

Preparation of carbon fiber/ZnO core-shell structure by a simple method

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Received February 20, 2009; accepted May 10, 2009

Carbon fiber/ZnO was prepared by surface modification precipitation in aqueous solution. Corresponding nucleation and crystal growth model was proposed for this structure. The effects of annealing temperature on the structure and absorptive properties of the composites were investigated. Results showed that obtained ZnO shell was ca. 200 nm on the surface of carbon fiber. The ZnO coating can protect the CFs from oxidation at a relatively high temperature. Energy bandgap calculated from the absorptive spectra was about 3.30 eV.

Keywords coatings, optical materials and properties

PACS numbers 81.15.-z, 42.70.-a, 74.25.Gz

1 Introduction

Carbon fibers used as microelectrodes are the important portion in the whole microelectrode family [1]. Moreover, carbon fibers are the basic part of the lightweight composite for high-performance materials [2]. Technology of carbon materials often requires addition of certain additives. Such a situation takes place during preparation of carbon-supported catalysts when various metals such as Mo, Pt or metal oxides are deposited on an activated carbon support [3].

ZnO with a large band gap ($E_g = 3.37$ eV at 300 K) used as an important N-type semiconductor is quite attractive because of its excellent optical and electrical properties, thus making it ideal to work as transparent conducting electrodes for diodes and solar cells [4–7]. Moreover, ZnO-based nanomaterials may serve as chemical sensors and catalyst for environmental and industrial applications [8–10]. It is well known that the performance of these devices is influenced by the structure, size and surface area of ZnO. Remarkable progress has been achieved concerning preparation of ZnO to optimize its physical and chemical properties [11–17]. Several methods have been employed to prepare ZnO nanocrystals, such as hydrothermal methods [11, 12], solution method [13, 14], vapor transport [15, 16], electrodeposition [17,

18], and carbon thermal reduction [19].

Though there were many reports on the fabrication and excellent properties of C/ZnO, in which the C is in the form of carbon nanotube [20, 21] or carbon spheres [22], few on carbon fiber/ZnO was reported. In this article, we synthesized the carbon fiber/ZnO composite structure by a surface modification precipitation process at low temperature. The morphology, UV-vis absorptive properties and thermal analysis of the samples were investigated. A model about how the ZnO shell formed was presented. The ZnO shell of this special structure can probably bring some special and interesting phenomena in photoluminescence and other properties.

2 Experimental

All the reagents are of analytical grade and used without any purification. For the deposition of ZnO, carbon fibers (CFs) were immersed in acetone for 2 h to clean the CFs surfaces, then CFs were treated with HNO₃ (65%) for 24 h at room temperature to introduce various functional groups (such as COOH, OH, and CO) on CFs surfaces. These functional groups can act as nucleation sites for ZnO nanoparticles on CFs. First, Zn(NO₃)₂ was dissolved in H₂O under vigorous agitation at 40°C. The solution was stirred for 0.5 h, and the as-treated CFs was

introduced to it. Second, the mixture was stirred for 5 h and ammonia was added by titration. The reaction was continued for another 2 h. Finally, the resultant product was centrifuged at 7000 r/min and washed with distilled water. The precipitate were then dried and annealed in air at different temperatures.

The as-synthesized composites were characterized by X-ray diffraction (XRD, Rigaku D/max-Ra) with $\text{Cu } K_{\alpha}$ $\lambda=0.15418$ nm, field emission scanning electron microscope (FESEM, JSM-6700F), and fourier transform infrared spectrophotometer (FTIR, UV-3101). UV-vis absorption spectra were recorded using a spectrophotometer (3100 UV-VIS-NIR), and careful background subtraction was performed. Thermal analysis was performed in air using a Mettler Toledo simultaneous thermal analyzer (TGA-/SDTA 851e) with a heating rate of $10^{\circ}\text{C}/\text{min}$.

3 Results and discussion

In order to analyze the phase transformation, X-ray diffraction (XRD) was used to characterize the as-obtained samples. As shown in Fig. 1, all the peaks can be indexed to wurtzite ZnO (JCPDS file No. 80-0075) for both precursor and as-obtained samples annealed at different temperatures. Therefore, ZnO had been formed before annealing, which might result from the condensation reaction in the preparation. ZnO was amorphous, and only broad and weak peaks of ZnO appeared for the sample until the annealing temperature was higher

than 200°C . With annealing temperature increasing, the intensity of the peak became stronger and sharper, indicating that ZnO was crystallized better and the particle-size was increased.

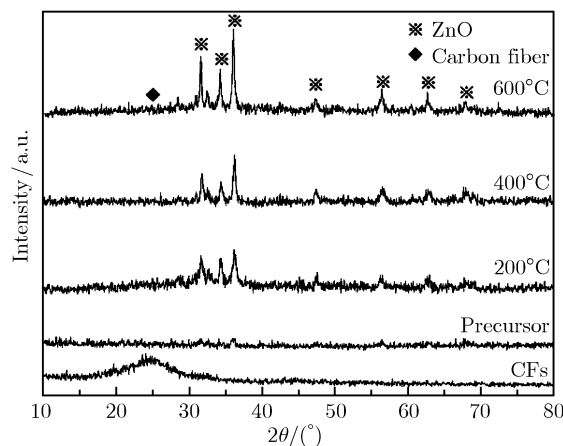


Fig. 1 XRD patterns of precursors and as-obtained samples annealed at different temperatures.

Figure 2 showed the FESEM of CFs and as-obtained samples from $0.08\text{M Zn}(\text{NO}_3)_2$. It can be seen that the carbon fibers were characterized by regular dimensions ($\sim 6\text{--}8\ \mu\text{m}$ in diameter), uniform and smooth surface (at the adopted resolution) [Fig. 2(a)]. Figure 2(b) showed that ZnO particles (the concentration of $\text{Zn}(\text{NO}_3)_2$ was 0.08M) were uniformly dispersed on the surface of the fibers and formed the whole shell. According to Fig. 2(c), the SEM image of a portion of the sample with bared surface, the thickness of ZnO shell was ca. $200\ \text{nm}$.

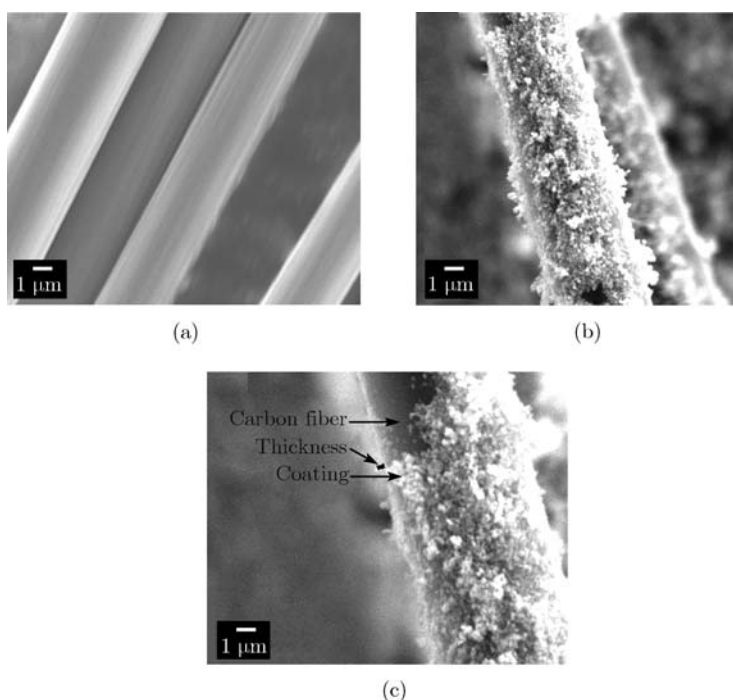


Fig. 2 SEM image of carbon fiber (a); SEM image of carbon fiber covered by ZnO with $0.08\text{M Zn}(\text{NO}_3)_2$ [(b), (c)].

To further investigate the coating process, FTIR analysis was carried out to probe the surface properties of CFs treated with HNO_3 (Fig. 3). Peaks at 2919 and 2845 cm^{-1} can be assigned to C–H stretching frequencies [23]. Vibrational features at 3400, 1634, and 1400 cm^{-1} were assigned to the O–H, C–O, and C–O stretching motion. Thus, some organic materials might have been absorbed on CFs. From the results stated above, it could be concluded that the possible process for the coating of ZnO onto CFs might be described as follows:

First, when CFs was treated with HNO_3 , functional groups such as O–H, C O were introduced on CFs surfaces, which can act as nucleation sites for ZnO particles. The added $\text{Zn}(\text{NO}_3)_2$ provided Zn^{2+} , and it was mixed well with CFs after 5 h stirring. Second, $\text{NH}_3 \cdot \text{H}_2\text{O}$ offered OH^- , which easily combined with Zn^{2+} and nucleated on the CFs with functional groups to form $\text{Zn}(\text{OH})_2$ initially and subsequently changed to ZnO as initial nucleation shell. Finally, ZnO was continually formed on the prior ZnO nucleation layer from Zn^{2+} and excessive OH^- to form a uniform and entire ZnO shell.

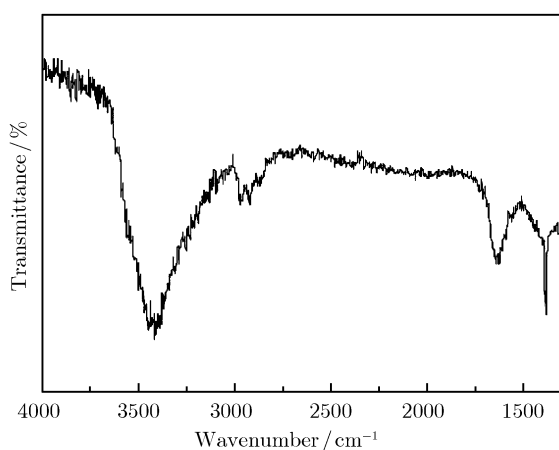


Fig. 3 FTIR spectrum of CFs treated with HNO_3 .

The band gap energy E_g for the ZnO nanoparticles can be determined by extrapolation to the zero absorption coefficient which is calculated from the following equation:

$$\alpha = \frac{2303A\rho}{lC} \quad (1)$$

where A is the absorbance of a sample; ρ is the density of ZnO; C is the concentration of the particles; and l is the optical path length. The optical absorption coefficient α of a semiconductor close to the band edge can be expressed by the following equation [24]:

$$\alpha = \frac{K(h\nu - E_g)^n}{h\nu} \quad (2)$$

where K is a constant, E_g is the band gap, and n is a value that depends on the nature of the transition. In this case, n is equal to 1/2 for this direct allowed tran-

sition. The band gap can be estimated from a plot of $(\alpha h\nu)^2$ versus photon energy.

The absorption spectrum of CFs/ZnO composite was shown in Fig. 4. The value of the absorption onset of the sample was about 376 nm and the absorption appeared red-shift with annealing temperature. The band gap E_g of ZnO can be determined by extrapolation of linear portion to the energy axis at the zero absorption coefficient, which is calculated from Eq. (2). The intercept of the tangent to the plot will give a good approximation of the band gap energy for this direct band gap material (shown in the inset of Fig. 4 for the sample annealed at 200°C). From this figure, the band gap of about 3.30 eV was deduced, which is very close to the intrinsic bandgap of ZnO.

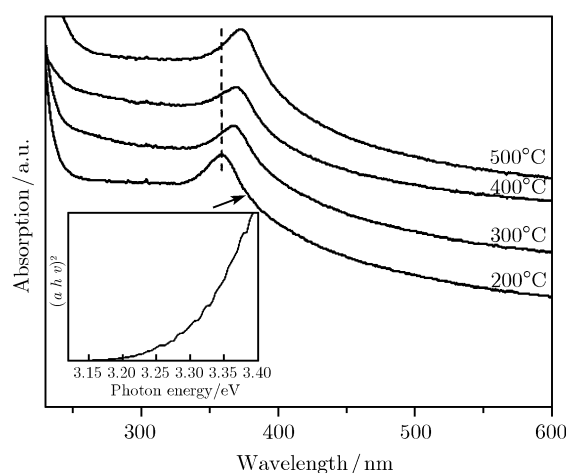


Fig. 4 Absorption spectra of CFs/ZnO composite.

Thermal analyses were performed on CFs and ZnO-coated CFs (Fig. 5). As for CFs, a mass loss at 370°C was attributed to the onset of oxidation of CFs. From 370 to 630°C, the mass loss was ca. 55%. Afterward, a quick mass loss (23%) occurred between 630 and 720°C accompanied with strong exothermic process (DTA) in this temperature range. No further mass loss was recorded above 760°C. The TG curve of ZnO-coated CFs showed a stepwise profile. A mass loss at 490°C was attributed

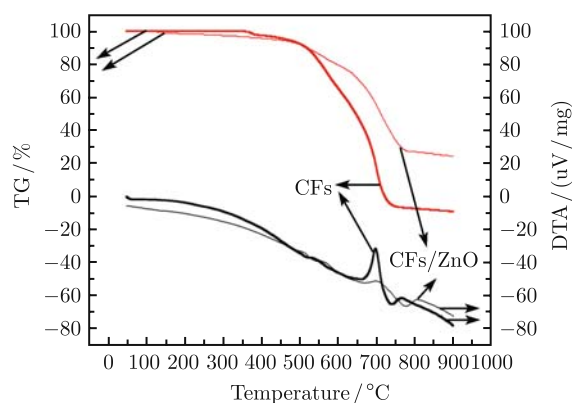


Fig. 5 Thermal analyses of CFs and ZnO-coated CFs.

to the onset of oxidation of CFs. From 490 to 650°C a mass loss (23%) occurred. The mass loss was ca. 59% between 650 and 760°C and showed a weak exothermic peak centered at this temperature range. From 760 to 900°C, no further mass loss was recorded. From the results of TG-DTA, it was concluded that the ZnO coating can protect the CFs from oxidation at a relatively high temperature and reduce the mass loss to some extent.

4 Conclusions

CFs/ZnO core-shell material was synthesized via a surface modification precipitation process in aqueous solution at low temperature. The precursor was ZnO before annealing and the crystalline quality improved with annealing temperature increasing. CFs/ZnO core-shell structure was obtained with 0.08M Zn(NO₃)₂, and the model was proposed for the growth of this structure. The energy band gap of ZnO calculated from the absorption spectra was about 3.30 eV. In addition, the ZnO coating can protect the CFs from oxidation at a relatively high temperature. The as-obtained composites may be suitable for application in sensors and catalysts for its high surface area.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 10374047).

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