One-step hydrothermal synthesis of shape-controlled ZnS-graphene oxide nanocomposites

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Abstract Shape-controlled ZnS–graphene oxide (GO) nanocomposites were successfully synthesized via an easy one-step hydrothermal method by changing the solvents. The sample prepared in ethyleneglycol and water (1:1 in volume ratio) yielded ZnS nanoparticles (NPs)–GO nano-composites. The sample prepared in ethylenediamine and water (1:1 in volume ratio) yielded ZnS nanowires (NWs)–GO nanocomposites. The sample prepared in ethylene-glycol, ethylenediamine and water (1:1:2 in volume ratio) yielded ZnS nanocomposites. The results showed that the GO in the composite were exfoliated and decorated with ZnS NPs, NWs and NRs. The photoluminescence intensity of the ZnS–GO nanocomposites exhibited a clearly quenching in comparison with that of ZnS.

1 Introduction

Graphene, as a new class of two-dimensional (2D) carbon material with a thickness of one atom, possesses excellent transparency (~97.7 %), superior mobility of charge carriers at room temperature (~10,000 cm² V⁻¹ s⁻¹) and

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D. Han · S. Yang Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Angeleric Changeleric 120022 Product relatively large surface area ($\sim 2,600 \text{ m}^2 \text{ g}^{-1}$), has received enormous attention for its potential applications in nanoelectronics, biosensors, supercapacitors, photocatalysts and transistors [1-5]. In the past few years, combining graphene oxide (GO) and semiconductors in one entity opens up broader avenues for improving its performance and developing novel optoelectronic devices [6-8]. Among these, zinc sulfide (ZnS) is an important wide band gap (Eg = 3.6 eV at 300 K) semiconductor, which is considered important for applications such as ultraviolet-lightemitting diodes, electroluminescent devices, flat-panel displays, sensors and injection lasers [9–13]. Numerous studies have demonstrated that assembling ZnS on GO can exhibit excellent electronical and optical performance [14-16]. Especially, the morphology of the ZnS/GO nanocomposites played an important role in determining the distribution of the carrier state density and affecting the carrier transport property [17-20]. Wang et al. [21] synthesized the ZnS quantum dot-graphene by the solvothermal method, which showed the interesting photovoltaic properties. He et al. [22] synthesized the novel ZnO nanowires (NWs)/reduced graphene oxide (RGO)/CdS quantum dot heterostructure via a facile three-step solution method, which possessed the enhanced photocatalytic activity. Therefore, understanding of the interaction between ZnS nanostructures [NWs, nanorods (NRs), nanoparticles (NPs)] and GO deeply will be beneficial to design and manufacture practical products. Up to now, the issue about how the morphology affecting the structure and optical properties of the ZnS-GO nanocomposites has still been blurry.

In recent years, researchers have not stopped trying to employ environmental friendly, simple and low-cost methods to fabricate the ZnS–GO nanocomposites. Herein, the shape-controlled ZnS–GO nanocomposites were

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successfully synthesized via an easy one-step hydrothermal method by changing the solvents, their structure and photoluminescence (PL) property were also investigated.

2 Experimental section

2.1 Materials

Zinc nitrate, thiourea, ethytleneglycol (EG), ethylenediamine (EN), graphite, sodium nitrate, sulphuric acid, potassium permanganate, hydrogen peroxide, hydrochloric acid are all analytical grade (Shanghai Chemical Reagents Co.), and used without further purification.

2.2 Preparation of graphene oxide (GO)

GO was prepared by a modified Hummers' method from flake graphite [23]. Briefly, 5 g of graphite were mixed with 5 g of NaNO₃ and 100 ml of H₂SO₄ under stirring for 1 h at 80 °C, and then the mixture was cooled to 0 °C in an ice bath. Then, 10 g of KMnO₄ were added slowly into the above mixture under stirring maintaining the temperature below 5 °C. The cooling bath was then removed and the mixture was stirred at 35 °C vigorously for 4 h. After that, 1,000 ml of deionized water were added, and the temperature was increased to 98 °C and kept there for 30 min. Then, 30 ml of 30 % H₂O₂ were added slowly till the color turned from brown to bright yellow. Finally, the as-prepared GO were washed alternately with 30 % HCl and deionized water until pH = 7, then dried at 60 °C for 24 h. 2.3 Preparation of ZnS/GO nanocomposites

In a typical process, 0.015 g of GO and 0.186 g of zinc nitrate were added into 20 ml of deionized water under stirring for 1.5 h and ultrasound for 1 h (solution A). 0.143 g of thiourea were put into the 20 ml of EG, EN, EG:EN = 1:1 under stirring for 2 h, respectively (solution B). Solution B was added to solution A drop by drop under vigorous stirring. After that, the mixture was transferred into a 50-ml Teflon-lined autoclave and kept at 180 °C for 12 h. After the reaction, the autoclave was taken out and cooled down to room temperature. The product was washed with ethanol and deionized water for several times and separated by centrifugation, and then dried at 60 °C for 1.5 h to get the powder. The scheme for the preparation of ZnS/GO nanocomposites can be seen in Fig. 1.

2.4 Characterization of products

X-ray diffraction (XRD) pattern was collected on a MAC Science MXP-18 X-ray diffractometer using a Cu target radiation source. Transmission electron micrographs (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken on JEM-2100 electron microscope. The specimen was prepared by depositing a drop of the dilute solution of the sample in ethanol on a carbon-coated copper grid and drying at room temperature. PL measurement was carried out at room temperature, using 325 nm as the excitation wavelength, He–Cd Laser as the source of excitation. The samples used for the XRD, PL measurements were solid power.



Fig. 2 XRD pattern of graphene oxide



Fig. 3 XRD patterns of ZnS and ZnS–GO nanocomposites synthesized in EG:W = 1:1; EN:W = 1:1; EG:EN:W = 1:1:2

3 Results and discussion

The XRD pattern of GO is shown in Fig. 2. The feature (001) diffraction peak of the GO appears at 10.3° with the interplanar spacing of 0.85 nm, which is much larger than that of the natural graphite (0.335 nm) [24–26], indicating the complete oxidation of the starting graphite [27]. The XRD patterns of the ZnS and ZnS–GO nanocomposites are shown in Fig. 3. All the diffraction peaks for the ZnS and ZnS–GO nanocomposites can be well indexed as the hexagonal wurtzite phase structure, which are consistent with the standard card (JCPDS No. 36-1450). It is possible to predict the growth direction by performing comparison of the full width at half maximum (FWHM) for different XRD peaks [28]. When the ratio of EG:W is 1:1, the



Fig. 4 a, b TEM and HRTEM images of ZnS–GO nanocomposites synthesized in EG:W = 1:1; **c, d** TEM and HRTEM images of ZnS–GO nanocomposites synthesized in EN:W = 1:1; **e, f** TEM and HRTEM images of ZnS–GO nanocomposites synthesized in EG:EN:W = 1:1:2

FWHM has no apparent change among all the diffraction peaks, indicating no change in the structural orientation and the formation of the NPs; When the ratio of EN:W is 1:1 and EG:EN:W is 1:1:2, the (002) diffraction peak is stronger and narrower than the other peaks, suggesting a preferential growth direction along the c-axis. Little difference among the diffraction peaks of ZnS and ZnS–GO nanocomposites also suggests that the presence of GO does not influence the crystal nature of ZnS. It may be due to the low amount of GO and relatively low diffraction intensity of GO in the ZnS–GO nanocomposites.

Figure 4 show the TEM and HRTEM images of the ZnS–GO nanocomposites. It can be seen that ZnS are well dispersed on the surface of the wrinkled GO. GO plays an important role in assisting ZnS dispersion on its surface, while ZnS helps to prevent the aggregation of GO. When the ratio of EG:W is 1:1 (Fig. 4a), the shape of the sample is ZnS NPs–GO nanocomposites. The HRTEM image

(Fig. 4b) shows that these NPs are well crystallized. When the ratio of EN:W is 1:1 (Fig. 4c), the shape of the sample is ZnS NWs–GO nanocomposites. The HRTEM image shows a well oriented and good crystallization in Fig. 4d. The displayed clear lattice spacing of 3.1 Å (Fig. 4d) is close to that of the wurtzite ZnS (002) plane. All of the evidence demonstrate that the growth direction of the NWs is (002), a preferential growth direction. When the ratio of EG:EN:W is 1:1:2 (Fig. 4e), the length of the NWs is decreased, the ZnS NRs–GO nanocomposites is formed. Also in Fig. 4a, c, d, the GO sheets can be clearly seen and the ZnS NPs, NWs and NRs is closely attached to the GO sheets, which indicates an intimate interfacial contact between the GO and ZnS.

So the ZnS NPs-GO nanocomposites would be formed in water and EG due to their inherent high symmetry in crystallographic structure. When using the mixture of EN and water as the reaction solvent, EN as a structure-directing agent will guide the growth of the crystal. Since EN can easily react with Zn and S to form the intercalated lamellar compound $ZnS \cdot EN_{0.5}$ [29], the zinc atoms in the compound are tetrahedrally coordinated by three sulfurs and one nitrogen from the EN molecule. During the hydrothermal process, solvent used would destroy EN from the complex, restrict the recrystallization process of the ZnS template, and the irregular shape would be formed [30–33]. For the hexagonal structure ZnS, the growth rate along the c axis under the action of EN is usually the fastest [34]. So, the anisotropic NWs would be formed in the mixture solution of the EN and water, which is consistent with the anisotropic wurtzite structure, i.e. the unique structural feature of the (001 h) facet and the existence of a 63-screw axis along the c-direction (Donnay–Harker law) [30, 35]. The decreased length of the ZnS NRs–GO nanocomposites (EG:EN:W = 1:1:2) compared with that of the ZnS NWs–GO (EN:W = 1:1) also prove the effect of the EN molecule on the growth of the ZnS NCs.

Figure 5 present the room temperature PL spectra of ZnS and ZnS-GO nanocomposites. The PL spectrum of ZnS (red line) is asymmetric. According to the energy diagram of the defects distributed in ZnS, the emission peaks can be attributed to the following origins: 418 and 450 nm to the sulfur vacancy and surface states [36, 37], 503 nm to the self-activated defect centers formed by the zinc vacancy inside the lattice [38], 541 nm to the sulfur species on the surface of ZnS NWs [39], the peak centered at 588 nm is rarely reported. Only Li et al. [39] observed the peak centered at 578 nm in the wurtzite ZnS NRs. The origin of this peak is still not clear and needs further study. The PL intensity of the above defects related emission in the ZnS NPs (EG:W = 1:1), NWs (EN:W = 1:1) and NRs (EG:EN:W = 1:1:2) is different. Since that the formation of the defects depends largely on the growth process by using different solvents, and the final morphology plays an



Fig. 5 Room temperature PL spectra of ZnS and ZnS–GO nanocomposites synthesized in EG:W = 1:1; EN:W = 1:1; EG:EN:W = 1:1:2

important role in affecting its optical properties [40]. Moreover, the PL intensity of ZnS–GO nanocomposites (black line) is much lower than that of ZnS, further proving the effective interfacial electron-transfer process between GO and ZnS. Since that GO is good electron acceptor and the excited ZnS is good electron donor, the interaction between GO and ZnS would lead to an increased transfer of the photogenerated electrons to GO [41] and reduce electron–hole pair recombination effectively.

4 Conclusions

In this paper, the shape controlled ZnS–GO nanocomposites were fabricated successfully by one-step hydrothermal method by changing the solvents used during the synthesis. When the ratio of EG:W is 1:1, the shape of the sample was ZnS NPs–GO nanocomposites. When the ratio of EN:W is 1:1, the shape of the sample was ZnS NWs–GO nanocomposites. When the ratio of EG:EN:W is 1:1:2, the length of the NWs was decreased, the ZnS NRs–GO nanocomposites was formed. The PL intensity of the ZnS– GO nanocomposites exhibited a clearly quenching in comparison with that of the ZnS.

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