considered as one of the most effective methods for the synthesis of nanoparticles and other novel nanoscale materials [16–18]. In our past work, we have also successfully synthesized various nanoparticles via a γ-radiation route [19–21]. The QDs have been proved to have potential applications in biology and medicine, but the biocompatibility and cytotoxicity of QDs might limit their wide applications in this area. Various coatings, such as ZnS shell, thiol-containing molecules, PEG, chitosan, peptide and other polymers, have been developed to modify QDs and they have proved to be very efficient in changing their cytotoxicity and biocompatibility [22–24]. Silk fibroin, a natural fibrous protein derived from silk, has excellent biocompatibility and has been used as biomaterials, drug delivery carrier and template to fabricate nanomaterials [25]. To our knowledge, the fabrication of silk fibroin coated impure QDs via a γ-radiation route has not been reported.

In this work, we have successfully fabricated silk fibroin coated Mn^{2+}-doped ZnSe quantum dots (SF-ZnSe:Mn^{2+} QDs) via a one-step γ-radiation route in an aqueous system at room temperature. The as-prepared QDs were characterized and analyzed with TEM, EDS, FT-IR, XRD, UV–vis, PL and SQUID methods. All results show that the SF-ZnSe:Mn^{2+} QDs were about 5 nm in diameter and exhibited excellent photoluminescence and superparamagnetic behavior. This method could be conveniently extended to fabricate other nanoparticles coated with silk fibroin.

2. Experimental details

2.1. Materials

$ZnAc_2$, $MnAc_2$, SeO_2 and $(CH_3)_2CHOH$ were analytic grade and purchased from Shanghai Chemical Company. Silk fibroin was

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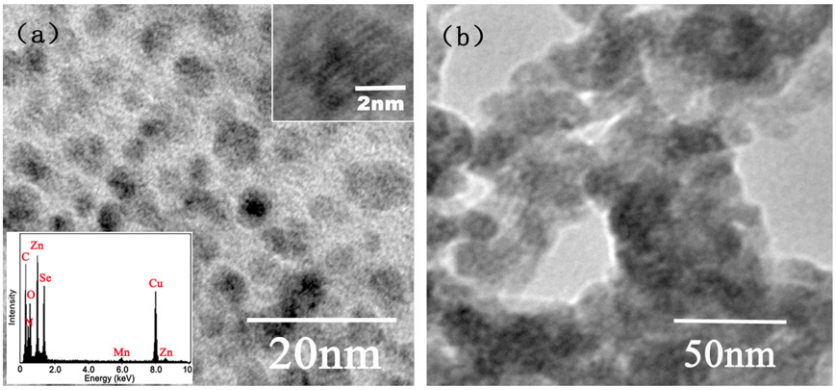

Fig. 1. TEM images and EDS spectrum of as-prepared products. (a) A typical TEM micrograph of SF-ZnSe:Mn^{2+} QDs; the insets are a high-resolution TEM image and the EDS spectrum. (b) A TEM micrograph of the product prepared through the same route but without silk fibroin.

prepared from the raw silk fibers following the reported methods [26,27].

2.2. *Preparation of* SF-ZnSe:Mn^{2+} *QDs*

SF-ZnSe:Mn^{2+} QDs were directly fabricated via a convenient γ-radiation route in an aqueous system at room temperature. A typical synthesis route was as follows: 5 ml $ZnAc_2$ (10 mM), 5 ml $MnAc_2$ (0.2 mM) and 10 ml SeO_2 (10 mM) were added into 70 ml deionized water containing 0.1% silk fibroin (SF, w/v); then 10 ml $(CH_3)_2CHOH$ was added into the above solution as a hydroxy free radical removal agent; afterwards, the solution was bubbled with pure nitrogen for 30 min to remove oxygen; then the solution was irradiated by γ-rays under a given absorbed dose (6 kGy h^{-1}, 20 kGy). After irradiation, the resulting solution was concentrated using a rotary evaporator, and then the synthesized QDs were separated from solution by centrifugation at 10,000 rpm for 10 min. The sample was washed three times with deionized water and stored in deionized water for further analysis.

2.3. *Characterizations*

Transmission electron microscopy (TEM) images were taken on a JEOL JEM-200CX transmission electron microscope. The elementary analysis was carried out with energy dispersion spectrometry (EDS). Fourier transform infrared (FT-IR) spectra were obtained on a NICOLET NEXUS870 FT-IR spectrometer. X-ray diffraction (XRD) patterns were recorded on a BRUKER D8-ADVANCE X-ray diffractometer with graphite-monochromatized Cu-$K\alpha$ radiation ($\lambda = 0.154178$ nm). Ultraviolet–visible (UV–vis) spectra were obtained at room temperature using a PERKIN-ELMER λ-17 spectrophotometer. The photoluminescence (PL) spectra were obtained with a HITACHI 850 spectrofluorophotometer. The magnetic properties were characterized with an MPMS XL-7 superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

3.1. *Morphology and structure characterizations*

TEM, EDS, XRD, and FT-IR characterizations were carried out to identify the morphology and structure of the as-prepared products. Fig. 1(a) is a typical TEM micrograph of the SF-ZnSe:Mn^{2+} QDs and it shows that the diameter of QDs is about 5 nm, with a narrow size distribution. Fig. 1(b) is a TEM micrograph of the product which was prepared through the same route but without silk fibroin. It shows that serious aggregation took place and ZnSe:Mn^{2+} QDs were not even successfully synthesized. Comparing Fig. 1(a) with Fig. 1(b), we can conclude that the silk fibroin played an important role in the formation of QDs. Silk fibroin provided a place for the nucleation and growth of nanocrystals in the entire reaction and controlled the final size of the products. The EDS spectrum of SF-ZnSe:Mn^{2+} QDs (the inset in Fig. 1(a)) indicates that the products mainly contain the elements Zn, Mn, Se, C, N and O. Table 1 gives the results of the EDS analysis, which reveals that the atomic content of Mn element in ZnSe QDs is about 0.73%. Fig. 2(a) shows the FT-IR spectra of the original silk fibroin and SF-ZnSe:Mn^{2+} QDs. Peaks of silk fibroin which appear at 1650 cm^{-1}, 1536 cm^{-1}, 1235 cm^{-1} and 699 cm^{-1} can be attributed to the amide I C=O, amide II C–N^+N–H, amide III C–N^+ N–H and amide IV O=C–N bonds. After the reaction, the peak around 1650 cm^{-1} shifts to 1688 cm^{-1}, revealing the chelation between the C=O and Zn^{2+} or Mn^{2+}. The changes of peaks around 1536 cm^{-1}, 1235 cm^{-1} and 699 cm^{-1} in SF-ZnSe:Mn^{2+} also indicate the interactions between the silk fibroin and QDs [28,29]. XRD patterns are shown in Fig. 2(b). Compared with the pattern of pure SF-ZnSe QDs, no great changes are observed in the pattern of SF-ZnSe:Mn^{2+} QDs, but a very slight shift of the diffraction peaks takes place. This slight shift of diffraction peaks might be attributed to the difference between the Mn^{2+} and Zn^{2+} ionic radii. The three observed peaks in the SF-ZnSe:Mn^{2+} QD pattern at 27.5°, 45.5°, and 53.3° can be indexed to the (111), (220) and (311) reflections for cubic ZnSe (JCPDS Card No. 37-1463). The above results indicate that Mn^{2+} had been doped in ZnSe without obviously changing the crystal form of ZnSe. The XRD peaks in SF-ZnSe:Mn^{2+} are broadened due to the small nature of nanocrystals, and the mean size of particles can be calculated to be about 4.8 nm by the Debye–Scherrer formula, which is consistent with the TEM results.

Table 1
The results of EDS analysis of SF-ZnSe:Mn^{2+} QDs.

Elements	Weight %	Atomic %
C	11.85	33.95
N	3.80	9.34
O	9.85	21.18
Zn	32.96	17.34
Se	41.11	17.92
Mn	0.42	0.26

3.2. *Photoluminescence of* SF-ZnSe:Mn^{2+} *QDs*

Fig. 3 shows the UV–vis and PL spectra of SF-ZnSe and SF-ZnSe:Mn^{2+} QDs. The absorption peaks of Mn^{2+}-doped and undoped SF-ZnSe QDs are at 401 nm and 396 nm, respectively, which show an obvious blue shift in the forbidden gap compared with the bulk ZnSe band gap (464 nm) [11]. The undoped SF-ZnSe QDs show an emission peak at about 422 nm, which is the typical luminescence of ZnSe resulting from the transition