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Letter

One-step synthesis of Cu₂S nanostructures with two different morphologies on either side of a copper substrate

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1. Introduction

Recently, transition metal chalcogenides semiconductors have attracted extraordinary research interest owing to their potential application in catalyst, solar cell, field emission, photoluminescence and optoelectronic devices [1,2]. It is well documented that the properties of inorganic nano/micro-materials depend strongly on their morphologies and sizes, thus the design and controlled synthesis of nano/micro-structures with different morphological configurations and size distribution are very important from the standpoint of basic research and the realization of advanced devices [3,4]. Cu₂S (chalcocite) is a p-type semiconductor with a bulk band gap of 1.21 eV and has been extensively investigated and used in solar cells [5,6]. Meanwhile, the availability of Cu₂S nanostructures with well-defined morphologies and dimensions should enable bringing new types of applications or enhancing the performance of currently existing photoelectric devices due to the quantumsize effects [7]. As a consequence, substantial efforts have been focused on the development of novel synthetic route for fabricating Cu₂S nanostructures with controlled shape and size. Up to now, various Cu₂S nanostructures, such as nanowire, nanotube, nanoplate and nanodisk have been synthesized by a variety of methods, including nanolithography techniques, template-directed synthesis, vapor-phase methods, solvothermal methods and so forth [8-12]. Moreover, some of these approaches have been

ABSTRACT

Cu₂S nanosheets and hexagonal nanoplates have been synthesized, respectively on either side of a copper substrate via a facile one-step hydrothermal process using ethylenediamine (en) and distilled water as co-solvent and cetyltrimethylammonium bromide (CTAB) as surfactant. X-ray diffraction (XRD), field emission scanning electron microscope (SEM), transmission electron microscope (TEM), selected area electron diffraction (SAED) and UV-vis spectra were used to characterize the obtained products. A reasonable formation mechanism of Cu₂S nanostructures was proposed based on the experimental results. © 2009 Elsevier B.V. All rights reserved.

> extended to grow semiconductor nanostructures directly on solid substrates. For example, seed-mediated synthetic process can grow ZnO nanostructures on silicon or glass substrates [13,14], and the natural surface-oxidation of metal foil with the assistance of surfactants can grow metal oxide nanostructures [15]. This strong adherence of thin film structure on the substrate surface is very convenient for device applications. Inspired by these, here, we describe a facile one-step hydrothermal process to synthesize Cu₂S nanostructures with two different morphologies on both sides of a copper foil, respectively. To the best of our knowledge, there have been no reports concerning the differences of two sides of a solid substrate. This is of great value to fundamental studies on oriented growth of semiconductor nanostructures and for practical applications in nanodevices.

2. Experimental

All chemicals were of analytical grade and used without further purification. Copper foils (10 mm × 10 mm × 0.5 mm, 99.9%) were washed with 1 M NaOH, 1 M HCl and deionized water before use. In a typical procedure, 0.2307 g cetyltrimethy-lammonium bromide (CTAB) was dissolved in 40 ml of co-solvent of distilled water and ethylenediamine (en) to form a homogeneous solution, then 0.001 mol Cu(CH₃COO)₂·H₂O and 0.003 mol thiourea were added into the CTAB aqueous solution, and its pH value was adjusted to 12 by addition of 1 M NaOH. The mixture was transferred into Teflon-lined autoclaves, and the previously cleaned copper foil was then immersed in the solution. The autoclaves was sealed and maintained at 160 °C for 10 h. After cooling to room temperature, the resulting copper foil at the bottom of the Teflon-lined autoclaves was taken out and thoroughly rinsed with ethanol and deionized water. For clarity, the top and bottom surfaces of the copper foil were defined as the front side and the back side, respectively. The obtained products were characterized by X-ray diffraction (XRD Shimadzhu XRD 6000, Cu Ka radiation), scanning electron microscope (SEM JEOL FESEM JEM-6700F), transmission electron

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Fig. 1. Typical X-ray diffraction patterns of the products obtained on different sides of the copper foil: (a) front side and (b) back side.

microscope (TEM, HITACHI H-8100), selected area electron diffraction (SAED) and UV-vis spectra (Shimadzu UV-2550).

3. Results and discussion

The phase composition and phase structure of the as-obtained samples were examined by XRD, as shown in Fig. 1. All peaks shown in both spectra can be readily indexed to the hexagonal-phase of Cu₂S (JCPDS card no. 84-0208) in addition to the peaks marked with asterisks that are attributed to the copper substrate (JCPDS 45-0937). The formation of hexagonal crystal structure of Cu₂S is reasonable because the present synthetic temperature (160 °C) is higher than its phase transition temperature (105 °C), at which Cu₂S undergoes a structural transition from monoclinic to hexagonal [7]. This result is consistent with previous report about the Cu₂S nanostructure [16].

The morphologies and microstructure of the products were further investigated by SEM. To our surprise, the obtained black films covering the two sides of the copper foil substrate exhibit completely different morphologies. Fig. 2 shows the images of the products obtained on the front side of the copper substrate. As the low-magnification SEM images in Fig. 2a and b revealed, the formed structures are composed of Cu_2S nanosheets in high



Fig. 2. SEM and TEM images of Cu₂S nanosheets obtained on the front side of the copper foil: (a–c) FE-SEM images at different magnifications, (d) flower-like structures composed of thin nanosheets, and (e) TEM image (the inset is the SAED pattern).



Fig. 3. SEM and TEM images of Cu₂S nanoplates obtained on the back side of the copper foil: (a and b) FE-SEM images at different magnifications, (c) TEM image (the inset is the SAED pattern).

density. The inset in Fig. 2b shows the flank of the nanosheets, which reveals that these Cu₂S nanosheets are approximately perpendicular to the surface of the substrate. The corresponding enlarged image in Fig. 2c clearly shows that, among the products, a proportion of nanosheets exhibit multilateral morphology, and others have crooked anomalous shape. The surface of the nanosheets is very smooth. The dimensions and thickness of the observed nanosheets are in the range of 350-600 and 15-25 nm, respectively. A more interesting morphology, flower-like structures composed of several petal-shaped thin nanosheets, is also observed (Fig. 2d), the petals assemble compactly through their bases and distribute on the substrate. A TEM image of several nanosheets, which shows their anomalous multilateral morphology, is seen in Fig. 2e. The six symmetrical electron diffraction spots shown in the SAED pattern (inset in Fig. 2e) that taken on the nanosheets, confirms its single-crystal structure and indicates that the nanocrystals have a preferred orientation. According to the SAED pattern, the surface of the nanosheets is made up of the (0001) planes of the hexagonalphase of Cu₂S, and the edges should correspond to the six $\pm [1 \ 0 \ 1 \ 0]$, $\pm [1\bar{1}00], \pm [0\bar{1}10]$ directions.

Fig. 3 shows the images of the products obtained on the back side of the copper substrate. As can be seen in a low-magnification SEM image (Fig. 3a), dense Cu₂S nanoplates are distributed on the copper substrate over a large area. An enlarged image of the structure shown in Fig. 3b further sheds light on the morphological characteristics of the Cu₂S nanoplates. These nanoplates have a regular hexagonal morphology with an edge length of 250–350 nm and thickness of about 150 nm. Moreover, we can also find a large amount of small hexagonal Cu₂S nanoplates and they are still in the state of growing. The inset in Fig. 3b is a representative contrastive TEM image of big and small hexagonal nanoplates, which clearly shows that they are all regular hexagons, with the adjacent edges forming angles of 120°, as indicated by arrows. The results

are further confirmed by the TEM image in Fig. 3c. The corresponding SAED pattern (inset in Fig. 3c) shows that the nanoplates lies on the (0001) plane, which is similar to the one in Fig. 2e, and in good agreement with the XRD results presented above.

The putative reaction relevant to the growth of Cu_2S nanostructures in an en solution can be simply represented by the following reactions [12,17]:

$$Cu^{2+} + nen \rightarrow [Cu(en)_n]^{2+} (n > 0)$$
 (1)

$$NH_2CSNH_2 + 2H_2O \rightarrow 2NH_3 + CO_2 + H_2S$$
(2)

$$[Cu(en)_n]^{2+} + Cu^0 + nen \to 2[Cu(en)_n]^+$$
(3)

$$H_2S + 20H^- \rightarrow S^{2-} + 2H_2O$$
 (4)

$$2[\operatorname{Cu}(\operatorname{en})_n]^+ + S^{2-} \to \operatorname{Cu}_2 S + 2n\operatorname{en}$$
(5)

En was selected as the solvent due to its special properties, such as strong chelating, certain solubility and reducing ability [18,19]. In our reaction system, en performs three major roles in the growth of Cu₂S nanostructures. Firstly, it is well known that en is a bidentate chelating agent, after copper salt is dissolved in an en solution, $[Cu(en)_n]^{2+}$ complex is formed, which can control the reaction rate by limiting the availability of free Cu²⁺ [12]. Secondly, en offers a basic alkaline environment, together with the high pH value, which can accelerate the thermal hydrolysis of thiourea; on the other hand, with the increase of temperature and pressure, the stability of the complex is decreased, and S^{2–} coming from the dissociation of thiourea immediately reacted with the $[Cu(en)_n]^+$ complex. The above-mentioned two reasons lead to the fast nucleation, growth and the final formation of Cu₂S nanostructures [18]. Finally, en as a reducing agent in many previous reports, its reducibility increases with temperature and pressure, thus, in our hydrothermal conditions, en helps to reduce copper.



Fig. 4. UV-vis absorption spectra of the products obtained on both sides of the copper foil: (a) front side and (b) back side.

In addition, an appropriate amount of water in the system may oxidize the copper surface [20], so the copper substrate can also continuously supply the copper source during the reaction. In our hydrothermal process, the copper substrate is at the bottom of the Teflon-lined autoclaves. For the front side of the copper substrate, a Cu ion concentration gradient is formed from it to the bulk solution [21], en could much more easily to coordinate with copper ions, as the Cu₂S nuclei are formed, the CTAB probably adsorb selectively on the preferred low-index facets, which restricts the deposition of Cu₂S on the CTAB passivated facets, so the crystal growth is limited in [0001] direction, and finally Cu₂S nanosheets are obtained. While for the back side of the copper substrate, it directly contacts the bottom of Teflon-lined autoclaves, there is no the concentration gradient. It is possible the subsequent different growth rates along [001] and {100} directions lead to the formation of nanoplates, as reported previously [16]. At the same time, the eroded substrate surface would be of higher chemical activity, so the nucleation rate in this case is faster, and finally a large amount of small hexagonal Cu₂S nanoplates exist. From the above results, it is clear that the growth conditions exert subtle control over the growth kinetics, which arouses anisotropic growth and leads to produce Cu₂S nanosheets and hexagonal nanoplates on both sides of the copper foil, respectively. Further investigation is under way to better understand the detailed growth mechanism for the morphological control.

The UV-vis absorption spectra of the as-prepared Cu_2S nanostructures are shown in Fig. 4. It is clear that the absorption edge of both samples is about 680 nm. A marked absorption peak appears at 310 and 305 nm for the Cu₂S nanosheets (Fig. 4a) and hexagonal nanoplates (Fig. 4b), respectively. The absorption shows obvious blue shift compared to that of bulk phase (1022 nm), which arises from a size quantum effect [6]. Additional, an absorption peak at 359 nm in Fig. 4a indicates the products on the front side have a slightly larger crystal size and a narrower size distribution than those on the back side [22].

4. Conclusions

In summary, Cu₂S with two different morphologies have been synthesized, respectively on both sides of a copper foil under mild hydrothermal conditions. This is the first time to concern the differences of both sides of a solid substrate. It is reasonable to expect that this simple method can be extended to fabricate other kinds of homologous semiconductor materials for practical applications in nanodevices.

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References

- [1] X. Duan, Y. Huang, R. Agarwal, C.M. Lieber, Nature 421 (2003) 241-245.
- [2] Q.Y. Lu, F. Gao, D.Y. Zhao, Angew. Chem. Int. Ed. 41 (2002) 1932-1934.
- [3] D.B. Kuang, A.W. Xu, Y.P. Fang, H.Q. Liu, C. Frommen, D. Fenske, Adv. Mater. 15 (2003) 1747–1750.
- [4] J. Matthew, Y.K. Bierman, L. Albert, S. Jin, Nano. Lett. 7 (2007) 2907–2912.
 [5] Z.C. Wu, C. Pan, Z.Y. Yao, Q.R. Zhao, Y. Xie, Cryst. Growth Des. 6 (2006) 1717–
- 1719.
 [6] Z.P. Liu, D. Xu, J.B. Liang, J.M. Shen, S.Y. Zhang, Y.T. Qian, J. Phys. Chem. B 109 (2005) 10699–10704.
- [7] X.S. Du, Z.Z. Yu, A. Dasari, J. Ma, Y.Z. Meng, Y.W. Mai, Chem. Mater. 18 (2006) 5156-5158.
- [8] L. Chen, Y.B. Chen, L.M. Wu, J. Am. Chem. Soc. 126 (2004) 16334-16335.
- [9] J. Chen, S.Z. Deng, N.S. Xu, Appl. Phys. Lett. 80 (2002) 3620–3622.
- [10] Z.Q. Li, H. Yang, Y. Ding, Y.J. Xiong, Y. Xie, Dalton Trans. 149 (2006) 149-151.
- [11] H.T. Zhang, G. Wu, X.H. Chen, Langmuir 21 (2005) 4281–4282.
- [12] S. Gorai, D. Ganguli, S. Chaudhuri, Mater. Lett. 59 (2005) 826-828.
- [13] L.E. Greene, M. Law, J. Goldberger, F. Kim, J.C. Johnson, Y.F. Zhang, et al., Angew. Chem. Int. Ed. 42 (2003) 3031–3034.
- [14] M.S. Wang, E.J. Kim, S.H. Hahn, C. Park, K.K. Koo, Cryst. Growth Des. 8 (2008) 501–506.
- [15] Y. Liu, Y. Chu, M.Y. Li, L.L. Li, L.H. Dong, J. Mater. Chem. 16 (2006) 192-198.
- [16] Z.B. Zhuang, Q. Peng, B.P. Zhang, Y.D. Li, J. Am. Chem. Soc. 130 (2008) 10482–10483.
- [17] S.K. Haram, A.R. Mahadeshwar, S.G. Dixit, J. Phys. Chem. 100 (1996) 5868– 5873.
- [18] S. Gorai, D. Ganguli, S. Chaudhuri, Cryst. Growth Des. 5 (2005) 875-877.
- [19] B. Li, Y. Xie, J.X. Huang, Y. Liu, Y.T. Qian, Chem. Mater. 12 (2000) 2614-2616.
- [20] S.K. Panda, S. Gorai, S. Chaudhuri, Mater. Sci. Eng. B 129 (2006) 265–269.
- [21] F. Lu, W.P. Cai, Y.G. Zhang, Y. Li, F.Q. Sun, J. Phys. Chem. C 111 (2007) 13385-13392.
- [22] P. Zhang, L. Gao, J. Mater. Chem. 13 (2003) 2007-2010.