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Solvothermal Synthesis of Superhydrophobic ZnS Film

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In this work, a superhydrophobic ZnS film was successfully synthesized by a simple solvothermal route using Zn foil and sulphur powder as raw materials in an absolute ethanol solution at 160 ºC for 24 h. The products were characterized by X-ray diffraction, energy dispersive spectroscopy, scanning electron microscopy and contact angle. Results show that the obtained films were high crystallinity and uniformity. A possible reaction mechanism was proposed and discussed. It is found that the ZnS film exhibits superhydrophobicity due to its special nanoflakes structure. The average thickness of the ZnS nanoflakes film is *ca.* 120 nm.

Key Words: Zinc sulphide, Nanoflake, Superhydrophobicity.

INTRODUCTION

Zinc sulfide (ZnS), as a kind of semiconductor from II-VI family has caused great attention due to its wide applications in different fields. Owing to wide band gap energy (E_g) of 3.7 eV at room temperature, large excition binding energy (60 meV) and small Bohr radius (2.4 nm), it can be used to fabricate optoelectric devices such as blue light-emitting diodes, optical coating, electroluminescence devices, photovoltatic devices, heterojunction solar cells, *n*-window layers and photoconductor[1-4]. Various techniques have been developed to prepare ZnS films, such as chemical bath deposition route[5], photochemical deposition technique[6], pulsed electrochemical deposition technique[7] and successive ionic layer adsorption and reaction method[8].

Recently, Wang *et al.*[9] reported a simple hydrothermal method for large-scale preparation fo ZnS nanoribbon film with high photocatalytic activity for dye degradation using Zn foil and S powder in hydrazine hydrate. Though the solvent of hydrazine hydrate is toxic, it opened a new way to *in situ* prepare ZnS film in a large scale. Followed by the idea, we use nontoxic anhydrous ethanol to replace hydrazine hydrate as a solvent to prepare ZnS film. Interestingly, a novel nanoflake structure was obtained, which shows excellent super hydrophobicity. To the best of our knowledge, this is likely to be the first report on the superhydrophobic property of ZnS film prepared by Zn foil and sulfur as raw materials.

EXPERIMENTAL

All chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and were used without further purification. In a typical procedure, a 1.5 cm × 1.5 cm Zn foil, pretreated by sonication in 0.1 M HCl solution and dried in air, was added to an autoclave (50 mL capacity) containing 35 mL anhydrous ethanol (dissolved with 0.12 g S powder). Then, the autoclave was sealed and put into an oven at 160 ºC for 24 h. After the solvothermal reaction, the foil was collected from the solution, rinsed with ethanol and water before it was dried at 80 ºC in a vacuum oven.

The crystal structure of the product was determined from the XRD, (type: Bruker D8 advance) meter with a Ni mono-chromator using Cu K_α radiation (λ = 1.5418 Å) in the range of 20-70 ºC at room temperature while the tube voltage and electric current were held at 40 kV and 40 mA. Morphology of the prepared ZnS film was studied by SEM, (type: Zeiss EVO LS-15), with an accelerating voltage of 15 kV equipped with an EDS. The contact angles were investigated by contact angle meter (Drop master 300, Kyouwa Interface (Co. Ltd).

RESULTS AND DISCUSSION

A typical XRD pattern of the resultant ZnS film is shown in Fig. 1. It is evident that strongest diffraction peak can be indexed to the cubic structure ZnS correspond to (002) (JCPDS card 1-792) except the signals of Zn foil from the substrate,

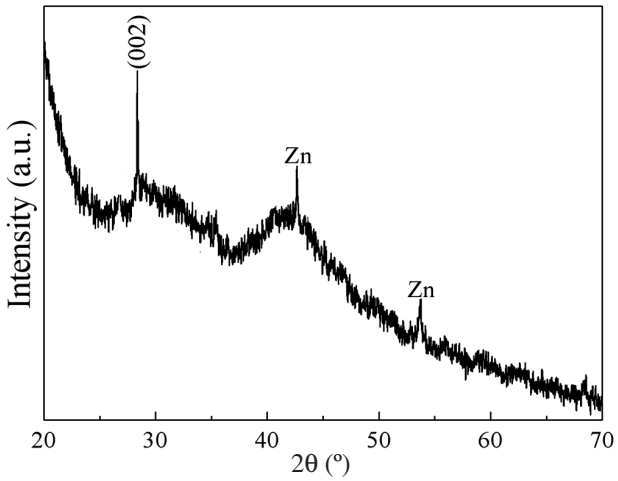

Fig. 1. XRD pattern of as-prepared ZnS film

which illustrates that the ZnS grew on the Zn foil has significantly preferred orientation in the direction of [0001]. The thickness of the nanocrystals (D) was calculated on the basis of the Scherrer formula, $D = \frac{k\lambda}{\beta \cos \theta}$, where k = 0.9 is the shape factor, λ is the X-ray wavelength of Cu K_α radiation (1.5418 Å), θ is the Bragg diffraction angle and β is the full width at half maximum (FWHM) of the (002) peak. The average nanocrystallite thickness of ZnS film was 125 nm. The composition of the obtained ZnS film is shown in Fig. 2 by the EDS analysis, which reveals the atomic ration (1:0.96) of ZnS and S in the products that is nearly equal to the stoichiometric ratio (1:1). The obtained ZnS on Zn foil is possible the result of the dissolution of the S powder, the transportation of the solvated S to the Zn foil and the production of ZnS *via* the S-Zn following reaction:

$$Zn(s) + S(l) \rightarrow ZnS(s)$$

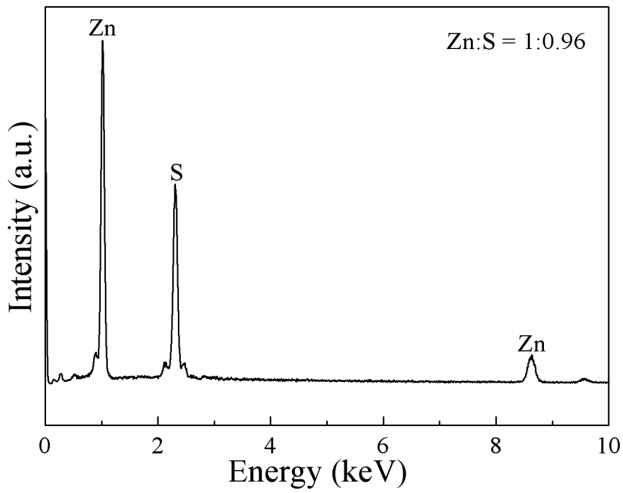

Fig. 2. EDS spectrum of as-prepared ZnS film

Fig. 3 shows the SEM morphologies of the as-prepared ZnS film. The ZnS film was mainly composed of many dense and uniform interconnected nanoflakes with the average thickness of *ca.* 120 nm. Most of the nanoflakes lie vertically to the substrate, which is consistent to the XRD result. The less thickness of the ZnS nanoflakes in [0001] direction (c-axis) indicated that the growth rate along the c-axis much higher than that along the Zn foil perpendicular to the c-axis. The anisotropic characteristics of the grow rate may attribute to the difference of the surface energy. The in-plane directions generally correspond to the lower surface energy. During this growth, the well-known oriented attachment (OA) mechanism[10] for the growth of a nanoflake microstructure by the condensation of nanocrystals drives the formation of the observed nanoflakes film. Previously, followed by the oriented attachment mechanism, our group have in-situ fabricated many semiconductive materials such as $AgSe_2$[11], CuSe[12], PbI_2[13] and Ag_2S[14]. More importantly, the novel structure reminded us to investigate the superhydrophobic property of the obtained film.

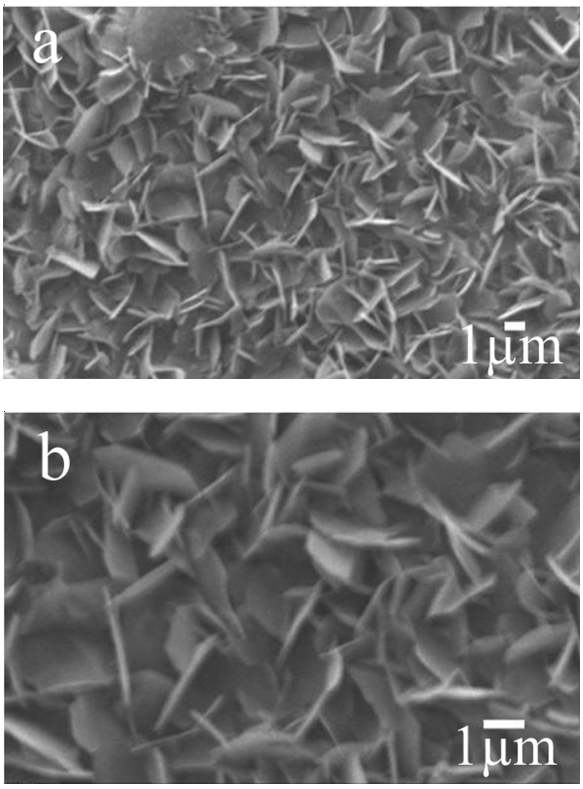

Fig. 3. SEM images of as-prepared ZnS film: (a) low magnification; (b) high magnification

Surface wettability of the prepared ZnS nanoflakes film was studied by contact angle measurement. When deionized water droplets *ca.* 5 μL were dropped on the surface, it yielded a nearly spherical shape at the microscopic level, as is shown in Fig. 4. The contact angle of Zn foil and ZnS film was *ca.* 75.4 ± 1.0º and 158.6 ± 2.0º, respectively. The super hydrophobicity of ZnS film exhibited a stable character in air with the contact angle showing no obvious change for a long time. Finally, the water droplet evaporated on the surface. Theoretically, a whole understanding of the super hydrophobicity phenomenon can be explained by the Cassie and Baxer equation[15]. For a composite surface, the water contact angle is affected significantly by the fractional areas of solid (f_1) *versus* air pockets (f_2): $\cos \theta = f_1 \cos \theta_1 - f_2$, ($f_1 + f_2 = 1$) where θ and θ_1 represent the water contact angles on rough and smooth surfaces, respectively. It is seen from the above equation that

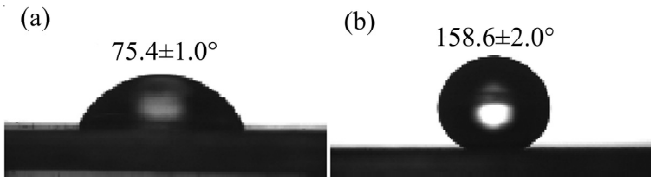

Fig. 4. Contact angles of (a) Zn foil and (b) as-prepared ZnS film

increasing the fraction of air (f_2) leads to increase of the contact angle on a rough surface (θ_r). According to the equation, the f_2 value of the Zn foil and ZnS film with nanoflakes microstructure is estimate to be 0.61 and 0.95, respectively. The larger fraction of air among the interspaces of the ZnS nanoflakes microstructure might contribute to the super hydrophobicity of the ZnS film, leading to the greatly increased air/water interface which is essential to super hydrophobicity and effectively prevent the penetration of water droplet into the interstices. It is revealed that the hierarchical and nanoflakes structure play an important role for preparation of super water-repellent structure.

Conclusion

In summary, the highly (002) oriented ZnS nanoflakes was synthesized by a simple solvothermal method using Zn foil and sulfur powder as raw materials in an absolute ethanol at 160 ºC for 24 h. The obtained film was high crystallinity and uniformity with novel nanoflakes microstructure. The average thickness of the ZnS nanoflakes is *ca.* 120 nm. It is found that the ZnS film exhibits super hydrophobicity due to the special nanoflakes structure.

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