Research Article

Synthesis and Fluorescence Property of Mn-Doped ZnSe Nanowires

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Water-soluble Mn-doped ZnSe luminescent nanowires were successfully prepared by hydrothermal method without any heavy metal ions and toxic reagents. The morphology, composition, and property of the products were investigated. The experimental results showed that the Mn-doped ZnSe nanowires were single well crystallized and had a zinc blende structure. The average length of the nanowires was about 2–3 μm , and the diameter was 80 nm. With the increase of Mn^{2+} -doped concentration, the absorbance peak showed large difference. The UV-vis absorbance spectrum showed that the Mn-doped ZnSe nanowires had a sharp absorption band appearing at 360 nm. The PL spectrum revealed that the nanowires had two distinct emission bands centered at 432 and 580 nm.

1. Introduction

As biomedical labeling reagents, high-quality colloidal luminescent semiconductor nanocrystals, such as CdSe, have attracted much attention because of their apparent, narrow, and symmetric photoluminescence, broad and intense absorption band, and tunable emission peak positions [1, 2]. However, many results indicate that any leakage of cadmium from the nanocrystals would be toxic and fatal to biological systems. Some attempts have been made to develop non-cadmium materials. Transition metal ion-doped quantum dots (d-dots) can meet this requirement. The sp-d exchange interaction between the semiconductor and the transition metal ions induces unique optoelectronic properties [3]; Mn-doped II-VI semiconductors arouse general interest in particular, [4–6]. As a wide-band-gap material, ZnSe is suitable for the fabrication of various optoelectronic devices, biolabeling, and hosts for the formation of doped nanocrystal [7–9]. Recent researches have been carried out to explore for the synthesis of transition metal ion-doped ZnSe nanocrystals such as Cu⁺, Mn²⁺, and Co-doped ZnSe nanomaterials. [10–12]

At present, the main method of preparing transition metal ion-doped ZnSe nanomaterials is colloid chemistry

route. The experiments are typically carried out with high temperature, toxic, and explosive chemical reagents. In particular, as-prepared products cannot be directly dispersed in the water phase due to their hydrophobic surfaces. A further reaction is needed to achieve the phase transfer for the aqueous environment. More recently, Nie and his co-workers [13] developed an alternative method to synthesize nanocrystals in aqueous solution. On the basis of those and other encouraging results [14, 15], we recently focused on the possibilities to synthesize metal ion-doped ZnSe directly in aqueous solution and explored the impact of system on morphology and performance of the nanomaterials.

In this paper, we report on the preparation of high-crystalline Mn-doped ZnSe nanowires (NWs) by a simple method, solution synthetic methodology using α -cyclodextrins as stabilizer, and investigated the relationship between the structures and the properties.

2. Experimental

All chemicals and solvents in our work were commercial products used as received without further purification. α -cyclodextrin (α -CD) was a product of Alfa Company, selenium powder (99.95%) was obtained from Beijing Reagent

Company. Zinc acetate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$), manganese acetate ($\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$), sodium sulfite, sodium hydroxide (NaOH), sodium citrate, and anhydrous ethanol were analytical grade and purchased from Beijing Reagent Company. Deionized water was used throughout all experiments.

The synthesis of ZnSe and Mn-doped ZnSe nanowires was adapted from a procedure developed for CdSe nanoparticles [16]. A brief description is provided as follows. A total of 0.2588 g of sodium citrate, 10 mL of 0.04 M $\text{Zn}(\text{OAc})_2$ solution and 0.08 mmol $\text{Mn}(\text{OAc})_2$ were added to 225 mL of deionized water. Under the magnetic agitation, 2 g of α -CD was introduced to the flask. After the pH value was adjusted to 10 with 1 M NaOH solution, the mixture was purged with N_2 for 30 min. Then 6 mL of 0.05 M Na_2SeSO_3 solution was added. When mixed uniformly, the solution was transferred to the vessel. It was laid to the oven with temperature 180°C for 4 days. After being naturally cooled to the room temperature, the mixture was centrifuged at 5000 rpm/min for 10 minutes and washed several times by deionized water and absolute ethanol. Having dried in vacuum at 80°C for 3 hours, the yellow products were obtained.

The transmission electron microscope (TEM) images were taken by H-800 microscope with an acceleration voltage of 80 kV. The high-resolution TEM images were obtained by employing a JEOL 3010 microscopy with a 300 kV accelerating voltage. Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid coated with carbon and were allowed to dry in air. The samples were characterized by X-ray diffraction (XRD), with scanning rate $10^\circ/\text{min}$, on D/max 2500 VB2+/PC X-ray diffractometer using graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The UV-vis absorbance spectra were obtained on a Shimadzu UV-3150 spectrophotometer in the range of 200–800 nm at room temperature. Optical densities were kept within 0.2 at the excitation wavelength. The photoluminescence (PL) spectra of the as-prepared Mn-doped ZnSe nanomaterials were measured using a Varian Cary-Eclipse fluorophotometer.

3. Results and Discussion

The XRD patterns of the ZnSe and Mn-doped ZnSe NWs are displayed in Figure 1. The XRD peaks of the undoped ZnSe NWs can be well indexed to zinc blende ZnSe crystals (JCPDS Card No. 37-1463). In the case of Mn-doped ZnSe NWs synthesized under the same conditions, the peaks are also indexed to zinc blende ZnSe. However, the main peaks of (111), (220), and (311) planes move 0.19° to the left because Mn was implanted to ZnSe internal lattice. The peak intensities at 2θ of $\sim 31.0^\circ$ [(200) plane] and $\sim 57.0^\circ$ [(222) plane] are markedly increased, which indicates that these Mn-doped nanowires have more advantages on growth along the two directions. The peaks which are observed at $\sim 38.0^\circ$ and 49.5° match those of wurtzite phase [(102) plane] and [(103) plane] because the synthesis process is affected by the introduction of impurity ions Mn^{2+} into the host lattice which can significantly affect the reaction rate, which is reflected by a reduction in the crystal phase [17].

FIGURE 1: XRD patterns of the ZnSe (a) and Mn-doped ZnSe (b) nanowires.

It is similar to the characters of the Mn-ZnSe nanoparticles reported by Mahamuni and coworkers [18]. A similar effect has also been reported for Mn^{2+} -doped ZnSe nanowires prepared using the high-temperature organometallic synthesis route [19]. The peak at $\sim 34.0^\circ$ is observed that matches those of MnSe [(200) plane] which indicates that there may be a small amount of MnSe produced.

Figure 2 shows the TEM images for Mn-doped ZnSe nanowires. The average length is about 2–3 μm . It reveals that they are all straight and have a smooth surface without any nanoparticle impurities. Their average diameter is 80 nm. This result is different from other cases. Colloidal Mn-doped ZnSe nanomaterials prepared in the solvent of the typical TOP/HDA/TOPO system are generally particles with the size of several nanometers. In an improved method, nanowires are obtained mostly with the diameter of several nanometers and length up to 200 nm [17].

The high-resolution TEM image of the nanowires and corresponding fast Fourier transformed electron diffraction (FFT ED) pattern are displayed, respectively. From the further analysis, it was found that the growths of crystal lattice are clear, even though the nanowires are very thick. The selected area ED pattern, consisted of discrete and bright spots, indicating that the nanowires are all typically single well-crystallized diffraction pattern of ZnSe. The ED pattern confirms that the zinc blende-structured ZnSe nanowires grow along the (200) direction. The image shows that the highly crystalline (200) planes, separated by $2.819 \text{ \AA}$, are close to that of cubic structured ZnSe crystal $2.834 \text{ \AA}$.

UV-vis absorption spectra of Mn-doped ZnSe NWs with different Mn^{2+} -doped concentrations are presented in Figure 3. An interesting pattern was revealed by this set of experiments. The absorption peaks of all samples are very strong. With the increase of Mn^{2+} -doped concentration, the absorbance shows large difference. The two weak absorption peaks of 5% Mn-doped ZnSe NWs emerge at 250 nm and 370 nm. While Mn^{2+} -doped concentration is increased to 10%, the location of absorption peak is at 360 nm with stronger absorption intensity, but the absorption peaks are

FIGURE 2: TEM images of the Mn-doped ZnSe nanowires, HRTEM, and its SAED pattern images (inset).

FIGURE 3: Absorption spectra of Mn-doped ZnSe with different Mn^{2+} -doped concentrations (a: 0; b: 5%; c: 10%; d: 20%).

FIGURE 4: Photoluminescence spectrum and the absorption spectrum (inset) of Mn-doped ZnSe.

similar with the pure ZnSe except of small red shift when the doped concentration is 20%. It has been reported that the transition metal ion-doped semiconductor could form a doping energy level with the band gap of ZnSe [20]. The doping concentration could have an influence on optical properties to a large extent.

In our case, when doping concentration is low (5%), the content of Mn is inadequate to reduce the band gap of ZnSe which results in ZnSe characteristic absorption and doped absorption emerging at the same time. The optimal doping concentration is 10%. The dopant can serve to retard charge traps and effectively reduce the band gap within the suitable concentration. When the doping concentration is too high (20%), the inconsistency of precipitation reaction may lead to precipitation separation and dopants failure to enter the internal lattice [20].

Figure 4 shows the optical absorption feature of Mn-doped ZnSe NWs (10% Mn^{2+} -doped concentration). A

sharp absorption band appears at 360 nm. A red shift in the absorption band compared with pure ZnSe nanoparticles [14] suggests that the injected metal ions are isomorphic to Zn^{2+} ions and decrease the band gap. The corresponding luminescence spectrum with 350 nm excitation wavelength shows signs of two distinct emission bands centered at 432 and 540 nm, respectively. These bands can be assigned to ZnSe trap state and $\text{Mn}^{2+} {}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ emission. The half-peak-wide of the highest emission peak is 29 nm, which is very narrow and almost symmetrical.

Band-edge luminescence and Mn^{2+} -related luminescence are competing processes. The absorption of a photon leads to the formation of an exciton. Luminescence results from recombination of the exciton as well as from the energy transfer to Mn^{2+} d-d levels. Mn^{2+} doping clearly leads the near-band-edge luminescence at 412 nm to the disappearance of, and the manganese orange emission band emerges at about 580 nm in Mn-doped ZnSe nanowires [18].

4. Conclusion

In summary, Mn-doped ZnSe nanowires were synthesized by hydrothermal method using α -cyclodextrins as stabilizer. It was a convenient, efficient method to obtain the transition metal ion-doped one-dimensional ZnSe nanomaterial which can be directly dispersed in the water phase. The average length of nanowires was about 2–3 μm , and the diameter was 80 nm. Mn-doped ZnSe NWs were indexed to zinc blende ZnSe crystals. After being doped, the peak of the absorption spectra of the nanowires appeared at 360 nm, and their emission band lied at about 580 nm. This method is simple for synthesizing Mn-doped ZnSe nanowires and provides a flexible approach for applications of biomedical labeling reagents.

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