Synthesis and enhanced field emission of zinc oxide incorporated carbon nanotubes

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ABSTRACT

Zinc oxide (ZnO) nanostructures were successfully incorporated into carbon nanotubes (CNTs) using an arc discharge method. Studies of the morphologies of ZnO incorporated CNTs (ZnO-CNTs) revealed that ZnO nanoparticles were attached on the exterior of CNTs. X-ray diffraction, Raman spectra and cathodoluminescence (CL) spectra revealed the existence of ZnO. The I_D/I_G ratios from Raman spectroscopy for the CNTs and ZnO-CNTs were 0.44 and 0.51, respectively, suggesting an increased degree of disorder of the CNT walls after the incorporation of ZnO. The deep red CL emission peak at 747 nm originated from ZnO defect emission in ZnO incorporated CNTs. X-ray photoelectron spectroscopy results revealed that sp^3-hybridized C—O bonds at 286.2 eV in ZnO-CNTs had higher intensities than CNTs, indicating presence of more C—O bonds in ZnO-CNTs. A low turn-on field of ~1.5 V μm^{-1} at a current density of 0.1 μA cm^{-2}, low threshold field of ~2.9 V μm^{-1} at a current density of 1 mA cm^{-2}, high field enhancement factor (5741), and stable emission current were obtained from ZnO-CNTs. The simplicity of synthesis, coupled with the promising emission results, make ZnO-CNTs a promising candidate for low-cost, compact CNT cold cathode materials.

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1. Introduction

Since electron field emission from carbon nanotubes (CNTs) was first demonstrated in 1995 [1–2], CNTs have attracted much attention as excellent field emission sources with potential applications such as field emission displays, X-ray sources and microwave devices [3,4]. High aspect ratios, good mechanical stiffness and large local field enhancement factors lead to low threshold voltages for electron emissions from CNTs [5–6].

As an important wide-band gap (3.37 eV) semiconductor with a large exciton binding energy of 60 meV, zinc oxide (ZnO) nanostructures have received widespread attention for use in electronics, optics and photonics systems [7–9]. Good thermal stability and oxidation resistance, and a high tendency to form stable nanostructures, makes ZnO nanostructures excellent candidates for field emission studies [10–12]. In particular, a key question is: will field emission properties improve and material applications extend if CNTs and ZnO nanostructures are combined?

ZnO-CNT combined nanostructures have been developed and field emission properties were reported [13–17]. Jo et al. reported a low

operating electric field from ZnO nanowires grown on carbon cloth [18]. CNT-bundle arrays have also been grown on vertically self-aligned ZnO nanorods and were found to have significantly enhanced field emission properties [19]. Yan et al. reported low turn-on and threshold fields, and stable emission currents for an ordered CNT-ZnO heterojunction [20]. A novel, stand-alone system of CNT-ZnO nano-contacts has been built to study the electronic structures and field emission properties using density functional theory. Ho et al. reported a significant enhanced field emission property for CNTs after ZnO nanoparticles was uniformly coated on the walls of CNTs [21]. Field emission arrays based on ZnO quantum dot/CNT hybrid nanocomposite exhibited significantly improved luminance intensity and emitting dot density when compared with the CNT-only arrays [22]. It is proposed that the introduction of the ZnO on the sidewall of CNTs can enhance the tunneling probability, and result in the improved field emission property for the hybrid emitters.

The synthetic method used plays a significant role in creating unique properties from nanostructured materials. Some of the synthesis routes described above either lack suitability for mass production or introduce undesired impurities. It is therefore highly desirable to develop an efficient, simple and economical method to mass-produce ZnO-CNT nanocomposites for industrial applications. Arc discharge is a simple, cost-effective, rapid technique that can easily be implemented and adapted for mass production. Varying

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the partial pressure, arc discharge current, process duration, and other physical conditions that constitute the arc discharge process can tune the surface morphologies of nanostructured materials prepared using the technique. To date, arc discharge has mainly been applied to synthesize carbon nanotubes and metal oxide nanostructures [23–24].

In this study we report a new strategy for incorporating ZnO into CNTs using an arc discharge method for large-scale production. The as-synthesized ZnO-incorporated CNTs had tube-shaped structures with smooth, clean surfaces along their entire length and they possessed better field emission properties than those from simple CNTs and ZnO nanostructures. This work highlights an excellent commercial opportunity in vacuum microelectronic devices using ZnO incorporated CNTs fabricated using a low-cost method with the ability to upscale production.

2. Experimental

2.1. Synthesis of ZnO incorporated CNTs

ZnO incorporated CNTs were synthesized using an arc discharge method in an arc discharge apparatus. A graphite rod (99.99% purity by weight; 7 mm diameter) was drilled to produce a 3.1 mm diameter hole in the center and served as an anode. A mixture of carbon (40 wt%), paraffin (20 wt%) and ZnO powder (40 wt%) was filled into the center hole produced in the graphite rod. A water-cooled graphite disc, 135 mm in diameter and 8 mm in thickness, with a purity of 99%, was used as the cathode inside the process chamber. The position of the anode was adjusted using a stepper motor to move up or down, facilitating an arc discharge with a steady current. During the experiment, ambient air was introduced into the chamber and the gas pressure inside the chamber was maintained at 500 Torr. After discharging for 20 s at 80 A, large quantities of black powder were observed adhering to the surface of the graphite substrate and the inner walls of the chamber.

ZnO incorporated CNTs were collected from the chamber and subjected to an oxidation treatment in air at 500 °C for 10 h. Heating in air oxidizes amorphous carbon and carbon nanoparticles such as fullerenes and other carbonaceous species, leaving only CNTs. Scanning electron microscopy (SEM) (JEOL 6500 F) and transmission electron microscopy (TEM) were used to characterize the as-synthesized materials. Effects of ZnO incorporation on CNT crystallinity were studied using X-ray diffraction (XRD) with Co K$_\alpha$ radiation. Raman and cathodoluminescence (CL) measurements were carried out at room temperature in a backscattering geometry. X-ray photoelectron spectroscopy measurements were carried out using photon energy of 900 eV in soft X-ray beamline at Australian Synchrotron, Australia.

2.2. Measurement of field emission properties

The CNTs were mounted onto a metallic substrate and electrically connected to a stainless steel block. In the set-up, CNTs worked as cathodes. The assembly was placed into a vacuum chamber that was evacuated to a residual gas pressure of 2×10^{-7} mbar. A highly polished stainless steel rod with a 4 mm diameter circular flat tip served as the anode. The anode was mounted on a micro-adjustment system (μm resolution) to set the anode-cathode separation. Field emission measurements were performed by applying different voltages across the stainless steel anode and cathode in the vacuum chamber. The emission current was measured using a Keithley 237 source measure unit as a function of anode-cathode separation between 50 and 120 μm. Fowler-Nordheim (FN) curves were plotted and used to determine field emission properties.

3. Results and discussion

Typical SEM image of ZnO incorporated CNTs is shown in Fig. 1(a). The image shows tube-shaped structures with smooth, clean surfaces along their entire length. CNT walls were not densely dotted with ZnO nanoparticles, which is in contrast with previous studies [13,15–16, 25]. Some small clusters distributed on the walls of CNTs were occasionally observed in SEM images and a TEM image of a specific particle structure among the clusters is shown in Fig. 1(b). It is clear that the particle structure had a diameter close to that of CNTs and had a polyhedral morphology.

A high-resolution TEM (HRTEM) image of the specific particle structure is shown in Fig. 1(c). The Fig. 1(c) shows a well-defined faceted structure with an inner hollow space (3–10 nm in diameter). ZnO particulates of were attached to the CNTs. Similar results were reported on ZnO nanoparticles coated CNTs prepared by atomic layer deposition (ALD) [13]. However, such structure has also been attributed to hollow, onion-like carbon particles formed from heating at around 2100–2500 K during arc discharge [26–27]. Fig. 1(d) shows a HRTEM image of a ZnO incorporated CNT synthesized using arc discharge. It is evident that the multilayer CNT sheets are stacked, with a lattice distance of approximately 3.35Å between each multilayer CNT sheet, which is lower than that for arc-derived carbon nanotubes (3.44Å). This result agrees well with boron-doped multi-wall CNTs, which feature decreased lattice space between multilayer CNT sheets after the incorporation of boron into CNTs [28]. The amorphous layers (less than 1 nm in thickness) can be seen at the top outside wall of the ZnO incorporated CNTs, which is likely from CNT defects or ZnO thin film layer coated on CNTs [13].

Fig. 2 shows the XRD spectra of CNTs and ZnO incorporated CNTs. The CNTs had similar crystal structures and phase purities as CNTs previously synthesized using the same method [29]. Typical patterns of crystallized materials consistent with the structure of the CNT orientations (002), (100) and (004) were observed in both samples, which further highlight the structural similarities between CNTs and ZnO-CNTs. Aside from peaks attributed to CNTs, the other diffraction peaks were readily indexed to the typical hexagonal structure of high-quality crystalline ZnO. This result confirms that high purity ZnO incorporated CNTs were successfully synthesized using arc discharge.

Raman spectroscopy provides a sensitive tool for characterizing carbon materials in general, and doped materials in particular [30]. Fig. 3 presents Raman spectra of CNT and ZnO incorporated CNTs in the wavenumber range 100–3000 cm^{-1}. The in-phase vibration of carbon atoms in the direction perpendicular to the nanotube axis, called the radial breathing mode (RBM), was observed in CNTs and indicated the existence of small CNTs (a few nanometers in diameter). The intensity of the RBM band was almost undetectable in ZnO incorporated CNTs. The ZnO dopant most likely hinders the collective in-and-out movement (breathing mode) of the carbon atoms of the nanotube [31].

A G-band at approximately 1581 cm^{-1} and a D-band at approximately 1354 cm^{-1} were observed in CNTs, and are associated with the stretching mode of the carbon-carbon bond in the graphite plane and defects/impurities in the CNTs. The G-band shifted to 1583 cm^{-1} and the D-band shifted to 1356 cm^{-1} for ZnO incorporated CNTs, consistent with the changing in-plane lattice constant and a weakening of either Zn—C or C—O in-plane bond strengths relative to that of a C—C bond. The D-band is normally present at approximately 1607 cm^{-1} in CNTs, but was not detected in this study. A peak at approximately 2702 cm^{-1}, which corresponded to the overtone of the D-band, was evident in both samples. The values of the intensity ratios between the D- and G- bands for the CNTs and the ZnO incorporated CNTs were 0.44 and 0.51, respectively, showing an increase in the degree of disorder of the CNT walls after the incorporation of ZnO. This ratio is useful for estimating the relative concentration of ZnO in CNTs when the amount of dopant present in the system is below the detectable level [32].