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Preparation of well uniform-sized and monodisperse ZnS nanoballs by γ-irradiation method

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Abstract

Well uniform-sized and monodisperse ZnS nanoballs with an average diameter about 120 nm were synthesized through γ-irradiation route by controlling appropriate irradiation time under ambient pressure and at room temperature. The products are characterized by field emission scanning electron micrograph (FESEM), transmission electron microscope (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectrometry (XPS). The influencing factors for the uniform-sized ZnS nanoballs e.g. irradiation time (dose), and pressure were also primarily investigated.

Keywords: ZnS; Nanoball; γ-irradiation; Monodisperse

1. Introduction

There is considerable interest on the fabrication of uniform-sized nanoballs. As one of the promising materials, Zinc sulfide (ZnS) nanoballs are attracting great attention and widely studied. ZnS, a direct wide band gap transparent semiconductor, is used in photonics research [1–3], and also has a variety of applications such as electroluminescent devices, solar cells, and other optoelectronic devices [4–6]. The most notable feature of nanosized ZnS particles is that its physical and chemical properties dramatically differ from that observed from bulk solid semiconductor, i.e. nanoparticles exhibit wider energy gap and quantum size confinement.

ZnS nanoparticles have been synthesized successfully via different preparation methods, including solid-state reaction, sol-gel process and hydrothermal method [7–9]. The γ-ray irradiation method, as a promising method, has been extensively used to prepare nanocrystalline metal, semiconductor hollow sphere, alloy, metaloxide, composites and metal sulfide in recent years [10–14]. In comparison with the other preparation method, the great advantage of this method is that the experiment can be carried out at very mild conditions, such as ambient pressure, room temperature and so on. In this letter, we report a simple and efficient method of preparing monodisperse and well uniform-sized ZnS nanoballs by γ-irradiating $ZnCl_2$, $Na_2S_2O_3{\cdot}5H_2O$ and polyvinyl pyrrolidone (PVP) mixed aqueous solution. The nanoballs were found to have a narrow size distribution when irradiation time was 24 h under ambient pressure at room temperature. Moreover, the influencing factors, like irradiation time (dose), the pressure, to the formation of ZnS nanoballs were studied.

2. Experimental

All chemical compounds used in the experiments were purchased from China Medicine Group, Shanghai Chemical Reagent Corporation, and used without further purification. Home-made high pressure reaction cell filled with high purity of N_2 (Maximum 80 atm) was used in our experiment. Solutions were prepared by dissolving an appropriate amount of analytically pure 1.36 g of $ZnCl_2$, 2.48 g of $Na_2S_2O_3{\cdot}5H_2O$, 0.75 g of PVP and 50 ml distilled water. After vigorously stirred for about 1 h at room temperature, solutions were then irradiated in the field of 2.59×10^{15} Bq ^{60}Co γ-ray source with a dose of 133.06 kGy. After reactions are finished, the white powders obtained were collected by centrifugation and washed with ethanol and distilled water several times till the final products had high purity. By keeping other conditions the same as above,

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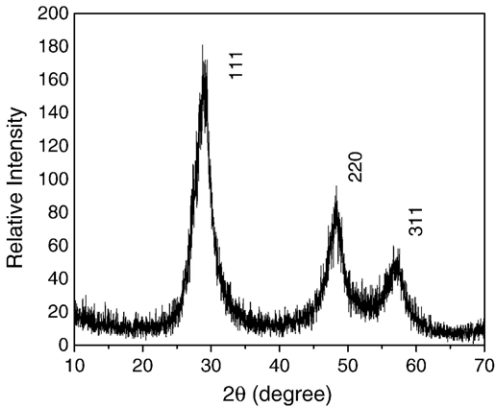

Fig. 1. XRD pattern of as-grown ZnS nanoballs.

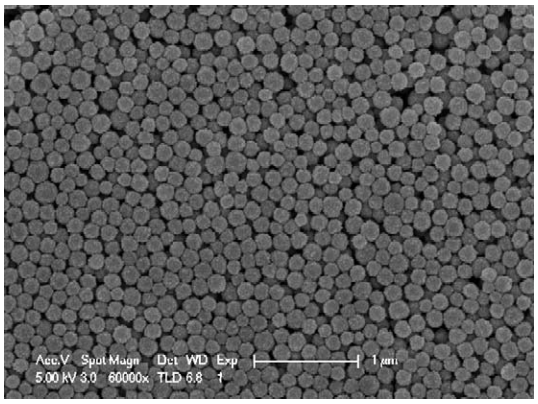

Fig. 3. FESEM image of as-grown ZnS nanoballs.

we also carried out parallel experiments by changing different irradiation times, or by changing different pressures.

The transmission electron microscopy (TEM) studies were carried out on a Hitachi Model H-800 (Japan) apparatus with an accelerating voltage of 200 kV. Field emission scanning electron micrography (FESEM) was carried out on a JEOL JSM-6700F. X-ray powder diffraction (XRD) patterns were collected on a Japan Rigaku D/max rA X-ray diffractometer equipped with graphite monochromated high-intensity Cu-Ka radiation ($\lambda = 1.5418$ Å). The accelerating rate was 0.06° S^{-1} in the 2θ range of 10°–70°. Further evidence for the composition of the product was inferred from X-ray photoelectron spectroscopy (XPS), using an ESCALab MKII X-ray photoelectron spectrometer with Mg Ka X-ray as the excitation source. The binding energies in XPS analysis were corrected by referencing C1s to 284.60 eV.

3. Results and discussion

XRD has been used to characterize the phase purity of the as-prepared product. Fig. 1 shows representative XRD pattern of as-grown products. It displays the overall phase composition purity of the products. The strong diffraction peaks at $2\theta = 28.9°$, 48.1° and 56.6° are assigned to (111), (220) and (311) planes of ZnS nanoballs, in which exhibit pure zinc blende crystal structure [15,16].

To further ascertain the phase of the final product, the XPS spectra of the sample were measured. In the survey spectrum (Fig. 2a) of the product, it shows the presence of Zn and S. The existence of C(1s) peak may be caused by the residual solvent or gas molecules, such as CO_2, absorbed by the surface of the sample. Higher resolution spectra of Zn and S regions are shown in the Fig. 2b and c. The centers of electron-binding energy of Zn($2P^3$) and S(2P) are 1022.80 and 162.70 eV, respectively, which are in a good agreement with the literature values [17]. All these indicate that the valence states of elements Zn and S are +2 and −2, respectively. Therefore, we can make sure that the product is ZnS through analyzing the XPS spectra and the XRD pattern of the as-grown product.

Fig. 3 shows FESEM of the products obtained for 24 h irradiating time under ambient pressure and at room temperature, it's clear that the products are nanoballs. The average diameter of the multi-layers monodisperse and uniform-sized nanoballs is about 120 nm. ZnS nanoballs are randomly and homogeneously distributed in all areas. These nanoballs were further examined by TEM. Fig. 5a shows a typical TEM photograph of ZnS nanoballs with well uniformity and monodispersed.

By changing irradiation time or adjusting the reaction pressure, we try to get better experimental conditions for the control of uniform-sized and monodisperse ZnS nanoballs. Fig. 4 shows experimental results carried out with different radiation times. The irradiation time was controlled for 6, 18, 24 and 30 h, and corresponding to the radiation doses 66.53 , 99.79, 133.06 and 166.33 kGy, respectively. It's found that the uniformity of the nanoballs was better when the radiation time was 24 h. The longer the irradiation time was, the larger the size of ZnS nanoballs formed was. The uniformity of nanoballs changed with the radiation time while keeping other conditions the same. Fig. 5 shows the TEM images and ED patterns of ZnS nanoballs under different pressures. It is observed that the size of the nanoballs (average diameter about 50 nm) under 40 atm is smaller than that (average diameter about 120 nm) under ambient pressure. The ED pattern in Fig. 5(b,d) shows the diffraction rings of ZnS, which can be characterized as 111, 200 and 311 diffraction from inner to outer. It is clearly shown that the diffraction rings of the product produced under 40 atm are stronger than those under ambient pressure, which indicates again that the size of nanoball at high pressure is smaller than that at low pressure. On the basis of the results of ED and TEM observed above, it's believed that the reaction pressure might affect the size of nanoballs.

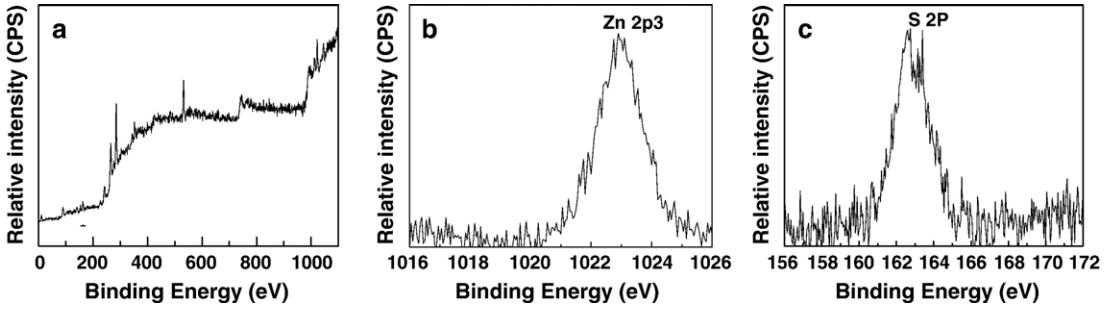

Fig. 2. XPS spectra of as-grown ZnS nanoballs: survey spectrum (a); Zn ($2P^3$) binding energy spectrum (b); S (2P) binding energy spectrum. (c).

The possible reaction processes for the formation of ZnS nanoballs could be described as follows:

$$H_2O \xrightarrow{\sim\sim} e^-_{aq}, H_3O^+, H\cdot, H_2, \cdot OH, H_2O_2 \quad (1)$$

Here, the symbol ($\sim\sim$) stands for irradiation and e^-_{aq} represents hydrated electron.

$$e^-_{aq} + S_2O_3^{2-} \rightarrow S^- + SO_3^{2-} \quad (2)$$

$$e^-_{aq} + S^- \rightarrow S^{2-} \quad (3)$$

$$Zn^{2+} + S^{2-} \rightarrow ZnS\downarrow \quad (4)$$

And then, the growth of the seeds continues whether the ZnS grows on the seeds (growth in a supersaturated solution), or by the process of Ostwald ripening whereby larger seeds grow at the expense of the smaller ones [18–20]. Generally speaking, if the main process of the nanoparticle growth is Ostwald ripening, there is a change in the nanoparticle size distribution with time or pressure. For the ZnS growth in this case, it's believed that the process of Ostwald ripening is dominant. Because when the irradiation time or the pressure was altered, the size of ZnS nanoballs was changed. As to why the pressure was adversely proportional to the size of ZnS nanoballs (<50 atm), it was not very clearly understood here, but one reason was probably that the chemical potential was not profitable for the growth of ZnS seeds in higher pressure.

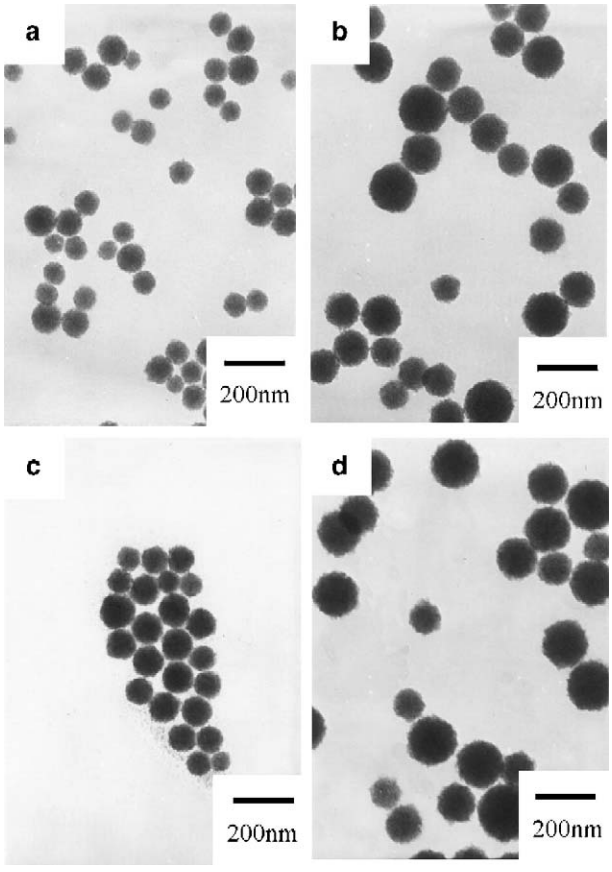

Fig. 4. TEM images of ZnS nanoballs at 1 atm. The radiance time is 6 h (a), 18 h (b), 24 h (c) and 30 h (d), respectively.

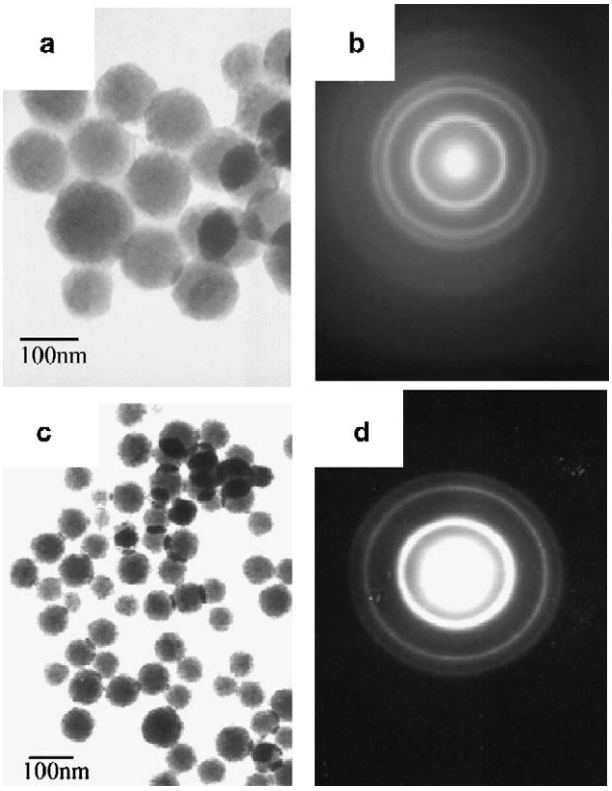

Fig. 5. TEM images of ZnS nanoballs at 1 atm (a) and 40 atm (c). ED patterns of ZnS nanoballs at 1 atm (b) and 40 atm (d).

4. Conclusion

In summary, highly monodisperse and uniform-sized ZnS nanoballs with an average diameter of 120 nm were successfully synthesized by a simple and effective γ-irradiation method. Moreover, the influencing factors for the formation of ZnS nanoballs, e.g. irradiation time, the pressure, were studied. It was found that irradiation time played an important role in the formation process of monodisperse and uniform-sized ZnS nanoballs, and the pressure affected the size of the ZnS nanoballs. Synthesis method used here may stimulate technological interest and also may prospect many applications in materials fields.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matlet.2006.04.017.

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