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Luminescence Properties of Nanostructure ZnO-Covered Carbon Fibers Prepared by Thermal Oxidation *

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We report on ZnO nanosheets and nanorods synthesized by thermal oxidation of zinc films deposited on carbon fiber surfaces. The structure and optical properties are characterized by x-ray diffraction, scanning electron microscopy and photoluminescence spectrum. An orange-red emission around 683 nm is found in the PL spectrum when the sample prepars at 400°C for four hours in air. With annealing temperature increasing from 400°C to 500°C, the blue shift is observed.

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Zinc oxide (ZnO) nanostructures have attracted considerable attention for their potential applications in many technologies such as dye-sensitized solar cells, UV photosensor, field effect transistors and photoluminescence.[1−3] Many techniques have been developed for synthesizing 1 dimension (1 D) ZnO nanostructures (ZNs), including solid-vapour deposition,[4] thermal evaporation,[5] metal-organic chemical vapour deposition[6] and aqueous solution method.[7] The electrodeposition shows several advantages with low cost, simple operation, and wide compatibility. The glass, polymer and semiconductor were used as substrates in the electrodeposition. Recently, the preparation, characterization and application of ZnO were extensively investigated. Qin *et al.*[8] synthesized the radial ZnO nanowires around Kevlar 129 fibers using hydrothermal approach. They studied the microfiber-ZnO-nanowire hybrid structure for energy scavenging. Additionally, the preparation of ZnO including nanorods, nanocastles and nanowires were widely reported.[9,10] However, there have been few reports on the ZnO-nanosheet-covered fibers fabricated by the thermal oxidation method. Because of the wide band gap (about 3.37 eV) of ZnO at room temperature and large exciton binding energy (about 60 meV),[11] ZnO is widely recognized as an ideal material for the application in exciton-related optoelectronic devices. In this study, carbon fibers with 3000 filaments were used. The diameter of a single filament was from 7 μm to 10 μm, and the length of the carbon fibers was about 100 m. The CF/Zn composite was prepared by electrodeposition. The fibers were cut to 80–100 mm in length before the surface treatment. They were coated by electrodeposition for 30 min. The current intensity was 20 mA. The CF/Zn composites were washed with distilled water followed by absolute alcohol. After being dried in air, they were annealed at 400°C, 450°C and 500°C for four hours in air, respectively. The heating rate was about 10°C/min. After they had cooled down naturally to room temperature, ZNs were obtained. In order to investigate the structure and the morphology ZNCFs were characterized using x-ray diffraction (XRD, X′ per pro) and field emission scanning electron microscope (FE-S4800). The room temperature PL spectrum was measured by RF-540 in 325 nm.

Figure 1 shows the XRD patterns of ZNCFs annealed at 400°C and 500°C for four hours in air. The results indicate that ZNs were obtained by annealing CF/Zn at different temperatures. In addition, the diffraction peaks of zinc are also observed.

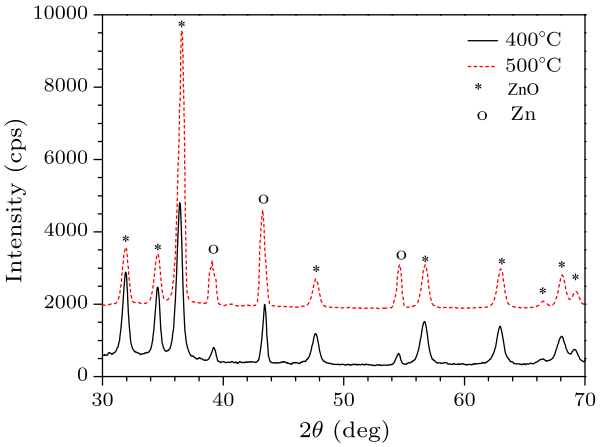


Fig. 1. XRD pattern of ZNCFs synthesized at 400°C and 500°C for four hours in air, respectively.

Figure 2 shows the SEM images of the Zn/CF with different magnifications after annealed at 400°C, 450°C and 500°C for four hours in air, respectively. The results show that the different morphologies are exhibited after CF/Zn annealed at different temperatures. ZnO-nanosheet-covered carbon fibers were obtained when annealed at 400°C (Figs. 2(a) and 2(b)). The nanosheets are aggregated and mingled in each other, which is ascribed to long-range

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electrostatic interactions among the polar charges of the {0001} planes.[12] When the temperature is increased to 450°C, the ZnO nanosheets become more fragmentary (Fig. 2(c)). Furthermore, the ZnO nanorods (Fig. 2(d)) were observed when CF/Zn annealed at 500°C. Therefore, the various morphologies may be related to source materials and reaction temperature.[13,14] The growth mechanism of ZnO-nanosheet-covered carbon fibers prepared by the thermal oxidation route has rarely been reported in the previous literature. In our experiment, the XRD results show that parts of metallic Zn were remained, and the content of Zn increases with the annealing temperature increasing (Fig. 1). The effect of the remained metallic Zn on the morphology of the ZnO surface layer is not clear at present. However, the detailed mechanism still needs further investigation.

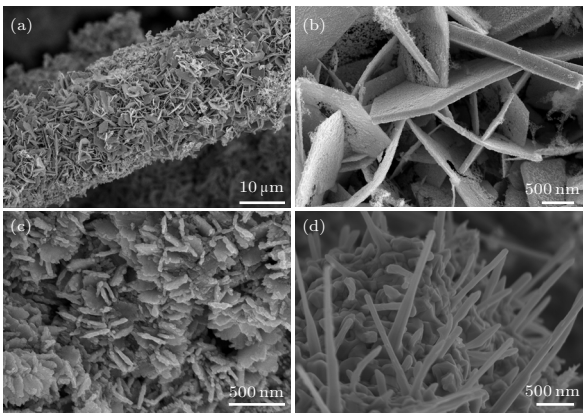


Fig. 2. SEM photographs of ZNCFs synthesized at different temperatures: (a) and (b) 400°C low and high magnification; (c) 450°C; (d) 500°C.

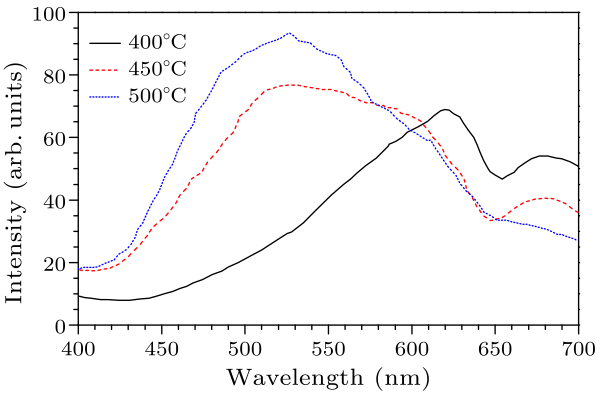


Fig. 3. Room-temperature PL spectra of the ZNCFs synthesized at temperatures 400°C, 450°C and 500°C.

PL spectra are used to evaluate the optical properties. Figure 3 shows that the PL spectra from the samples synthesized at temperatures 400°C, 450°C and 500°C for four hours in air, respectively. All the spectra have a broad emission covering the range from 430 nm to 700 nm. The intensity of the luminescence band in visible spectral range increases with the increasing annealing temperature. The blue shift from 683 nm to 500 nm is more pronounced with the increasing annealing temperature. Interestingly, the PL spectra of ZnO nanosheets exhibit a broad orange-red emission covering the range from 620 nm to 700 nm. The nanoneedle-like samples exhibit broad green and yellow defect emission. They are possibly ascribed to surface defects.[15]

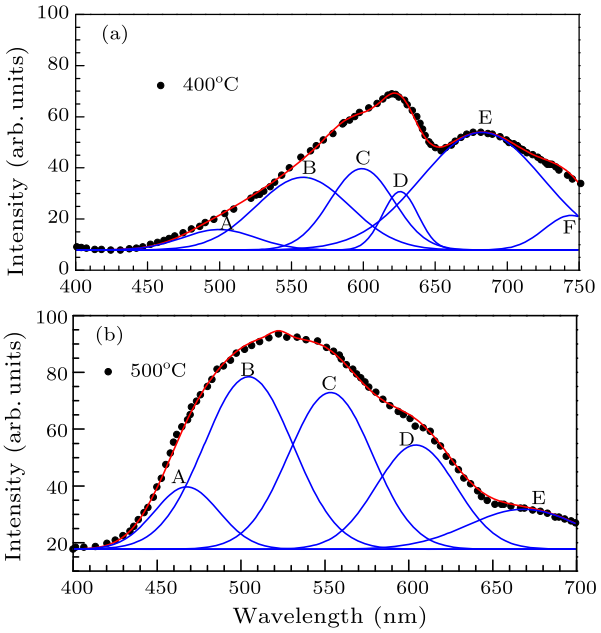


Fig. 4. Multi-peak Gaussian fitting result of the samples synthesized at temperatures (a) 400°C and (b) 500°C.

By multi-peak Gaussian fitting, it is found that the broad emission is composed of many peaks (Fig. 4). Peak F in Fig. 4(a) is caused by the background of the instrument during the PL measuring. Peaks A, B and C in Figs. 4(a) and 4(b) have been previously reported, respectively. The visible emissions are dependent on oxygen vacancies, oxygen interstitials, zinc vacancies and zinc interstitials.[16–18] In our experiment, the zinc was oxidized first on the zinc thin film surface, and then the nanostructure grew into inner zinc films. This process was achieved by atomic diffusion. Inevitably, there exist different internal defects. Therefore, yellow, green and cyan emissions were observed with the morphological ZNCFs changing. Chen *et al.*[19] reported that the different defects in ZnO were probably caused by the combination of graphite and carbon tubes producing carbon and oxygen from the atmosphere. When the graphite and carbon tubes were used as starting reagents, they supply carbon atoms to the Zn layer; the out diffusing C atoms may reach the ZnO layer and react with O there. One of the evidences is the reduction of ZnO at higher annealing temperature as can be seen from Fig. 1, the reflections of metallic Zn become stronger. C atoms may also diffuse into the ZnO layer combining the O at lattice sites thus producing the defects inside the ZnO crystals.[19] In our experiment,

ZNCFs on the carbon fiber surfaces were synthesized by the thermal oxidation method. Carbon atoms were used as an interstitial of the lattice of ZnO nanosheets when zinc films were oxidized at 400°C. Therefore, ZnO nanosheets exhibit clearly orange-red emission spectra. Additionally, compared with the diffraction peaks of ZNs, zinc shows relatively stronger diffraction peaks with the increasing annealing temperature (Fig. 1). Therefore, it is possible that parts of oxygen in ZnO were replaced by carbon, and zinc increases. Meanwhile, the carbon atoms in ZnO were oxidized into CO_x complex exporting carbon and introducing new defects,[19] so orange-red emission was obviously weakened. Further, elevating the oxidation temperature to 500°C, the combination of the carbon and oxygen atoms become more remarkable, the oxygen vacancies appears in the ZnO lattice, and this leads to the typical green emission. Therefore, we consider that the orange-red emission results from the interstitial carbon of ZNCFs, and green emission results from the oxygen vacancies and zinc interstitials.[16−18] However, the detailed mechanism of the PL properties needs further research.

In summary, ZnO nanosheets and nanorods have been synthesized by plating zinc on carbon fiber surfaces, then annealed at 400°C, 450°C and 500°C for four hours in air, respectively. The optical properties of ZNs are investigated. Interestingly, the orange-red emission of ZnO-nanosheet-covered carbon fibers is found. The PL spectra of CF/Zn annealed at different temperatures cover the range from 430 nm to 700 nm. With the increasing annealing temperature, the blue shift is clearly observed, and the intensity of all the sample peaks become stronger. We consider that the orange-red emission result from the interstitial carbon of ZNCFs, and green emission results from the oxygen vacancies.

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