Fabrication of Luminescent Cadmium Sulfide Nanofibres in Inverse Microemulsion *via* PEG-400 as the Template by γ-Irradiation

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Luminescent cadmium sulfide nanofibres with average diameters of 100 nm and lengths up to 3 μm were successfully prepared in large scale in inverse microemulsion under γ-irradiation and the addition of polyethylene glycol-400 (PEG-400) as the template at room temperature and under ambient pressure, which was confirmed by the observation of transmission electron microscopy, field-emission scanning electron microscopy and X-ray powder diffraction. Additionally, the chemical composition of cadmium sulfide nanofibres was determined with X-ray photoelectron spectroscopy and the optical properties of cadmium sulfide nanofibres were characterized by ultraviolet-visible and photoluminescence spectroscopies.

Key Words: Nanomaterials, Nanoparticels, Non-linear optical, Radiation, Semiconducting II-VI materials.

INTRODUCTION

The properties of nanocrystals depend not only on their composition, but also on their structure, phase, shape, size and size distribution. Furthermore, the architectural control of nanosized materials with well-defined shapes is important for the success of bottom-up approaches toward future nanodevice[1,2]. And such nanodevices have potential applications in nanoelectronic devices, nanooptical devices and chemical sensors[3,4], *etc*. So, how to develop ways of tailing the nanomaterials with desired morphologies is quite important and difficult. The ability to manipulate the morphology, size and size distribution of inorganic nanomaterials remains an important goal in modern material chemistry. The shape of inorganic nanocrystals has much influence on their widely varying physical properties[5,6]. Thus, the synthesis of inorganic nanocrystals of controlled shape arouses great interest. A series of relevant efforts has been paid on the shape' control, the synthesis of single crystalline nanocrystals with advanced structure is still in the developing stage.

The construction and integration of functional nanodevices based on the one-dimensional semiconductor materials have advanced rapidly in recent years. Nano devices such as transistors[7], light emission diodes[8] and gas and chemical sensors[9] have been reported, demonstrating exciting progress in the bottom-up approach for building new generation electronic and photo electronic systems with reduced size, higher efficiency and less energy consumption. As an important application of semiconductor materials, photodetectors or optical switches are essential elements in imaging techniques and light wave communications and possibly in future memory storage and optoelectronic circuits[10]. Various semiconductor materials, including group IV elements (Si, Ge), group III-V compounds (GaN, GaAs, InP) and group II-VI compounds (ZnS, CdS, CdS), have been used for the fabrication of photodetectors. And the large variety of band gaps of these materials leads to a wide spectral response ranging from far-infrared to ultraviolet light[11].

The size, shape and structure of semiconductor nanocrystals are important factors in adjusting their electronic, optical and other physical properties[12,13]. Thus, the synthesis of nano-to microscopic-scale semiconductive materials with controlled size and shape are of great interest owing to their novel properties and potential application in optics, electronics, catalysis, magnetism and biology[14-16]. Semiconductor nanomaterials exhibit a wide range of electrical and optical properties that depend sensitively on both size and shape and gain a great of interest for both fundamental and technological researches[17-19]. It is well-known that CdS is a typical inorganic semiconductor material used for light-emitting diodes. When it exists in a polymer matrix, the polymer is expected not only to provide good mechanical and optical properties, but also to confer a high kinetic stability on nanometer-sized semiconductor particles. In addition to the specific electronic and

TABLE-1
PREPARATION OF CdS NANOFIBRES IN INVERSED MICROEMULSION AND γ-IRRIDIATION

CdS nanofibres	OP-4 (g)	OP-10 (g)	PEG (mg)	H_2O (mL)	Shape	Length (um)
Nanofibre A	3.819	3.247	60	4.4	Fibres	1
Nanofibre B	3.012	2.016	60	4.4	Fibres	3

optical properties of CdS nanocrystals, the composite will possess excellent film process stability. Thus, the good optical quality thin films of the composite can be easily obtained[20].

Cadmium sulfide as important semiconductive II-VI material, has a typical wide band gap of 2.42 eV at room temperature and displays excellent optical properties and various luminescence properties, such as photoluminescence and electroluminescence. Its wide applications involve laser light-emitting diodes, solar cells and other optical devices based on its nonlinear properties[21-23]. It is well known that the fantastic properties of nanoscaled semi-conductive materials are dependent on the size, shape and crystallinity. Thus many efforts have been developed to those points. Cadmium sulfide nanocrystal as an important II-VI semiconductor material, quite different approaches has been applied to achieve one-dimensional CdS nanocrystal with the controlled morphology and size. Those approached include solvothermal route[24], liquid crystal template[25], irradiation technique[26], polymer controlled growth[27] and electrodeposition on a porous template[28].

γ-Ray radiation-induced to prepare inorganic or organic materials could be carried out at room temperature under normal pressure and it is hardly influenced by temperature and very convenient. Because there is no chemical initiator in the polymerization, the final product is not polluted. Several groups have taken advantage of γ-irradiation method to prepare functional nanomaterials[29,30] under ambient conditions. In this paper, we describe the processes that give rise to the synthesis of unusual CdS luminescent nanofibres structures by reaction of $Na_2S_2O_3 \cdot 5H_2O$ and $CdCl_2$ in inverse microemulsion under γ-irridiation and the addition of PEG-400 as the template and characterized by transmission electron microscopy and field-emission scanning electron microscopy.

EXPERIMENTAL

$Na_2S_2O_3 \cdot 5H_2O$, $CdCl_2$, isopropanol, octylphenyl poly(ethylene glycol) ether (n = 4) (OP-4) and octylphenyl poly(ethylene glycol) ether (n = 10) (OP-10) were purchased from Shanghai chemical reagent central factory and polyethylene glycol-400 (PEG-400) from acros. Distilled water (DI) was obtained from a Milli-Q® Gradient System from Millipore equipped with a Quantum™ cartridge. All of the reactants and solvents are of analytical grade and used without any further purification.

The nonionic surfactants OP-4 and OP-10 were selected as emulsifiers and cyclohexane was used as the continuous oil phase. In a typical experiment, OP-4 (3.819 g) and OP-10 (3.247 g) were dissolved in cyclohexane (50 mL) to form the continuous phase. $Na_2S_2O_3 \cdot 5H_2O$ (0.8432 g), $CdCl_2$ (0.201 g), PEG-400 (60 mg) and isopropyl alcohol (0.5 mL) (a scavenger of the oxidative radicals such as ·OH) were dissolved in distilled water (4.4 mL). The aqueous solution was added dropwise into the surfactants solution with constant stirring.

Afterwards, the inversed microemulsion was obtained by the supersonic emulsification. Another microemulsion was obtained by changing the amounts of surfactants and distillated water: OP-4 (3.012 g), OP-10 (2.106 g) and distilled water (3.5 mL).

After the inversed microemulsion was degassed by ultrasonic deaeration for 20 min and then bubbling with nitrogen for 40 min to remove the oxygen dissolved in the system, the microemulsion was irradiated in a field of 2.59×10^{15} Bq by a ^{60}Co γ-ray source at a dose rate of 50 Gy/min for an absorbed dose of 30 kGy. The whole reaction was performed under ambient conditions. After the reaction completed, the microemulsion was destabilized by adding ethanol. The light yellow precipitate of CdS nanofibres were separated by centrifugation, washed with cyclohexane and ethanol to remove the residual surfactants and dried under vacuum at room temperature for 24 h.

Transmission electron microscopy (TEM) images were performed on a Hitachi model H-800 TEM instrument with an accelerating voltage of 200 kV, high resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) were performed on a Hitachi model JEOL 4000EX at 400 kV, FESEM (JEOL JSM-6700) with an acceleration voltage of 5 kV. X-ray photoelectron spectroscopy (XPS) was recorded on ESCALAB MKII photoelectron spectrometer using a nonmonochromatic Al K_α radiation (1486.6 eV) under about 10^{-11} mbar. The samples were also identified by X-ray powder diffraction (XRD) employing a scanning rate of 0.02 deg/s in the 2θ range from 10 to 70º, using a Japan Rigaku D/max γA X-ray diffractometer equipped with graphite monochromatized CuK_α radiation (λ = 0.154178 nm). Ultraviolet-visible (UV-VIS) absorption spectrum was recorded by dispersing CdS nano-crystal in distilled water on a UV-2100 Shimadzu spectrophotometer at room temperature. The photoluminescent spectrum was taken on a Hitachi 850 fluorescence spectrometer with a Xe lamp at room temperature. The wavelength of excitation light is 350 nm.

RESULTS AND DISCUSSION

Cadmium sulfide nanofibres with different shapes were prepared under various conditions to investigate the influences of surfactant concentrations on the formation of CdS nanofibres. The recipes and results were summarized in Table-1.

The shape and size of CdS nanofibres were characterized by TEM as shown in Fig. 1. Fig.1a shows that the TEM images of the CdS nanofibres A, Fig.1b shows the TEM images of the CdS nanofibres B. From the figure, it is find that over 95 % of the particles were electron dense crystalline fibers, up to 3 μm in length and between 50 and 200 nm in width (Fig. 1a and 1b). Many fibers appeared to be flattened in cross-section and twisted into a tapelike morphology. Contrast the TEM images of Fig.1a and 1b, it is noted that the CdS nanofibres were

formed in large scale in the inverse emulsion under γ-irridiation and the addition of PEG-400 as the template. The CdS nanofibres B are thinner and longer when the surfactants are more. The CdS nanofibres were also identified by FESEM, Fig. 1c and 1d shows us the FESEM of CdS nanofibres A and B, the samples with average diameters of 100 nm and 50 nm, lengths up to 1 μm and 3 μm, respectively. They are in good agreement with TEM results. HRTEM and SAED images in Fig. 2 suggest that CdS nanofibres are single-crystalline and grow along $(2\bar{1}\bar{1}0)$ direction.
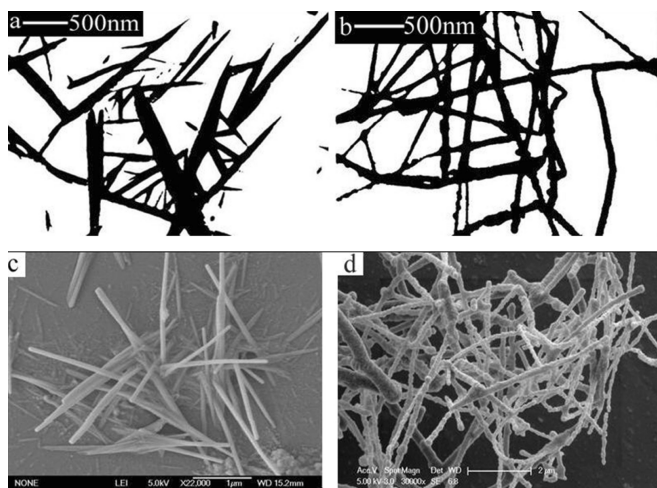

Fig. 1.   TEM and FESEM image of nanofibres for different surfactant (a) nanofibres A, (b) Nanofibres B, (c) nanofibres A, (d) nanofibres B
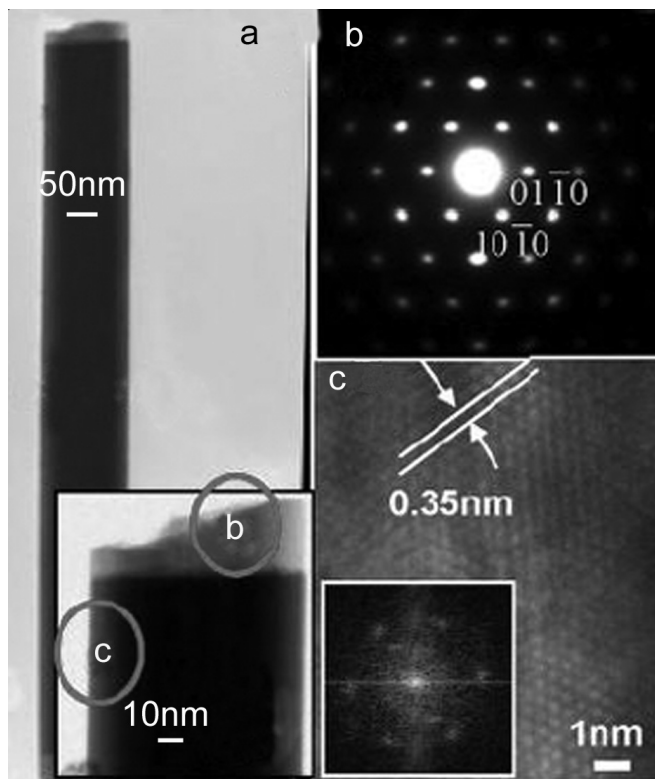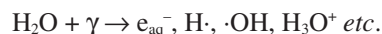

Fig. 2.   (a) TEM images of a single CdS nanofibre. Inset is a high magnification TEM image of the nanofibre end; (b) electron diffraction pattern from the corresponding circled area in (a). (c) HRTEM image from the corresponding circled area in (a) and its FFT pattern (the inset)

When the microemulsion was irradiated under γ-rays, the radiolysis of water produces many active species such as e_{aq}^-, H· and ·OH. Then, the e_{aq}^- could reduce sulfur source to S^{2-}, which reacted with Cd^{2+} to generate CdS. Meanwhile, isopropyl alcohol could eliminate the influence of oxidative radicals on the formation of S^{2-} anion. The possible reactions are described as follows:
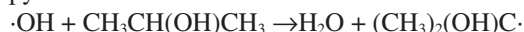
Radiolysis of water:

$$H_2O + \gamma \rightarrow e_{aq}^-, H·, ·OH, H_3O^+ \ etc.$$

Reduction of $Na_2S_2O_3$:

$$e_{aq}^- + S_2O_3^{2-} \rightarrow S^- + ·SO_3^{2-} \text{ and } e_{aq}^- + S^- \rightarrow S^{2-}$$

Combination: $S^{2-} + Cd^{2+} \rightarrow CdS$

Aggregation: $nCdS \rightarrow (CdS)_n$

Some oxidative radicals such as ·OH were scavenged by isopropyl alcohol.

$$·OH + CH_3CH(OH)CH_3 \rightarrow H_2O + (CH_3)_2(OH)C·$$

The inversed microemulsion can act as a nano-reactor to form nanoparticles. In this experiment, PEG-400 is a long-chain macromolecule with many hydroxy groups. In the water pool of the microemulsion, the long molecular chain is unfolded and acts as the template. When Cd^{2+} ion meets with S^{2-} ion, CdS nanocrystal grew along the long straight template and CdS nanofibres might be formed in the nano-reactors.

The formation of CdS nanofibres was also confirmed with XRD analysis. XRD pattern of CdS nanofibres was shown in Fig. 3, indicating that CdS nanofibres are in the hexagonal phase, that is, a wurtzite structure with lattice parameters (a = 4.134 Å and c = 6.723 Å). The results are very close to the reported data (JCPDS card file, no. 41-1049).
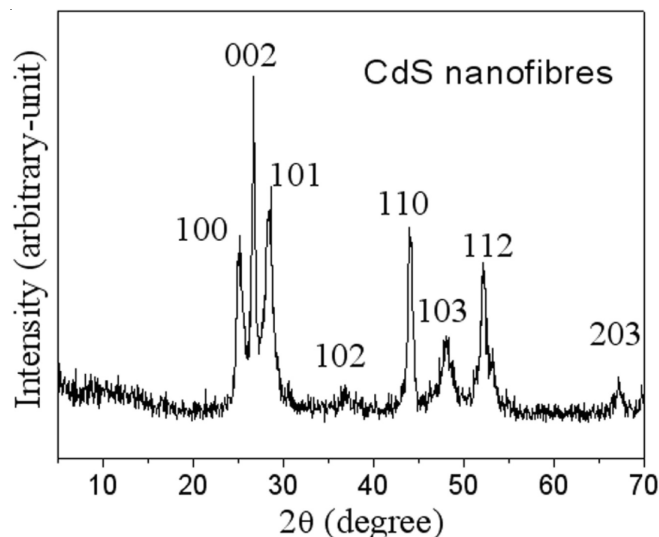

Fig. 3. XRD pattern of CdS nanofibres

The chemical composition of CdS nanofibres was determined with XPS, XPS was recorded on ESCALAB MKII Photoelectron spectrometer using a nonmonochromatic Al K_α radiation (1486.6 eV) under about 10^{-11} mbar, as shown in Fig. 4. The XPS is similar and close to the typical CdS spectrum reported by other work[31]. Fig. 4a is the typical survey spectrum of CdS nanofibres, showing the presence of Cd and S from the nanofibres, from the background and C and O from the absorbed gaseous molecules. Detailed spectra were taken at Cd and S regions. The two strong peaks Cd_{3d} and S_{2p} electron

binding energies were 405.70 ev and 162.20 eV, which indicates the valence states of Cd and S being +2 and -2, respectively. The calculated ratio of Cd atoms to S atoms is Cd : S is about 49.4 : 50.6, which indicates the formation of CdS compounds.
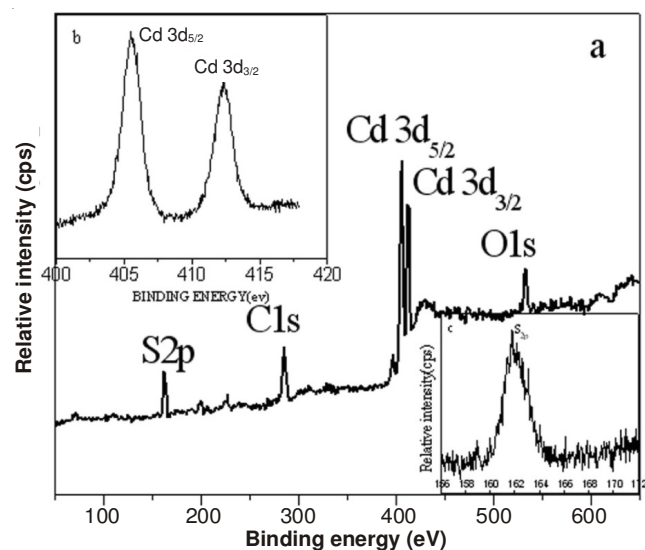

Fig. 4.   Typical XPS spectra of CdS nanofibres: (a) XPS survey spectrum of CdS nanofibres; (b) detailed scan for Cd3d$_{5/2}$ Cd3d$_{3/2}$; (c) detailed scan for S$_{2p}$

Fig. 5 Illustrates the UV-VIS absorption and the photoluminescence spectrum of the CdS nanofibres dispersed in distilled water with an excitation wavelength of 350 nm. Photoluminescence spectrum was taken on a Hitachi 850 fluorescence spectrometer with a Xe lamp. The wavelength of excitation light is 350 nm. As shown in Fig. 5(b), the appearance of a strong emission peak at -430 nm, which blueshifts about 60 nm from that of CdS bulk materials, similar to the previously reported result[32], can be ascribed to a high level transition in CdS semiconductor crystallites. It has been reported that this kind of bandedge luminescence arises from the recombination of excitons and/or shallowly trapped electron-hole pairs[33]. The location of the emission peak of CdS nanofibres derived under different synthetic conditions can shift to the red region with an increase in the nanorod length relating to the product's morphology and surface excess of S^{2-} or Cd^{2+} vacancies[34].
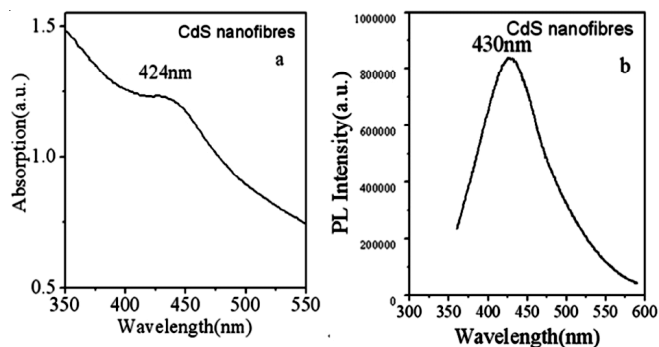

Fig. 5.   (a) UV-VIS absorption spectrum of CdS nanofibres and (b) PL spectrum of CdS nanofibres (lex = 350nm)

Conclusion

In conclusion, we have developed a novel method for the synthesis of the single-crystalline CdS nanofibres. Luminescent cadmium sulfide nanofibres with average diameters of 100 nm and lengths up to 3 μm were successfully prepared in large scale in inversed microemulsion under γ-irradiation, its shape and size can be controlled by the PEG-400 template, water-to-oil ratio and surfactants concentration. The results shown the nanoscale water pools can provide ideal nano-reactors for the formation of nanoparticles and PEG-400 template plays an important role in controlling the morphology of CdS nanofibres. The UV-VIS and photoluminescence spectroscopies showed us that the fibres have some luminescent.

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