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THE INVESTIGATION ON SYNTHESIS AND OPTICAL PROPERTIES OF ZnS:Co NANOCRYSTALS BY USING HYDROTHERMAL METHOD

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ZnS:La nanocrystals were directly synthesized in hydrothermal condition by using zinc acetate, cobalt acetate and thioacetamide (TAA) as main sources. The XRD and TEM experimental results showed that as-prepared approximately spherical ZnS and ZnS: Co nanoparticles have a cubic zinc blende structure and narrow size distribution with average diameter at about 40nm and 35nm. The particle diameter calculated using the Scherer's formula was 4.2~5.2nm which indicated nanoparticles have polycrystalline structure. From spectrum data of UV-vis characterization, the calculated band gap of nanocrystals was 3.79ev which is blue shifted from that of bulk materials (3.66ev) and confirmed quantum size effect of nanocrystals. The optical properties of ZnS: Co nanocrystals were determined by using photoluminescence (PL) spectra, which showed that the products exhibited good optical properties with maximum emission peak at about 470nm. In addition, the change of intensity of photoluminescence was investigated by varying the reaction time and concentration of Co doped in ZnS matrix. The intensity of luminescence first increased then decreased with increase of reaction time and concentration of Co and the detailed mechanism was discussed.

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1. Instruction

The synthesis procedure and optical properties of II-VI sulfide semiconductor nanomaterials have been intensity studied in the past decade due to their wide applications in photovoltaics, electroluminescence devices, bioimaging technologies, light emitting devices, catalysis and sensors, solar energy cells, etc [1-6]. Doping the impurities into nanomaterials is an effect approach for tuning the electronic, optical, mechanical and magnetic properties of matrix nanomaterials [7-11]. ZnS is a prominent sulfide semiconductor with wide band gap (3.66ev) and has important applications in photoluminescence (PL), electroluminescence (EL) and cathodoluminescence (CL) devices compared to other chalcogenides such as ZnSe, HgS, PbS [12-14]. Nano-sized ZnS doped with various transition metal ions such as Mn, Cu, Ag has attracted great deal of attention in view of advanced electronic and optoelectronic properties different from that of bulk materials [10,11,15]. For example, Li Ya-dong et al. have prepared luminescent ZnS: Mn one dimensional nanostructures by halid-transport chemical vapor deposition method, the prepared products show strong tunable PL emission from blue to green and yellow-orange emission, which is caused by the doped elements into ZnS nanowires and nanobelts [16]. Geng Baoyou et al. have synthesized ZnS: Cu nanorods by a solution phase thermal decomposition molecule precursor route and studied the doped ZnS nanocrystals optical properties [17].

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Recently, various synthetic schemes have been developed for the size- and shape-controlled doped ZnS nanocrystals such as high temperature solid phase sintering, chemical vapor transport method, sonochemical method, microwave irradiation, colloidal synthesis, solvothermal, hydrothermal and soft template routes *etc* [18-21]. Among these synthesis methods, hydrothermal route has attracted considerable attention because it requires a relatively low temperature, as compared to the traditional methods mentioned above, the reaction system is closed, which can effectively avoid oxidation phenomena and environmental pollution. In this paper, we adopt a method of hydrothermal to prepare Co-doped ZnS nanocrystals and investigate their optical properties by Uv-vis adsorption and photoluminescence (PL) spectroscopy. X-ray diffraction (XRD) and transmission electron microscopy (TEM) have also been carried out to study the structure and morphology of the ZnS: Co nanocrystals.

2. Experimental section

Zinc acetate, cobalt acetate and thioacetamide (TAA) were purchased from Sinopharm Chemical Regent Co., Ltd, China. All chemicals were of analytical reagent grade without further purification. In a typical process, 1mol·L^{-1} zinc acetate 5mL and 0.01 mol·L^{-1} cobalt acetate solution were mixed with different mole ratio (Mn^{2+}: Zn^{2+}=0, 0.02%, 0.04%, 0.2%, 0.4%, 0.8%), sodium polyphosphate (2.5g) deionized water solution was prepared and transferred to above solution. The mixed solution was further magnetically stirred for 1h. Then TAA solution was added into as-prepared solution with vigorous stirring for 30min and mole ratio of Zn: S was 1:1.15. Total volume of solution was 50mL. The final suspension was transferred to a Teflon vessel, heated in an oven at 150℃ for 3h. To obtain ZnS: Co nanocrystals, the collected solid-state products high speed centrifuging at 12,000rpm, were washed with deionized water and ethanol, then dried in a vacuum at 50℃ for 24h.

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8Advance X-ray powder diffractometer with graphite monochromatized Cu Kα (λ=0.15406nm). A scanning rate of 0.05 deg/s was applied to record the pattern in the 2θ range of 20~70°. The morphological features of the ZnS: Co nanocrystals were observed on a JEOL JEL-100 transmission electron microscopy (TEM) operated at 300kv. To prepare TEM samples, a 5μL droplet of dilute alcohol solution was dripped onto a carbon coated cooper grid and then dried at room temperature. A Shimadzu UV-2550 ultraviolet-visible (UV-vis) spectrophotometer was used to carry out optical absorbance measurements, samples were placed in quartz cuvettes (1cm path length). A Hitachi F7000 instrument was used to record the photoluminescence (PL) spectra.

3. Results and discussion

Fig. 1 shows X-ray diffraction (XRD) patterns of ZnS nanocrystals and ZnS: Co (0.02%-0.8%) nanocrystals. It reveals that the as-synthesized nanocrystals are cubic zinc blende phase of ZnS (JCPDS NO. 05-0566) and these features correspond to the {111}, {220} and {311} planes, which show obviously broad result from quantum-size effect of nanoparticles. It can be found that Co doping do not change crystalline structure of ZnS nanocrystals. The crystalline sizes of the ZnS and ZnS: Co nanoparticles can be calculated by Scherrer's equation below

$$D = \frac{k\lambda}{\beta\cos\theta}$$

where D is the mean crystalline size, k is the constant (shape factor), λ is the X-ray wavelength (1.54056 Å for Cu-Kα)， β is the full width at half maxium (FWHM) of the diffraction peak and θ is the Bragg diffraction angle. The estimated average sizes are 4.27nm (ZnS), 4.49 nm (0.02%), 5.22nm (0.2%) and 5.16nm (0.8%) respectively.

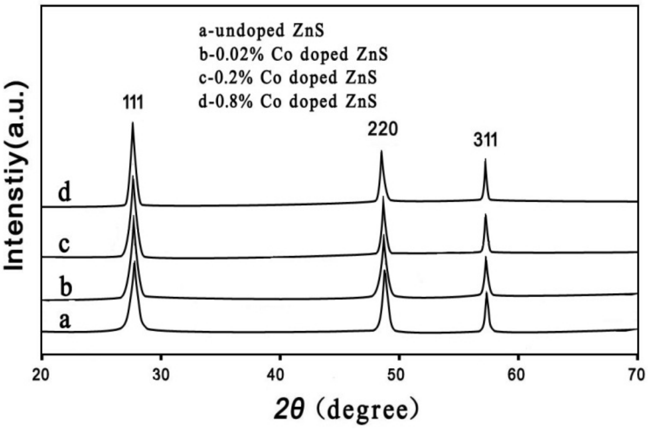

Fig. 1 XRD patterns of ZnS and ZnS: Co nanocrystals.

The representative TEM micrograph of undoped and 0.4% Co doped ZnS nanoparticles are shown in Fig. 2(a) and (b). From the figures, undoped and Co doped ZnS nanoparticles are approximately spherical with average diameter 40nm and 35nm. The grain size of undoped and Co doped ZnS nanocrystals as calculated by Scherrer's equation is 4.2~5.2nm. The nanoparticles size of the sample estimated from the TEM pictures is much larger than that obtained from XRD data, which indicates the obtained products are polycrystalline particles.

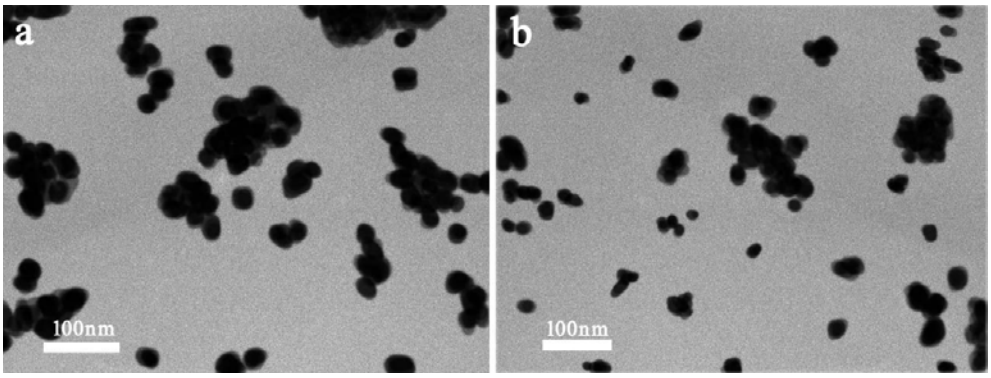

Fig. 2 TEM images of (a) undoped ZnS and (b) 0.4% Co doped ZnS nanoparticles.

Fig. 3 shows photoluminescence (PL) emission spectra for nanocrystalline ZnS: Co samples with different Co ion doped concentrations (0.02~0.8%). The emission maximum intensity was detected at wavelength of about 470 nm, excited by the 365 nm wavelength (λ_{ex}). From the spectra, the intensity of PL peak first increases with the increasing of Co ions from 0.02% to 0.4%. However, the intensity of the peak decreases when the content of doped Co ions is up to 0.8%. It is postulated that during the incorporation of Co ions into ZnS nanocrystals, the doping element, Co, has entered the lattice by substitution for Zn ions or occupation interstices of the lattice. The emission peak originates from the recombination of an electron from a shallow delocalized donor level just below the conduction band at the Co impurity. So the intensity of PL peak increases with increasing of doped Co ions. On the other hand, the excessive content of doped Co can result in fluorescence quenching in ZnS matrix.

The PL spectra of 0.4% Co doped ZnS nanocrystals with different reaction time (10min~4h) were determined (see in Fig. 4). From the figure, we can observe the intensity of PL peak at about 470nm first increase with reaction time from 10min to 3h, then decreases with longer time. The intensity reaches the highest value when the reaction time is 3h. With the increase of reaction time, the nanocrystals gradually grow which can reduce the defects of crystals. Radiationless transition resulting from defects of crystals decreases, which enhance the intensity of PL peak. Too longer reaction time, however, might enable Co ions diffuse to the surface of ZnS nanocrystals, which lead to direct quenching effect of luminescence. Finally, the intensity of PL peak comes to decrease.

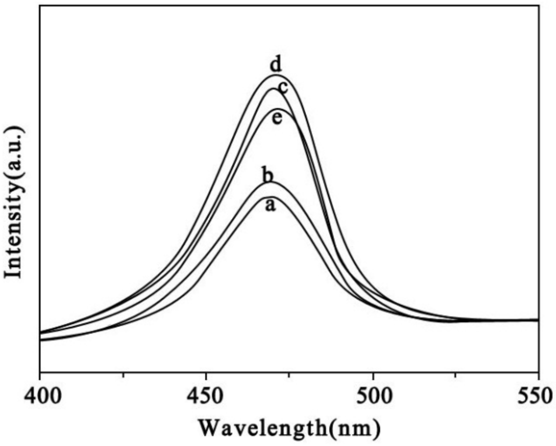

Fig. 3 Photoluminescence (PL) spectra of Co doped ZnS nanocrystals with different mole ratio a: 0.02%, b: 0.04%, c: 0.2%, d: 0.4%, e: 0.8%

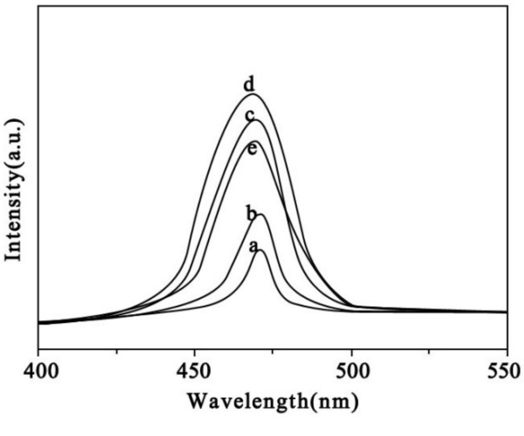

Fig. 4 Photoluminescence (PL) spectra of Co doped ZnS nanocrystals with different reaction time a: 10min, b: 30min, c: 1h, d: 3h, e: 4h.

Fig. 5 shows the UV–visible absorption spectrum of as-prepared 0.4% Co doped ZnS with 3h reaction time. On account of quantum size effect a broad absorption peak without maximum is observed. The band gap of semiconductors can be calculated by the followed formula

$$\alpha(v) = A(hv/2 - E_g)^{m/2}$$

where $\alpha(v)$ is the absorption coefficient and E_g is the band gap. A plot of $(\alpha E_{phot})^2$ vs. E_{phot} is constructed and the value of E_{phot} extrapolated to a=0 gives the band gap, E_g. The band gap of ZnS: Co nanocrystals calculated from formula is 3.79eV, which is blue shifted from that of bulk ZnS (3.66 eV) due to quantum confinement effects.

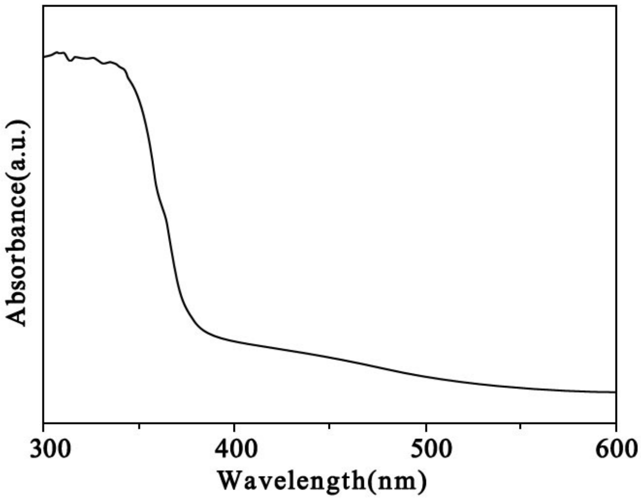

Fig. 5 UV-vis spectrum of Co doped ZnS nanocrystals

4. Conclusion

In summary, high-quality ZnS: Co luminescent nanoparticles have been synthesized using a facile method. XRD and TEM characterizations indicated that ZnS: Co nanocrystals have a cubic zinc blende structure with average diameter 35~40nm. The maximum peak of photoluminescence (PL) spectra was at about 470nm and the intensity changed with different reaction condition. UV-visible absorption spectrum showed the strong blue shift in absorption edge compared to bulk materials due to size quantum effect. These as-prepared nanocrystals can be potentially used as labels for biological macromolecules and important application in optoelectronic devices.

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