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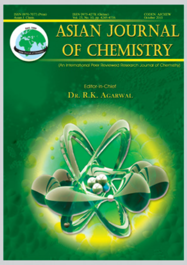

Growth of ZnO Nanorods Coated Carbon Nanotubes Structures by Aqueous Solution Method

NAISEN YU*, WENJIE XIONG, YAN CONG and YUNFENG WU

Institute of Optoelectronic Technology, School of Mathematics and Physics, Dalian Nationalities University, Dalian 116600, P.R. China

*Corresponding author: Fax: +86 411 87656135; Tel: +86 411 87656135; E-mail: yunaisen@dlnu.edu.cn

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Zinc oxide (ZnO) nanostructures are grown on carbon nanotubes (CNTs) using low temperature aqueous solution method. The growth is carried out in a two-step process, including synthesizing ZnO seeding layer and forming ZnO nanorods. Scanning electron microscopy (SEM) shows the ZnO nanorods have well-distributedly grown on the carbon nanotubes. The field electron emission of carbon nanotubes and ZnO-coated carbon nanotubes are also measured. The results show that ZnO nanostructures grown onto carbon nanotubes exhibit a high emission current density and field-enhancement factors, which make it a potential candidate for further applications.

Key Words: ZnO, ZnO-coated carbon nanotubes, Aqueous solutions.

INTRODUCTION

Due to their unique physical and chemical properties, carbon nanotubes (CNTs) have gained great attention due to their unique structure and physical properties[1,2]. Recently, efforts have been focused on modification of carbon nanotubes with semiconductive metal oxides such as TiO_2, CdS, SnO_2, ZnO[3-6]. Incorporation of metal oxides with carbon nanotubes will lead to nanocomposites possessing the properties of both components, which would be useful in the field of optics, catalysis, antibacterial properties. Simultaneously, ZnO has received widespread attention due to its excellent optical and electrical properties. So many scientists have paid considerable attention to assemble ZnO to carbon nanotubes. The ZnO/carbon nanotubes materials have been fabricated using many methods, such as plasma-assisted sputtering technique[7], chemical vapour deposition[8]. However, most of these materials were produced *via* chemical vapour deposition process at high temperature. In comparison with the high-temperature strategy, a wet chemical method is considered an economic and reasonable choice for its mild, productive and flexible reaction route.

In the paper, we grew ZnO nanorods on carbon nanotubes *via* a two-step wet chemical approach. This involved the coating of ZnO nanocrystals seeding layer, followed by simply growth ZnO nanorods in aqueous solution. The ZnO nanorods coated carbon nanotubes were characterized by XRD and SEM. The results showed that the wurtzite ZnO structure nanorods had well-distributedly grown on the carbon nanotubes. Meanwhile, the electron field emission properties were also investigated, the ZnO nanorods substantially enhanced the emission, the ZnO nanorods coated carbon nanotubes exhibited a high emission current density and field-enhancement factors.

EXPERIMENTAL

The carbon nanotubes were purchased from Shenzhen Nanotech Port Co. Ltd., China. The carbon nanotubes were first seeded by dipping into 20 mM zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] solution for 48 h under constant stirring. Then annealing at 200 ºC to achieve a good adhesion between the coating and the carbon nanotubes. Followed by growth ZnO nanorods in aqueous solution. In a typical experiment an equimolar (0.05 M) aqueous solution of zinc nitrate [$Zn(NO_3)_2$] and hexamethyltetramine ($C_6H_{12}N_4$) was prepared. All chemical reagents in the experiments were of analytical grade (AR) and used without further purification. The seeded multiwalled nanotubes were putted into the above solution of 90 ºC for 8 h. After deposition, the sample was cleaned with deionized water and then dried in an air atmosphere.

Structural characteristics of as-grown ZnO nanostructures were investigated using X-ray diffraction (XRD). Field emission scanning electron microscopy (FE-SEM Hitachi S-4800) was used to investigate the morphology. Field emission experiments were performed in a vacuum chamber at room temperature. The distance between an indium tin oxide anode and a tip of ZnO nanorods/carbon nanotubes was 145 mm. The measured emission area was 28 mm^2.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD of ZnO nanocrystals coated carbon nanotubes. The diffraction peaks are all assigned to multiwalled

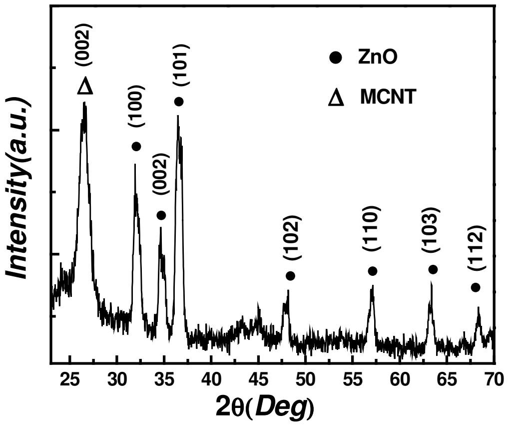

Fig. 1. XRD pattern of ZnO nanocrystals on carbon nanotube surfaces

nanotubes and hexagonal ZnO. The peak around 26º is attributed to the carbon nanotubes. The other diffraction peaks with strong intensity can be indexed as those from the known wurtzite structure of ZnO, which match the hexagonal structure of wurtzite ZnO according to the standard card (JCPDS 36-1451).

Fig. 2 displays the general morphology of typical seeded carbon nanotubes with different magnification. Fig. 2(a) clearly indicates that most carbon nanotubes are covered with ZnO nanoparticles. From the high magnification of Fig. 2(b), the nanocrystalline ZnO evenly coats on carbon nanotubes. The existence of the seed layer makes heterogeneous nucleation on carbon nanotubes possess lower free energy of activation compared with homogeneous nucleation in solution by providing a good structural match, so the ZnO crystalline nanostructures can preferentially be formed on the carbon nanotubes. Fig. 2(c) shows low magnification of as-grown ZnO nanorods/carbon nanotubes structures, it can be clearly seen that most of the carbon nanotubes are uniformly covered with ZnO nanorods. Fig. 2 (d) displays the magnified image reveals that the ZnO nanorods surround randomly the surface of carbon nanotubes. The ZnO nanorods obtained are uniform in size and coated evenly onto the outer walls of carbon nanotubes. And the diameter and length of ZnO nanorods are uniformly around 50 and 300 nm, respectively. Furthermore, ZnO nanorods were grown in a random direction, which was in agreement with the XRD results. The ZnO nanorods were grown in a random direction ascribed to the uncontrollable orientation of ZnO nanocrystal seeds on carbon nanotubes.

Fig. 3 illustrates the emission current density (*J*) as a function applied electric field (E) from as-grown ZnO/carbon nanotube and carbon nanotubes samples. The as-grown ZnO/carbon nanotubes and carbon nanotubes exhibit significantly different emission behaviours. It reveals that the electron emission performance of the ZnO/carbon nanotubes sample has been dramatically improved. For example, the maximum current density (under the field of 7 V/μm^{-1}) has been increased from the original 6.3-71.2 mA/cm^2. At the same time, the turn-on field has been reduced from 4.6-4.2 V/μm^{-1} at current density of 0.1 mA/cm^2.

The emission I-V curves were converted by using the Fowler-Nordheim (F-N) equation and plotted as ln (I/V^2) *versus* 1/V, as shown in the Fig. 4. The curves exhibits linear dependence which indicates that the emission satisfies the F-N mechanism. The field emission characteristics of the synthesized ZnO nanostructures are analyzed through the modified F-N equation.

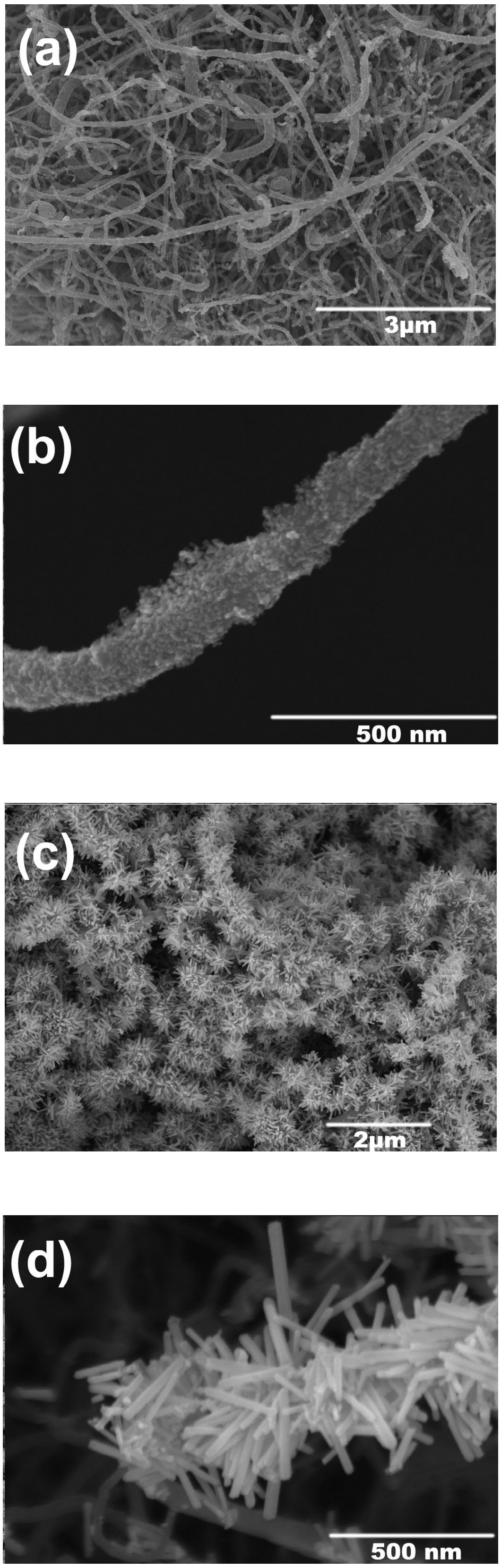

Fig. 2. SEM mircrographs showing ZnO nanorods grown on carbon nanotubes. (a) Low and (b) high magnification of the seeded carbon nanotubes, (c) low and (d) high magnification of ZnO nanorods/ carbon nanotubes heterostructures

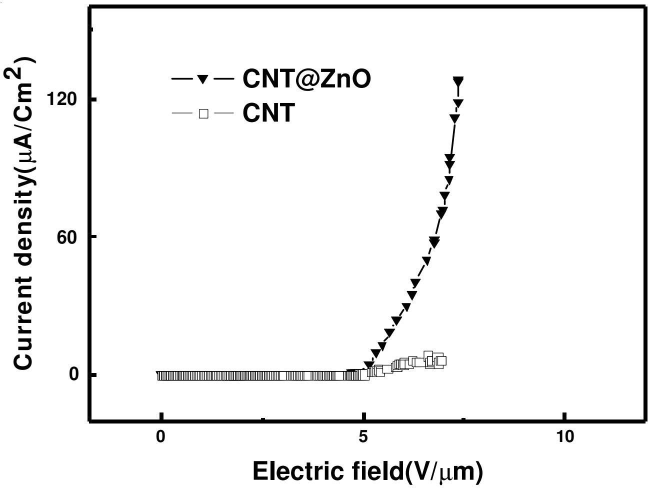

Fig. 3. Emission current density (*J*) as a function applied electric field (E) from as-grown ZnO/carbon nanotubes and carbon nanotubes samples

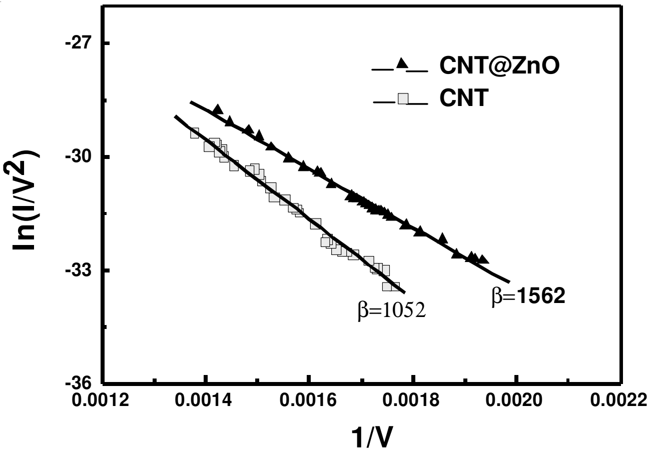

Fig. 4. F-N plots of as-grown ZnO/carbon nanotubes and carbon nanotubes samples

$$k = \frac{B\varphi^{3/2}d}{\beta}$$

where φ is the work function of ZnO, d is the emitting distance and $B = 6.83 \times 109\ VeV^{-3}/2\ m^{-1}$ and the field enhancement factor β can be calculated from the slope ($k_{F\text{-}N}$) of the F-N plot if the work function of the emitter is known. By taking 5.2 eV as a fixed work-function value for ZnO nanorods[9] and carbon nanotubes to 4.5 eV[10]. It came out to be 1562 and 1052 for carbon nanotube and ZnO/carbon nanotube, respectively. The improvement of field-enhancement factors is believed to occur *via* lowering of the Schottky barrier at the metal-semiconductor interface. Meanwhile, the nanorods were formed from randomly oriented one to aligned one, which offer higher numbers of emission sites.

Conclusion

In summary, ZnO nanorods structures were successfully grown onto the carbon nanotube surface by the aqueous solution method at low temperature. The results show that wurtzite ZnO structure nanorods have well-distributedly grown on the carbon nanotubes. Meanwhile, ZnO nanorods grown onto the carbon nanotube surface can increase the emission, sites. The ZnO-coated carbon nanotube exhibit a high emission current density and field-enhancement factors, which make it a potential candidate for further applications.

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