

In Situ Fabrication of Superhydrophobic Zinc Sulfide Films on a Flexible Zinc Foil Substrate

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A superhydrophobic ZnS film was successfully fabricated by a simple solvothermal method using Zn foil and S powder as raw materials in an absolute ethanol solution at 160 °C for 8 h. The products were characterized by X-ray diffraction (XRD), energy-dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and contact angle (CA) measurements. The results show that the obtained ZnS film was hexagonal phase, composed of many dense and uniform interconnected nanoflakes of average thickness ca. 120 nm. A possible reaction mechanism was proposed and discussed. It was found that the ZnS film exhibits superhydrophobicity owing to its special nanoflake structure.

Zinc sulfide (ZnS), a semiconducting material from group II–VI, has attracted great attention because of its wide applications in different fields. Owing to its wide band gap of 3.7 eV, it can be used to fabricate optoelectric devices such as blue light-emitting diodes, optical coatings, electroluminescent devices, photovoltaic devices, heterojunction solar cells, n-window layers, and photoconductors.^{1–4} Various techniques have been developed to prepare ZnS films, such as chemical bath deposition,⁵ photochemical deposition techniques,⁶ pulsed electrochemical deposition techniques,⁷ and successive ionic layer adsorption and reaction methods.⁸

Recently, “in situ preparation” methods have been widely used to fabricate thin metal sulfide films because of their simplicity, low cost, and ease of control of morphology.^{9,10} For example, Lei et al.¹¹ reported a CuS nanosheet structure prepared in situ on a Cu foil substrate. Jia et al.¹² fabricated In₂S₃ nanoflake arrays for hybrid solar cells by an in situ method on a sputtered In coating on an ITO substrate. Usually, a metal foil or coating and a certain amount of S powder with an appropriate solvent are put in an autoclave, followed by hydrothermal treatment. Inspired by this idea, Wang et al.¹³ prepared a ZnS nanoribbon film with high photocatalytic activity for dye degradation by an “in situ growth” strategy using Zn foil and S powder in hydrazine hydrate solvent. However, hydrazine hydrate is toxic, so it is still necessary to find an environmentally friendly solvent to replace the toxic hydrazine hydrate solvent for in situ preparation of ZnS films on a large scale. Here, we use nontoxic anhydrous ethanol to replace hydrazine hydrate as the solvent for preparing ZnS films. Interestingly, a novel nanoflake structure was obtained, which shows excellent superhydrophobicity. To the best of our knowledge, this is likely to be the first report on the superhydrophobic properties of ZnS films prepared using Zn foil and S as raw materials.

The synthesis of the ZnS film was carried out using a solvothermal-assisted method. All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (analytical reagent grade; Shanghai, P. R. China). Typically, a 1.5 × 1.5 cm² 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 of anhydrous ethanol (with 0.12 g of dissolved S powder). Then, the autoclave was sealed and put into an oven at 160 °C for 8 h. After the solvothermal reaction, the foil was removed from the solution, rinsed with ethanol and water, and dried at 80 °C in a vacuum oven.

The sample was characterized by X-ray diffraction (XRD) (Bruker D8 Advance diffractometer) using a Cu K α radiation source, and scanning electron microscopy (SEM; Zeiss EVO LS-15). X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos AXIS-UI TRA system equipped with a standard and monochromatic source (Al K α). For all XPS measurements, the binding energy (BE) was calibrated against C 1s at 284.8 eV. The contact angles (CAs) were investigated using a CA meter (Drop Master 300, Kyouwa Interface Co., Ltd.).

A typical XRD pattern of the resultant ZnS film is shown in Figure 1. In order to avoid the diffraction peak of the Zn foil substrate, the fabricated ZnS film was scratched from the Zn foil substrate. It is evident that the strongest diffraction peak can be indexed to the hexagonal structure of polycrystalline ZnS, corresponding to (002) ($a = b = 3.777$ Å, $c = 6.188$ Å, JCPDS file No. 80-0007), which illustrates that ZnS grown on the Zn foil has a significantly preferred orientation in the [0001] direction. The composition obtained by energy dispersive spectroscopy (EDS) analysis of the scratched ZnS powder is shown in the inset of Figure 1; it reveals an atomic ratio (1:0.94) of Zn and S in the products that is nearly equal to the stoichiometric ratio (1:1). The obtained ZnS particles on the Zn foil possibly originated from dissolution of the S powder, transportation of the solvated S to the Zn foil, and the production of ZnS via the following S–Zn reaction: Zn(s) + S(l) → ZnS(s).

The surface element composition of the prepared ZnS film was also studied by XPS analysis, as shown in Figure 2. In the XPS measurements, the BE scale was calibrated against the BE of C 1s at 284.8 eV. In Figure 2a, there are two separate peaks at

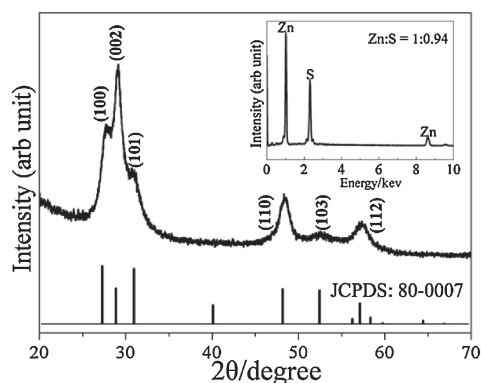


Figure 1. XRD pattern and (Inset) EDS spectrum of ZnS particles scratched from the Zn foil.

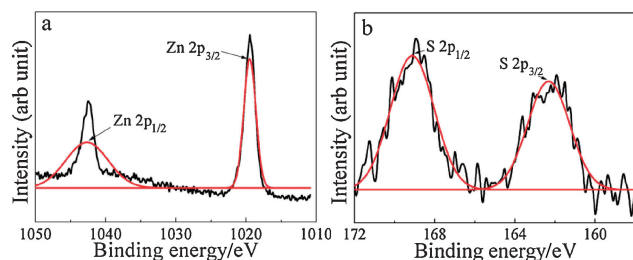


Figure 2. XPS spectrums of the prepared ZnS film: (a) spectrum of Zn 2p; (b) spectrum of S 2p.

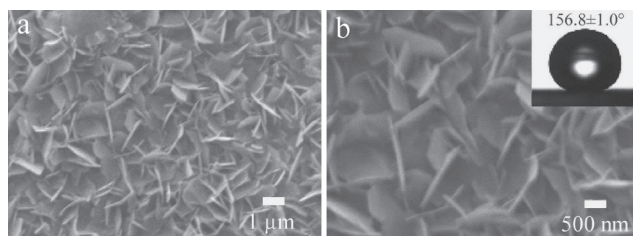


Figure 3. SEM images of ZnS film on Zn foil: (a) low magnification; (b) high magnification; (Inset of b) contact angle of ZnS film on Zn foil.

1042.8 and 1020.2 eV, which were contributed by Zn2p_{1/2} and Zn2p_{3/2}, respectively. In Figure 2b, the two peaks at 169.1 and 162.3 eV were attributed to S2p_{1/2} and S2p_{3/2}, respectively.

Figure 3 shows the SEM images of the as-prepared ZnS film on Zn foil. The ZnS film was mainly composed of many dense and uniform interconnected nanoflakes of average thickness ca. 120 nm. Most of the nanoflakes lie vertically to the substrate, which is consistent with the XRD results. The smaller thickness of the ZnS nanoflakes in the [0001] direction (*c* axis) indicates that the growth rate along the *c* axis was much higher than that along the Zn foil perpendicular to the *c* axis. The anisotropic characteristics of the growth rate may be attributed to differences in the surface energy. The in-plane directions generally correspond to lower surface energies.¹⁴ During this growth, the well-known oriented attachment (OA) mechanism¹⁵ for the growth of a nanoflake microstructure by the condensation of nanocrystals drives the formation of the observed nanoflake film. Previously, based on the OA mechanism, our group carried out in situ fabrication of many semiconducting materials such as AgSe₂,¹⁶ CuSe,¹⁷ PbI₂,¹⁸ and Ag₂S.¹⁹ More importantly, the novel structure prompted us to investigate the superhydrophobic properties of the obtained film.

The surface wettability of the prepared ZnS nanoflake film was studied by CA measurements. When deionized water droplets of about 5 μL were dropped on the surface, they yielded nearly spherical shapes at the microscopic level. The CAs of the ZnS film and Zn foil were about (156.8 ± 1.0)° (in the inset of Figure 3b) and (75.4 ± 1.0)° (see the Supporting Information²¹), respectively. The superhydrophobicity of the ZnS film was stable in air, with the CA showing no obvious change for a long time. Finally, the water droplet evaporated on the surface. A complete theoretical understanding of the superhydrophobicity phenomenon can be obtained using the Cassie and Baxter equation.²⁰ For a composite surface, the water CA is affected significantly by the fractional areas of the solid (*f*₁) versus air pockets (*f*₂): $\cos \theta_{CA} = f_1 \cos \theta_{1CA} - f_2$ (*f*₁ + *f*₂ = 1), where θ_{CA} and θ_{1CA} represent the water CAs on rough and smooth surfaces, respectively. The above equation

means that increasing the fraction of air (*f*₂) leads to an increase in the CA on a rough surface (θ). According to the equation, the *f*₂ values of the Zn foil and ZnS film with a nanoflake microstructure are estimated to be 0.61 and 0.95, respectively. The larger fraction of air among the interspaces of the ZnS nanoflake microstructure might contribute to the superhydrophobicity of the ZnS film, leading to a greatly increased air/water interface, which is essential for superhydrophobicity and effectively prevents the penetration of water droplets into the interstices. It is revealed that the hierarchical and nanoflake structure plays an important role in the preparation of super-water-repellent surfaces.

In conclusion, a highly (002)-oriented ZnS nanoflake layer was synthesized by a simple solvothermal method, using Zn foil and S powder as the raw materials, in absolute ethanol at 160 °C for 8 h. The obtained film had high crystallinity and uniformity, with a novel nanoflake microstructure. The average thickness of the ZnS nanoflake film was ca. 120 nm. It was found that the ZnS film exhibited superhydrophobicity as a result of the special nanoflake structure.

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References and Notes

- J.-U. Kim, Y.-S. Kim, H. Yang, *Mater. Lett.* **2009**, *63*, 614.
- M. J. Murcia, D. L. Shaw, E. C. Long, C. A. Naumann, *Opt. Commun.* **2008**, *281*, 1771.
- I. O. Oladeji, L. Chow, *Thin Solid Films* **2005**, *474*, 77.
- G. Boutaud, W. M. Cranton, D. C. Koutsogeorgis, R. M. Ranson, C. Tsakonas, C. B. Thomas, *Mater. Sci. Eng., B* **2009**, *165*, 202.
- P. Roy, J. R. Ota, S. K. Srivastava, *Thin Solid Films* **2006**, *515*, 1912.
- M. Gunasekaran, R. Gopalakrishnan, P. Ramasamy, *Mater. Lett.* **2004**, *58*, 67.
- N. Fathy, R. Kobayashi, M. Ichimura, *Mater. Sci. Eng., B* **2004**, *107*, 271.
- M. A. Yildirim, A. Ateş, A. Astam, *Physica E (Amsterdam, Neth.)* **2009**, *41*, 1365.
- M. Tang, Q. Tian, X. Hu, Y. Peng, Y. Xue, Z. Chen, J. Yang, X. Xu, J. Hu, *CrystEngComm* **2012**, *14*, 1825.
- Y. Gao, Z. Zheng, Y. Tian, Y. Zhang, Y. Zhang, *Eur. J. Inorg. Chem.* **2011**, 4198.
- Y. Lei, H. Jia, Z. Zheng, Y. Gao, X. Chen, H. Hou, *CrystEngComm* **2011**, *13*, 6212.
- H. Jia, W. He, X. Chen, Y. Lei, Z. Zheng, *J. Mater. Chem.* **2011**, *21*, 12824.
- C. Wang, Y. Ao, P. Wang, S. Zhang, J. Qian, J. Hou, *Appl. Surf. Sci.* **2010**, *256*, 4125.
- L. Yao, M. Zheng, S. He, L. Ma, M. Li, W. Shen, *Appl. Surf. Sci.* **2011**, *257*, 2955.
- Y. Cheng, Y. Wang, D. Chen, F. Bao, *J. Phys. Chem. B* **2005**, *109*, 794.
- D. Li, Z. Zheng, Z. Shui, M. Long, J. Yu, K. W. Wong, L. Yang, L. Zhang, W. M. Lau, *J. Phys. Chem. C* **2008**, *112*, 2845.
- D. Li, Z. Zheng, Y. Lei, S. Ge, Y. Zhang, Y. Zhang, K. W. Wong, F. Yang, W. M. Lau, *CrystEngComm* **2010**, *12*, 1856.
- Z. Zheng, A. Liu, S. Wang, Y. Wang, Z. Li, W. M. Lau, L. Zhang, *J. Mater. Chem.* **2005**, *15*, 4555.
- D.-P. Li, Z. Zheng, Y. Lei, F.-L. Yang, S.-X. Ge, Y.-D. Zhang, B.-J. Huang, Y.-H. Gao, K.-W. Wong, W.-M. Lau, *Chem.—Eur. J.* **2011**, *17*, 7694.
- A. B. D. Cassie, S. Baxter, *Trans. Faraday Soc.* **1944**, *40*, 546.
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