Preparation and characterization of nano ZnS by ion exchange resin method

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Abstract. D113 macroporous ion exchange resins were used as the supplier of Zn\textsuperscript{2+} ions and the regulator of ZnS morphology to prepare nano ZnS materials. The morphology and structure of the products were researched using the traditional batch method including Na\textsubscript{2}S concentration, temperature and resin addition time. Some means of characterization, such as SEM, XRD and FT-IR, were adopted well. The results showed that when Na\textsubscript{2}S concentration was lower for 0.05 mol/L, the product is well dispersed, showing a fine nano-particle size of about 100 nm; and when Na\textsubscript{2}S concentration was higher for 0.3 mol/L, the products liked a multi-petal flower in bloom with a thickness of less than 100 nm. When the reactive temperature was 30 °C, the characteristic diffraction peak has higher intensity and wider half-peak width. Under the resin addition time of 5 min, the product is mainly needle-like, like a cluster of pine leaves. When the resin addition time reached 20 min, the products showed a flaky structure. FT-IR was positively used to confirm the feasibility of this method.

1. Introduction

As a II – VI semiconductor compound material, Zinc sulfide (ZnS) has attracted wide attention[1], showing remarkable versatility and promise for novel fundamental properties and diverse applications, including light-emitting diodes (LEDs)[2], sensors, lasers[3], infrared windows[4], electroluminescence[5], and flat panel displays[6], etc. In addition, some elemental or inorganic materials are doped in ZnS, which makes the application of ZnS wider, such as ZnS/Cu, ZnS/Mn, ZnSe/ZnS, CdSe/ZnS, etc.[7-9]. When ZnS is prepared into nanometer size, the application range of ZnS is further expanded. This is due to the nonlinear optical properties, luminescent properties, quantum size effects and other important physical and chemical properties[10,11] of nano ZnS materials. Nano ZnS materials have many excellent properties in the fields of electricity, magnetism, optics, mechanics, catalysis and so on [12-16]. These excellent properties largely depend on the size of ZnS nanoparticles. Therefore, the preparation of ZnS nanoparticles with different particle sizes and narrow distribution becomes a frontier research topic in inorganic inorganic materials chemistry. At present, there are many preparation methods of ZnS, including ion exchange reaction method, chemical precipitation method, microemulsion method, hydrothermal method and so on[17-19]. These methods have the problems of complex operation, large energy consumption, and complicated follow-up treatment.
In this paper, D113 macroporous ion exchange resins were adopted as the supplier of Zn$^{2+}$ ions to prepare nanostructure ZnS materials, they were also as the regulator of ZnS morphology because of the special internal structure of ion exchange resins. In the process of preparation, the operation was simple, the energy consumption was lower, the products and the resins could be separated quickly. By controlling the amount of resins, the product could be directly further applied without washing. In addition, in view of the recyclability of ion exchange resins, the resins could be recycled repeatedly. The traditional batch method was used, and the effects of Na$_2$S concentration, temperature and resin addition time on nano ZnS were discussed systematically and in detail. Moreover, the effects of experimental conditions on the products were fed back from the microscopic perspective by means of multiple characterizations.

2. Experimental

2.1. Preparation

All of the chemical reagents used in this work were analytical grade and were obtained from the Chinese Xilong Chemical Co., Ltd. D113 resins used were purchased from Chemical plant of Nankai University. Table 1 summarized the physical and chemical properties of the D113 resins selected. Deionized water was used in all of the experiments. Firstly, the ion exchange resins were pretreated to make them into Na form, and then reacted with a certain concentration of ZnSO$_4$ to prepare resins in Zn form. A certain concentration of Na$_2$S solution was placed in a grinding cone bottle, and then the conical bottle was placed in a constant temperature water bath oscillator. The resins in Zn form were added into batches in the case of excessive resin. The concentration of Na$_2$S solution was changed for 0.05, 0.1, 0.2, 0.3 mol/L, the adding time of resins was controlled within 5, 8, 12, 20 min, and the oscillating temperature was kept at 20, 30 $^\circ$C, respectively. With the continuous addition of resins, the solution gradually became cloudy, which attributed to the ZnS suspension. After adding all the resins, the oscillating reaction lasted 60 minutes for better nucleation and growth. Finally, the resins and the suspended solids were separated through a filter net. The suspended solids were collected and dried under 80 $^\circ$C for further study, and the separated resins were used for the following experiment in view of their recyclability[20]. The related reaction equations are shown in formulas (1) and (2).

| Items                      | Properties                                           |
|----------------------------|------------------------------------------------------|
| Name                       | D113                                                 |
| Polymer structure          | Macroporous weak acid acrylic acid                   |
| Functional group           | -COOH                                                |
| Total exchange capacity    | (a) $\geq$ 10.8 mmol/g (dry, H form); (b) $\geq$ 4.2 mmol/mL (wet, H form) |
| Physical form              | Milky or yellowish opaque spherical beads            |
| Effective size (mm)        | 0.315-1.25                                           |
| Maximum service temperature ($^\circ$C) | 100                                                 |
| pH range of application    | 5-14                                                 |

2.2 Characterization

After the reaction, the morphology of the dried powdered solid was observed and analyzed through Scanning Electron Microscope (SEM, JSM-6360LV, JEOL, Japan). Effective components of the dried solid were then determined with an Empyrean X-ray Diffraction spectrometer (XRD, D8 Advance, Bruker, Germany). The products synthesized under the optimal reaction conditions were analyzed and characterized by Fourier Transform Infrared Spectroscopy (FT-IR, PerkinElmer, USA).
3. Results and discussion

3.1 Effect of Na2S concentration

3.1.1 SEM

Figure 1 and 2 are SEM diagrams of ZnS prepared at concentration of 0.05, 0.1, 0.2, and 0.3 mol/L, the former magnification is 5000, while the latter is 10000. The micro-morphology of the product can be observed from the SEM diagram so as to judge the effect of Na2S concentration on the micro-morphology of the product.

![Figure 1](image1)

**Figure 1.** SEM diagrams of products prepared under different Na2S concentrations (Magnification: 5000, A: 0.05mol/L; B: 0.1mol/L; C: 0.2mol/L; D: 0.3mol/L)

![Figure 2](image2)

**Figure 2.** SEM diagrams of products prepared under different Na2S concentrations (Magnification: 10000, A: 0.05mol/L; B: 0.1mol/L; C: 0.2mol/L; D: 0.3mol/L)

As can be seen from Figure A, the product is well dispersed, showing a fine nano-particle size of about 100 nm; Figure B shows that the product tends to agglomerate between small particles, from the previous plain into gullies or hills, which is especially clear from Figure 2-B; Figure C also shows a certain agglomeration, which appears sheet structure adsorbed on the surface of a massive solid, like clusters of lush grass carved in relief technique on the material surface; Figure D looks particularly interesting under Na2S concentration of 0.3 mol/L, it likes a multi-petal flower in bloom with a thickness of less than 100nm as shown in Figure 2-D.

In the internal of macroporous ion exchange resins, there are many channels. At the same time there are a large number of exchangeable ions in the interior wall of channels and in the exterior surfaces of resin particles, as shown in Figure 3. At a certain time and temperature, when the ion exchange resin was excessive and the concentration of Na2S is low, S2- ions could diffuse freely into the resin channels, react with the free Zn ions to form ZnS precipitation, and then the solid quickly passed through the channels, entered into the solution, and became a suspension. With the increase of Na2S concentration, a large number of ZnS particles were formed in the resin channels, and the collision probability of ZnS particles increased, which caused "congestion" and eventually led to agglomeration. At the same time, a part of S ions and Zn ions met and combined on the surface of resin particles, and the smooth surface of the resins provided a powerful place for product formation, which led to the formation of sheet structures. On the one hand, the macroporous resins used could provide sufficient exchangeable ions with large ion exchange capacity. On the other hand, the special channel structure in macroporous resins could restrain the growth of the product and regulate their morphology [21].

3.1.2 XRD

Figure 4 shows XRD curves of ZnS prepared under Na2S concentration of 0.05, 0.1, 0.2, and 0.3 mol/L. It can be seen from the figure that the characteristic peaks at 2θ = 28.6, 33.2, 47.6, 56.4 marked as asterisk belong to ones of ZnS, the position and intensity of the diffraction peaks are basically the same as those of PDF card No.65-0309, which is ascribed to sphalerite structure. With the decrease of
concentration, the intensity of characteristic diffraction peak increases and the width of peak widens, indicating that ZnS crystal structure is better and the particle size is smaller at low Na$_2$S concentration. Meanwhile, when the concentration of Na$_2$S is 0.05 mol/L, there are no other impurity peaks, which explain that the product is a single cubic sphalerite structure with high purity. Therefore, taking into account the above SEM results, Na$_2$S concentration of 0.05 mol/L is more suitable.

3.2 Effect of temperature

3.2.1 SEM

Figure 5-A and -B are SEM diagrams of products prepared at reaction temperature of 20 and 30 ℃, respectively. It can be seen from Figure 5-A (20 ℃) that the agglomeration of the products is serious and the morphology is poor. However, when the reaction temperature is raised to 30 ℃, the regular lamellar structure appears, pieces of ZnS products are stacked together, and the agglomeration is greatly improved. This is due to the low ambient temperature could slow down the dissociation rate of Zn$^{2+}$, Na$^+$, S$^{2-}$, etc. in the solution, while the product could not quickly leave the channels and surface of resins, and then the deposition and agglomeration occurred. Conversely, the higher ambient temperature was conducive to dispersion and molding of products.

3.2.2 XRD

Figure 6 presents XRD curves of ZnS prepared under 20 and 30 ℃. This figure indicates that the XRD spectra obtained at different temperatures have certain impurity peaks, and the peaks marked in asterisks are characteristic peaks of ZnS. The position and intensity of the diffraction peaks are basically the same as ones of PDF card No. 65-0309, which is sphalerite structure. The sharp peak shape at 20 ℃ indicates that the crystal size was larger, while the characteristic diffraction peak at 30 ℃ has higher intensity and wider half-peak width, and the characteristic peak is very obvious. In addition, combined with the analysis results of Figure 5, 30 ℃ is confirmed to be an optimal reaction temperature.
3.3 Effect of resin addition time

3.3.1 SEM

Figure 7. SEM diagrams of products prepared under different resin addition time (Magnification: 5000, A: 5min; B: 8min; C: 12min; D: 20min)

Figure 8. SEM diagrams of products prepared under different resin addition time (Magnification: 10000, A: 5min; B: 8min; C: 12min; D: 20min)

Figure 7 and 8 are SEM diagrams of ZnS prepared under resin addition time of 5, 8, 12, and 20 min at 30 °C, the former magnification is 5000, while the latter is 10000. As can be seen from Figure A, the product is mainly needle-like, the needle tip size is less than 100 nm, and the length is more than 5 μm, like a cluster of pine leaves. In Figure B, needle-like structures can still be observed, but most of the needle tips are bent, their size is basically the same as one of the product shown in Figure A. Figure 7-C shows a clear agglomeration, resulting in an obscure boundary, but in Figure 8-C a small number of slender needle-like structures can be seen. Figure 7-D shows a photo of the resin addition time for 20 min. The size of the product is significantly larger than before, showing a flaky structure, which is more obvious from Figure 8-D, just like the petals of a chrysanthemum flower. In short, the morphology of the product changes with the different addition time of resin. Therefore, the resin addition time is one of the key factors affecting the morphology of the product.

As the resin is gradually added, the S\(^{2-}\) ions in the solution react with the Zn\(^{2+}\) ions which are exchanged by Na\(^{+}\) from the resin to form ZnS. The supplying rate of Zn\(^{2+}\) ions is controlled by the resin addition rate and reaction temperature. The resin addition rate can be controlled by adjusting the resin addition time after determining the amount of resin added and reaction temperature. The shorter the time of resin addition just as 5 min, the faster the supplying rate of Zn\(^{2+}\) ions is and the faster the nucleation rate is, at the same time the nucleation rate is obviously higher than that of the nucleus growth, which makes the product size smaller. When the resin is added for a long time just as 20 min, the supplying amount of Zn\(^{2+}\) ions in unit time is less, the nucleus growth rate is faster, and it is easier to get larger size products.
3.3.2 XRD

Figure 9 exhibits XRD curves of ZnS prepared under different resin addition time at 30 °C. It is distinct that the characteristic peaks at $2\theta = 28.6, 33.2, 47.6, 56.4$ marked as asterisk belong to ones of ZnS, which is ascribed to sphalerite structure. With the increase of time, the intensity of characteristic diffraction peak decreased and the width of half-peak narrowed, which indicated that the structure of ZnS crystal obtained was better and the grain size was smaller when the resin was added in shorter time. Combining the analysis results of Figure 7 and 8, it is concluded that 5 min is the optimal resin addition time for preparing ZnS materials in this work.

3.4 Characterization of FT-IR

FT-IR of products prepared under the optimal reaction conditions including Na$_2$S concentration of 0.05 mol/L, 30 °C, and resin addition time of 5 min, is shown in Figure 10. The peaks at 1647 and 2865 cm$^{-1}$ are attributed to the absorption peaks of water molecules, the former is the bending vibration of H-O-H, and the latter is the antisymmetric stretching vibration of O-H. The strong vibration absorption peaks near 1121, 996, 626 cm$^{-1}$ belong to ZnS. In addition, there is no tensile vibration peak corresponding to ZnO in the FTIR spectra between 420 and 460 cm$^{-1}$, which indicates that no oxidation reaction occurs to form ZnO during the preparation process and the stability is better. So it is further confirmed that ZnS could be obtained successfully by using ion exchange resins through FT-IR characterization. This method is particularly feasible.

4. Conclusions

In this paper, nanostructured ZnS materials were successfully prepared by ion exchange resin method. The effects of Na$_2$S concentration, temperature and resin addition time on the products were systematically discussed, and the prepared materials were characterized by SEM, XRD and FT-IR. The results showed that with the increase of Na$_2$S concentration, the products gradually tended to agglomeration from the dispersed state. Under Na$_2$S concentration of 0.3 mol/L, the products liked a multi-petal flower in bloom with a thickness of less than 100 nm. The reactive temperature and resin addition time affected the diffusion rate of exchanged ions, and then influenced the nucleation and growth rate of ZnS. With the increase of resin addition time, the products had different morphologies from needle-like structure to layered structure. In addition, XRD patterns indicated that the structure of ZnS crystal obtained was better and the grain size was smaller when the resin was added in shorter time. Finally, FT-IR of products prepared under the optimal reaction conditions further confirmed the feasibility of the ion exchange resins method for preparing ZnS.

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