

Controlled-Synthesis of $\text{CuC}_2\text{O}_4/\text{ZnO}$ Heterostructures Using CuC_2O_4 Microspheres as Templates

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Abstract One-dimensional $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures were successfully prepared *via* hydrothermal reaction for 10 h at 120 °C using CuC_2O_4 microspheres as templates. Thermal gravimetric analysis (TGA), field-emission scanning electron microscope (FESEM), energy dispersive X-ray spectrometry (EDX), transmission scanning electron microscope (TEM) and powder X-ray diffraction (XRD) were used to characterize the structure and morphology of the products. Results show that the obtained products are $\text{CuC}_2\text{O}_4/\text{ZnO}$ nanorod bundles with 500 nm in diameter and 1 μm in length. Each rod bundle consists of many nanorods which grow along the same orientation. TEM image and EDX spectra show that the product is a uniformly heterostructured material formed from CuC_2O_4 and ZnO.

Keywords $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures, controlled-synthesis, template

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Since the landmark publication on carbon nanotubes^[1-3] one-dimensional (1D) semiconductor metal oxide nanostructures, such as nanowires, nanobelts, and nanotubes, have attracted considerable attention due to their potential applications in nanoscale electronic, optoelectronic devices and catalysis. However, the properties and applications of those nanomaterials are limited by their simple binary systems^[4], such as ZnO, TiO_2 , SnO_2 . Therefore, the synthesis of complex functional nanomaterials with controlled size and morphology, such as core/shell quantum dots^[5], doped structure^[6], heterostructures^[7], and 1D arrays^[8] are highly desirable.

In this article, we report the hydrothermal synthesis of 1D $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures using CuC_2O_4 as templates. $\text{CuC}_2\text{O}_4/\text{ZnO}$ is an important precursor to synthesize the CuO/ZnO composites which used for the gas sensor^[9] hydrogen production^[10-11] and photodegradation^[12].

1 Experimental

1.1 Apparatus and reagents

X-ray powder diffraction (XRD) was carried out on a Rigaku (Japan) D/max- γ_{A} X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.154\ 178\ \text{nm}$). Field emission scanning electron microscopy (FE-SEM) images were recorded on a Hitachi S-4800 electron microscope. Transmission electron microscopy (TEM) image was obtained on a JEOL-2010 transmission electron microscope at an accelerating voltage of 200 kV. An energy-dispersive X-ray spectroscope (EDX) was attached to the TEM instrument. Thermal gravimetric analysis (TGA) of the samples was carried out on a Shimadzu TA-50 thermal analyzer at a heating rate of 10 K/min

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from room temperature to 800 °C in N_2 atmosphere.

All chemicals, $\text{Zn}(\text{NO}_3)_2$, hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, HMT) and poly(acrylamide-co-diallyldimethylammonium chloride) (PAM-CTAC) were of analytical grade and used without further purification.

1.2 Preparation of $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures

0.108 g of $\text{Zn}(\text{NO}_3)_2$, 0.3 g of PAM-CTAC and 0.0492 g of HMT were added into an alcohol/water mixture solvent ($V(\text{alcohol}):V(\text{water}) = 3:2$, 10 mL), respectively, and then the solution was added into another alcohol/water mixture solvent ($V(\text{alcohol}):V(\text{water}) = 3:2$, 10 mL) containing 0.0543 g CuC_2O_4 microspheres^[13] under stirring. The reaction mixture was transferred into a Teflon-lined autoclave with 50 mL capacity and sealed. The autoclave was heated in an oven kept at 120 °C for 10 h, followed by cooling to room temperature. The resulting powder was collected and washed with dilute water alcohol solution for several times, and dried in vacuum at 60 °C for 4 h.

2 Results and discussion

2.1 Phase analysis of CuC_2O_4 and $\text{CuC}_2\text{O}_4/\text{ZnO}$ with XRD diffraction

XRD patterns of the as-prepared CuC_2O_4 and $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures are given in Fig. 1. All the peaks in Fig. 1a are indexed to the monoclinic structure of CuC_2O_4 (JCPDS card No. 21-297). In the Fig. 1b, besides the strongest diffraction peak from CuC_2O_4 phase the diffraction peaks of hexagonal structure ZnO, are observed which is very close to that given by JCPDS file No. 36-1451. So, it can be concluded that the products are composite of CuC_2O_4 and ZnO.

2.2 The morphology analysis

The morphologies of CuC_2O_4 and $\text{CuC}_2\text{O}_4/\text{ZnO}$ products were characterized by SEM. The morphology of CuC_2O_4 is porous microsphere with diameter of 400 ~ 540 nm (Fig. 2A). Higher magnification SEM image (inset of Fig. 2A) shows that each porous sphere is made of many nanoparticles with size around 50 ~ 80 nm. Some porous spheres have formed hollow porous spheres in the centre part. When using CuC_2O_4 microsphere as template, the $\text{CuC}_2\text{O}_4/\text{ZnO}$ nanorod bundles with diameter of 500 nm and length of 1 μm are obtained (Fig. 2B). Each bundle consists of many nanorods which grow along the same orientation. From Fig. 2C, we can see some hollow bundle rods with the similar structure as hollow porous sphere CuC_2O_4 obtained. Above results show that $\text{CuC}_2\text{O}_4/\text{ZnO}$ nanorod bundles are formed on the porous CuC_2O_4 microsphere.

The TEM image of the $\text{CuC}_2\text{O}_4/\text{ZnO}$ rodlike-bundles is shown in Fig. 3A. There are no particles on the surface of each rod, and it does not possess obvious core/shell structure. HRTEM images may reveal the formation of $\text{CuC}_2\text{O}_4/\text{ZnO}$ rodlike-bundles. However, no clear lattice fringe image of $\text{CuC}_2\text{O}_4/\text{ZnO}$ was obtained since its instability toward electronic irradiation during HRTEM imaging.

EDX spectrum of single nanorod is given in Fig. 3B. The discernable peaks of C, Zn, Cu, O indicate that the product is just composed of Zn, Cu, C and O with the atomic ratio of C:O:Cu:Zn about 27.79:51.90:11.20:7.62. The EDX spectra of different locations on a single nanorod have no obvious difference. According to EDX and TEM results, we conclude that CuC_2O_4 and ZnO are co-crystallized in the reactive system forming uniform composite $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures.

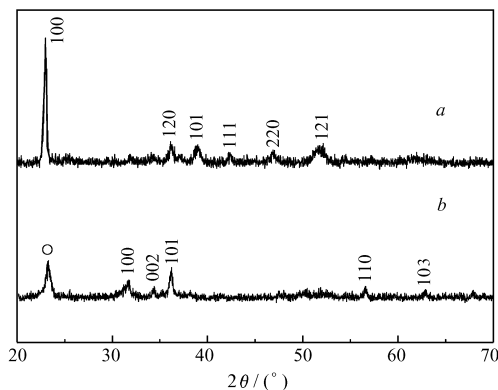


Fig. 1 XRD patterns of CuC_2O_4 (a) and obtained $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures (b)

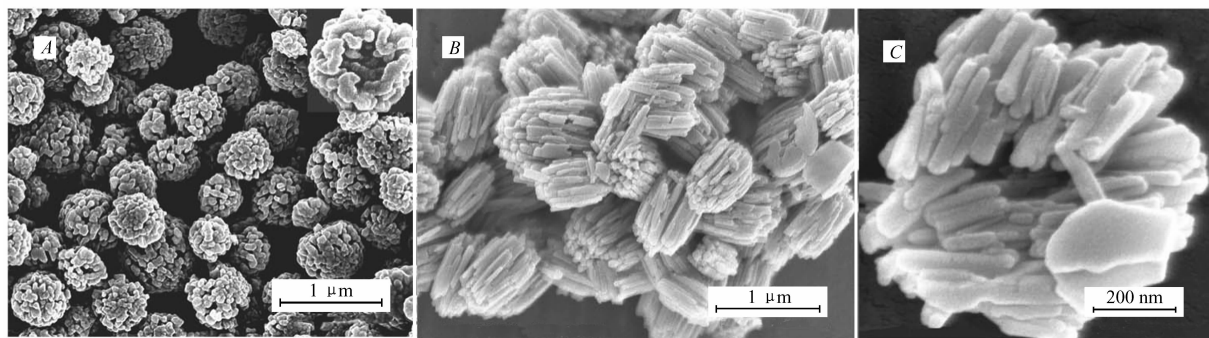


Fig. 2 SEM images of CuC_2O_4 microspheres(A) , $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures(B,C)

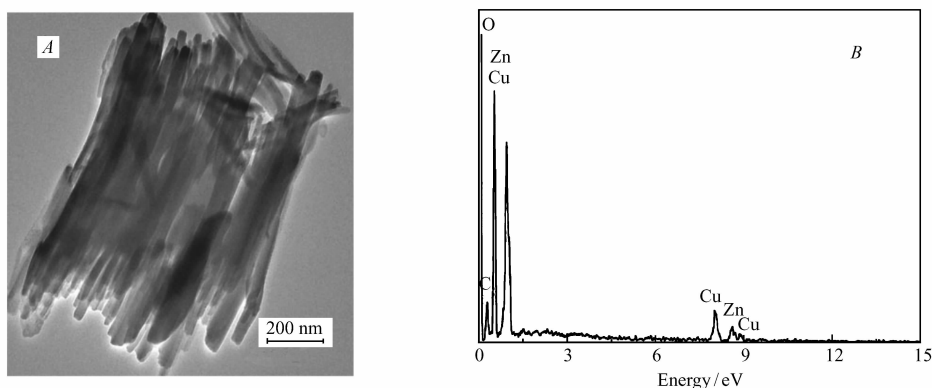


Fig. 3 TEM image(A) and EDX spectrum(B) of as-prepared $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures

2.3 The TGA curves of CuC_2O_4 and $\text{CuC}_2\text{O}_4/\text{ZnO}$

The TGA curves of the CuC_2O_4 microspheres and $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures are shown in Fig. 4. There are two mass loss steps on the TGA curve of CuC_2O_4 microspheres. In the range of 50 ~ 285 °C , the mass loss is mainly attributed to the evaporation of H_2O , while the second one could be ascribed to the decomposition of the copper oxalate at 285 ~ 315 °C . The mass loss at the second step is about 49.2% , which is close to the theoretical mass loss value (47.4%) of CuC_2O_4 decomposition. In comparing with CuC_2O_4 , the TGA curve of $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures has two mass loss steps at the temperature of 25 ~ 250 °C and 250 ~ 440 °C , respectively. The first one is also attributed to the evaporation of H_2O , whereas the second one is ascribed to the decomposition of the copper oxalate. The mass loss at the second step is about 35.0% , which is close to the theoretical mass loss value(34.2%) of CuC_2O_4 decomposition in $\text{CuC}_2\text{O}_4/\text{ZnO}$ and consistent with the result from EDX spectrum. These results show that the decomposition rate of the CuC_2O_4 is slower and its decomposition temperature is lower for $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures.

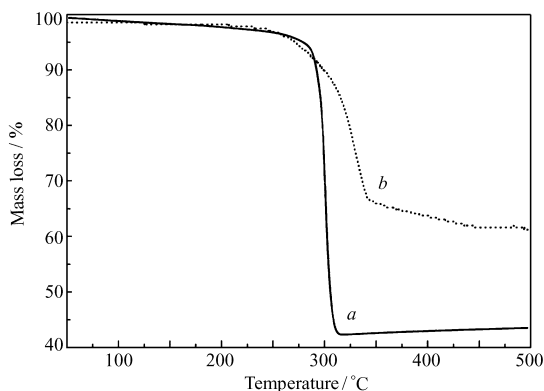


Fig. 4 TGA curves of the CuC_2O_4 microsphere(a) and $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures(b)

2.4 The formation mechanism of $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures

To understand the formation mechanism of $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures, the SEM image of the product obtained at 120 °C for 2 h was shown in Fig. 5. In this image, there are two kinds of morphologies including

the nanoflakes and the sphere consisting of shorten nanorods. Its XRD pattern (data not given here) showed the mixture of ZnO and CuC_2O_4 , and EDX spectra (data not given) showed that the flake-like structures contained Zn and O elements, and the similar rod-bundles contained Cu, O, C and Zn elements, but the content of Zn atom was less. These results implied that ZnO nuclei first grew on the surface of CuC_2O_4 nanoparticle, then grew along certain orientation with the reaction time prolonged. At the same time, polycrystalline CuC_2O_4 dissolved and recrystallized on the growth surface of the ZnO with increasing temperature, and finally grew up to uniform composite $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures with the presence of morphology-controlled agent PAM-CTAC.

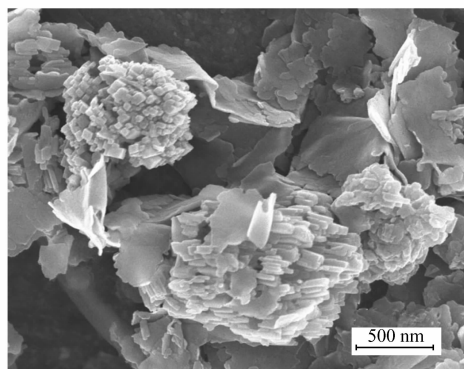


Fig.5 SEM image of the obtained products at 120 °C for 2 h

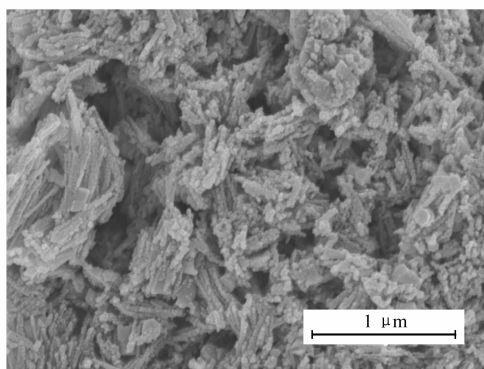


Fig.6 SEM image of the CuO/ZnO nanorod bundles

2.5 The characterization of CuO/ZnO prepared from $\text{CuC}_2\text{O}_4/\text{ZnO}$

Upon the calcination of the obtained $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures at 420 °C in air, all the $\text{CuC}_2\text{O}_4/\text{ZnO}$ was converted into CuO/ZnO nanorod bundles made of many nanoparticles (Fig. 6). These CuO/ZnO nanorod bundles have large surface area, therefore it might find applications as absorbents and catalysts.

3 Conclusions

In summary, aligned $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures were successfully synthesized at 120 °C for 10 h by simple hydrothermal method using CuC_2O_4 microspheres as template. The prepared $\text{CuC}_2\text{O}_4/\text{ZnO}$ heterostructures were uniform composite materials, and have been characterized by means of XRD, SEM, EDX and TGA. The catalysis, optics, electron of this new structure material properties is under investigation.

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以 CuC₂O₄ 微球为模板可控合成 一维 CuC₂O₄/ZnO 异质结构

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摘 要 以 CuC₂O₄ 纳米微球为模板,通过水热法在 120 ℃、1 h 时成功合成了一维 CuC₂O₄/ZnO 异质结构。采用热重分析(TGA)、场发射扫描电子显微镜(FE-SEM)、能量散射 X 射线谱(EDX)、透射电子显微镜(TEM)和 X 射线粉末衍射(XRD)等测试技术对产物的结构和形貌进行了表征。结果表明,所得产物为一维 CuC₂O₄/ZnO 纳米棒束,长约 1 μm,直径约 500 nm。每个棒束由许多纳米棒沿同一方向组装而成。TEM 照片和 EDX 光谱表明,CuC₂O₄ 和 ZnO 形成了均匀的异质结构。

关键词 CuC₂O₄/ZnO 异质结构,可控合成,模板