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# Electron transport behavior of individual zinc oxide coated single-walled carbon nanotubes

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## Abstract

Uniform zinc oxide coated single-walled nanotubes (SWNTs) were fabricated by ultrasonic irradiation with acid-treated SWNTs, zinc acetate, and triethanolamine at low temperature in aqueous phase processing. The ZnO coating process did not decrease the dark current of the SWNTs, but a real decrease in the steady state negative photocurrent was observed after ZnO coating, suggesting a clear photosensitization effect. Transport measurements reveal that the negative photocurrent in s (semiconducting)-SWNTs@ZnO could be described by electron-hole compensation behavior attributed to the ZnO layer under ultraviolet excitation. This simple coating method for one-dimensional material can open up new possibilities for multifunctional nanodevices.

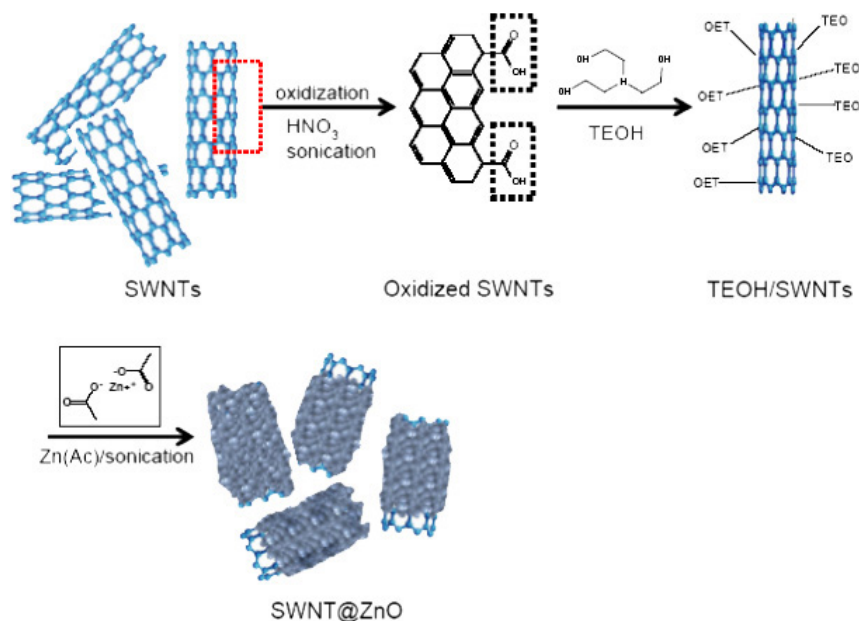
(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Semiconducting nanoparticles have been widely investigated due to their potential applications in photocatalysis, solar energy conversion, and optoelectronic devices [1–6]. The assembly of isotropic nanoparticles into one-dimensional (1D) structures leads to the formation of new nanocomposites which may lead to new nanodevices [7–9]. Recently, single-walled carbon nanotubes (SWNTs) have become one of the most studied 1D nanostructures for new nanocomposites, due to their excellent structural and electronic properties [10, 11]. In order to prepare multifunctional nanodevices, several methods have been developed to coat carbon nanotubes (CNTs) with metallic and semiconducting or insulating materials, such as Au, Ag, SnO<sub>2</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> [7, 12–16].

Zinc oxide (ZnO) is a wide band gap semiconductor (3.4 eV) with a large exciton binding energy (60 meV) that has been extensively investigated because of its excellent performance in sensors and optoelectronic systems [17–20]. There are several methods to fabricate ZnO clusters, nanoparticles, and nanostructures [21, 22], but little work has been done using CNTs. Recently, Zhu *et al* [23] and Ravindran *et al* [24] have reported the coating of ZnO nanoparticles on multi-walled carbon nanotubes (MWNTs) by sputtering and/or by an electrostatic coordination approach, but they showed that it is difficult to form a continuous coating on the CNTs. This reveals that different coating mechanisms of CNTs still need to be further investigated. So far, to our best knowledge, there have been no further and systematical investigations on the synthesis and photonic and electrical properties of ZnO-coated CNTs through a wet-chemical process in aqueous solution at lower temperatures. The dual role of carbon nanotubes can

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**Scheme 1.** Illustration of the synthesis process of SWNTs@ZnO (core-shell) nanocomposite. TEOH stands for triethanolamine,  $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ .

facilitate charge transfer and promote charge transport in a ZnO-CNT composite.

In this study, it has been demonstrated that the ZnO coating can not only modify the optical properties but also the electron transport behavior of metallic or semiconductor SWNTs. The design of such a ZnO-coated carbon nanotube composite with dual roles can provide a convenient strategy to develop next generation photochemical solar cells. Therefore, in this work, a simple method was proposed to fabricate ZnO-coated SWNTs (SWNT@ZnO) at low temperatures via ultrasonic processing with acid-treated SWNTs, zinc acetate, and triethanolamine. Furthermore, the developed SWNTs@ZnO will be characterized using high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, atomic force microscopy (AFM), and electron transport measurements.

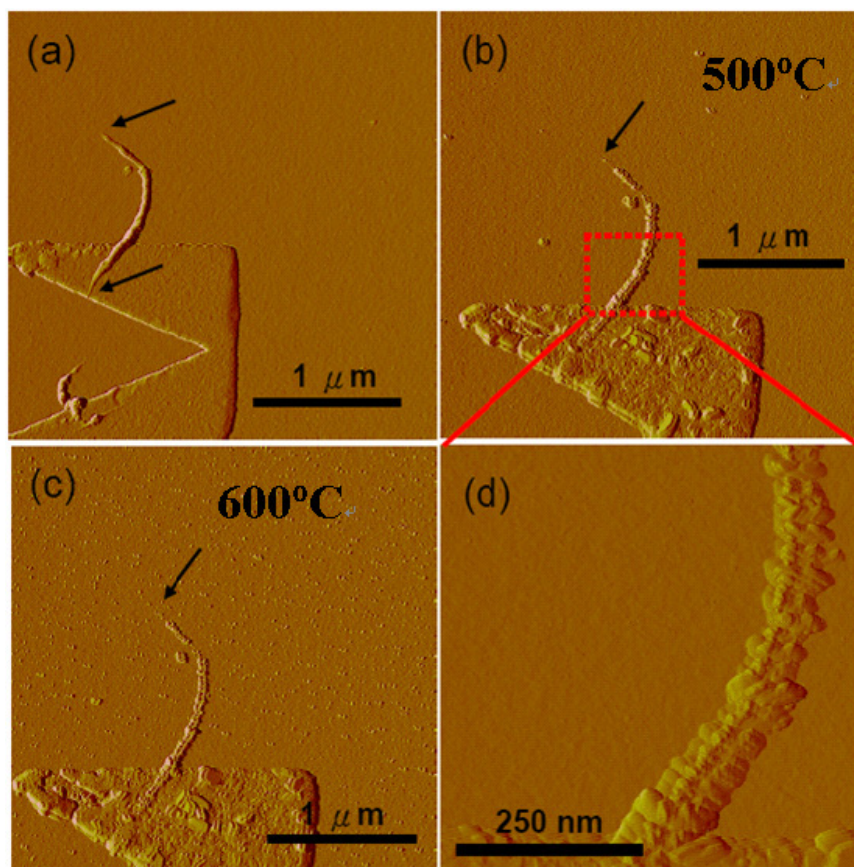
## 2. Experimental details

In this study, SWNTs produced by the HiPCO process were obtained from Rice University. These nanotubes were sonicated in concentrated nitric acid ( $\text{HNO}_3$ ) for 10 min. This treatment is well known to produce short nanotubes and to create defects on the sidewalls, which contain carboxyl and hydroxyl groups [25]. The schematic representation of the reactions done on the SWNTs for the preparation of the ZnO nanocomposite is given in scheme 1. The acid-treated SWNTs were dispersed in 20 ml distilled water. The suspension containing SWNTs was then heated to  $95^\circ\text{C}$  with intense ultrasonication. Subsequently, solutions containing  $0.005\text{ mol l}^{-1}$  of zinc acetate and  $1.5\text{ mol l}^{-1}$  of triethanolamine (TEOH) were dropped slowly into the SWNT suspension. The mixture solution was further ultrasonicated for 2 h at  $95^\circ\text{C}$ . The thickness of the ZnO coating can be

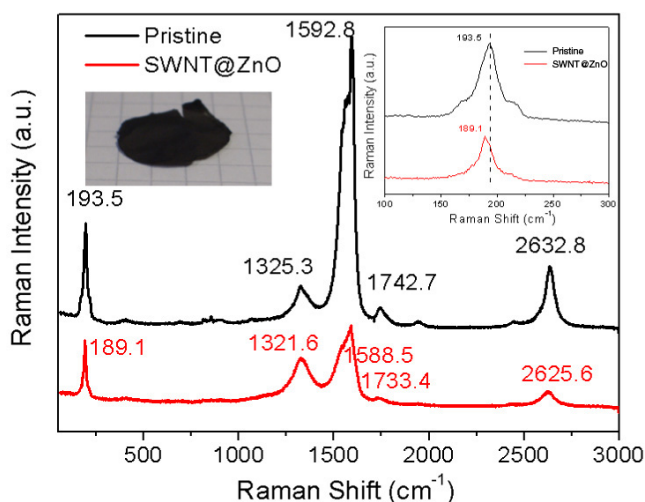
adjusted by changing the reaction time and the concentration of zinc acetate. In the transport measurement, a gold and a palladium electrode which act as source and drain were deposited on top of a  $\text{SiO}_2$  layer on a silicon substrate that was used as the gate. Individual SWNTs and SWNTs@ZnO were placed across the two noble metal electrodes.

## 3. Results and discussion

According to our previous study [25], the average diameter of pristine SWNTs (made with the HiPCO method) was about 1.6 nm. After the coating process, the average diameter of the SWNTs increased to 8 nm (as determined by AFM). An individual SWNT@ZnO nanotube, shown in figure 1(a), was fixed on the patterned silicon chip; it presented uniform surface morphology on the median part of nanotube. X-ray diffraction analysis (not shown here) indicated that the coated ZnO layer on the SWNTs presented poor crystallinity. It was believed that after the SWNTs were subjected to oxidization in  $\text{HNO}_3$  solution and treated at  $95^\circ\text{C}$ , the addition of zinc acetate into the SWNT aqueous solution probably promoted the formation of the crystallinity of the ZnO. In order to demonstrate that a continuous ZnO layer had been successfully coated on the SWNT, the SWNT@ZnO was heated at 500 and  $600^\circ\text{C}$  in air for 30 min, as shown in figures 1(b) and (c). On heating at more than  $500^\circ\text{C}$  in air atmosphere, the SWNTs will be generally removed by complete oxidation and a discontinuous ZnO coating on SWNTs is expected to appear. However, AFM observation of the same area reveals linear features formed at the positions where SWNT@ZnO was previously observed, suggesting that the SWNT had been uniformly coated with ZnO. Figure 1(d) shows the surface morphology of a ZnO nanowire (heated in air at  $500^\circ\text{C}$ ). An enhanced crystalline



**Figure 1.** AFM images of the same SWNT@ZnO. (a) Before heating, (b) after heating in air at 500 °C for 30 min, (c) after heating in air at 600 °C for 30 min, and (d) high-magnification image of (b). (The arrows point out the area without ZnO coating.)



**Figure 2.** Resonant micro-Raman spectra on bucky-paper SWNTs and SWNTs@ZnO. (Inset: bucky-paper image and local region Raman spectrum.)

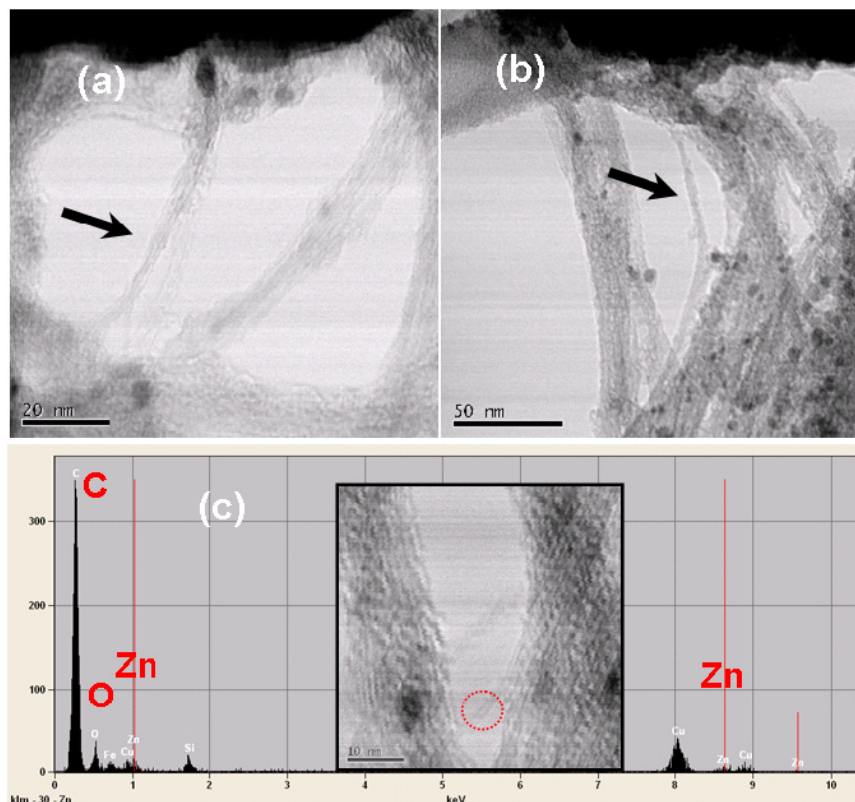
structure with linear features can be observed, which could be ascribed to the reduced defects in the ZnO coating layer.

Next, micro-Raman spectroscopy was used to observe the tiny variations on SWNTs coated with or without continuous ZnO materials, as shown in figure 2. The Raman spectra were

measured with a Jobin Yvon LabRam Raman spectrometer equipped with a microscope and utilizing the 633 nm excitation wavelength with on-sample intensity of about  $0.2 \text{ mW } \mu\text{m}^{-2}$ . The main features in the Raman spectra of SWNTs are the radial breathing modes (RBMs), which appear in the frequency range  $100\text{--}400 \text{ cm}^{-1}$ , the G band ( $1600 \text{ cm}^{-1}$ ), arising from the tangential vibrations of the carbon atoms, and the D band ( $1280 \text{ cm}^{-1}$ ), associated with disorder,  $\text{sp}^3$ -hybridized a carbon present as impurities and SWNT defects [26]. Therefore, the increase in the D-band intensity observed for the SWNTs@ZnO can be attributed to the functionalization of the SWNTs. The Raman spectra of bucky-paper SWNTs@ZnO show a peak shift of the RBMs by about  $2\text{--}5 \text{ cm}^{-1}$  at lower frequencies (inset figure), which can be attributed to the chemical interaction between the carbon atoms and the triethanolamine-Zn (TEOH-Zn).

The SWNT@ZnO nanocomposites were also analyzed by transmission electron microscopy (TEM). Figures 3(a) and (b) present TEM pictures of the ZnO-coated SWNTs; the arrows point to the continuous layer of non-crystalline material coating the SWNTs. Energy-dispersive x-ray (EDX) measurements were made with VG501 scanning TEM to analyze the elemental composition of the thin non-crystalline layer. The EDX spectrum shown in figure 3(c) was obtained by focusing an electron beam with a spot size of 1.0 nm directly on the coated SWNTs. Zinc, oxygen, and a significant carbon



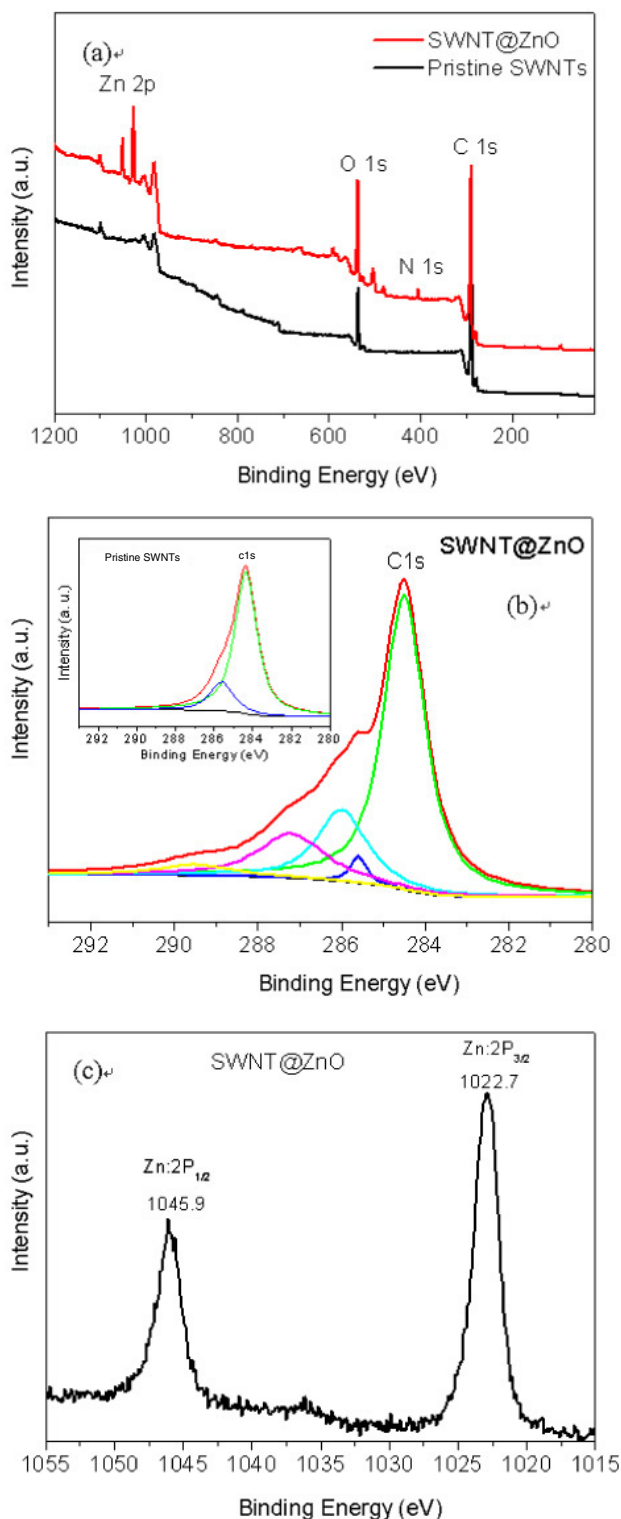


**Figure 3.** Typical TEM images and EDX analysis of SWNTs@ZnO. (a) and (b) present low-magnification TEM images. (c) element composition analysis of an individual SWNT@ZnO. (Inset: high-magnification scanning TEM image of a coated SWNT; the circle indicates the area used for the EDX analysis.)

peak could be clearly obtained after a long acquisition time. The elemental composition of the sample was also determined by x-ray photoelectron spectroscopy (XPS). The XPS spectra of the SWNTs@ZnO show the presence of carbon, oxygen, zinc, and nitrogen (figure 4(a)). Compared to the uncoated SWNTs, the C 1s peak position shifted to higher binding energies after the ZnO coating. The Gaussian decomposition of the C 1s peak of the coated and uncoated SWNTs is shown in figure 4(b). The spectrum consists of two main components in pristine SWNTs. In general, the peak at 284.5 eV is attributed to the graphite-like carbon atoms of the carbon nanotube walls, and the peak around 285.7 eV is attributed to surface hydroxyl groups. On the other hand, the spectrum of the SWNTs@ZnO could be decomposed into three peaks. The graphite-like carbon peak is shifted to higher binding energy and the peaks at around 286.0 eV and 287.2 eV are attributed to the C–N and C=O groups, respectively. Moreover, it could be observed that the intensity of the O 1s peak increases, and the peaks tend to shift to lower binding energies after the coating. This suggests that the oxygen in ZnO and in C=O has lower binding energy than the oxygen in C–O. Figure 4(c) shows the Zn 2p spectra of the SWNTs@ZnO. The peak positions are shifted towards higher binding energy by about 0.5 eV. It seems that Zn 2p peak shift could be due to the formation of some Zn–C bonds [27].

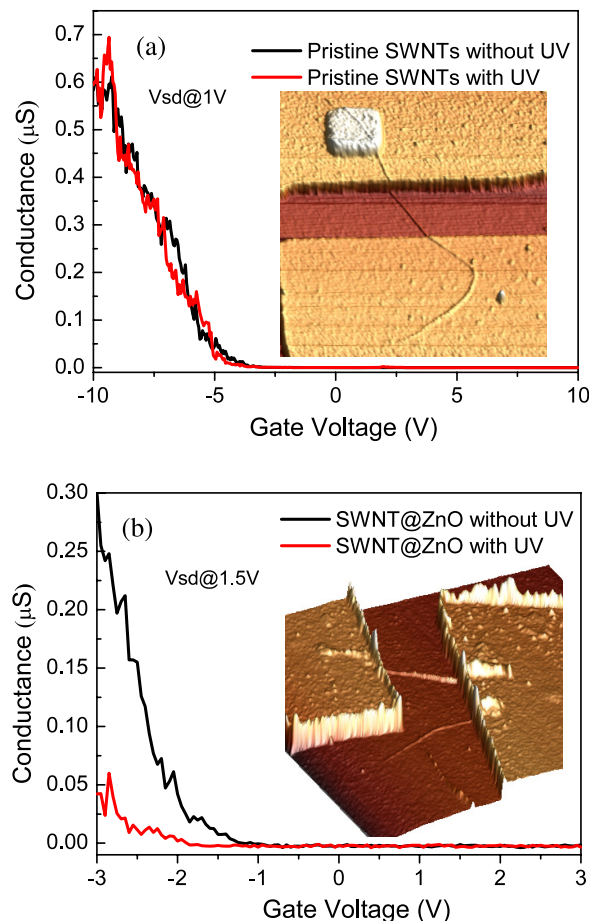
In order to measure the electrical transport, SWNTs were deposited on a doped silicon substrate with a thermally grown SiO<sub>2</sub> layer. Au/Pd electrodes were then applied in a two-probe configuration by standard electron beam lithography.

The electrical transport was measured on several individual SWNT@ZnO tubes by applying ultraviolet (UV) light on the tubes, at room temperature [23]. A series of conductance curves was obtained from pristine SWNTs showing p-type field-effect transistor (FET) characteristics. During the conductance measurements, UV light was irradiated on the device, but no change was observed for the conductance value, which is about  $0.6 \times 10^{-6}$  S, (figure 5(a)). Similar experiments have been reported previously by two research groups [28, 29]. They observed a clear decrease of the conductance during the UV irradiation on the SWNT device, and suggested that this phenomenon could be due to (a) hot electrons attached to adsorbed molecules to induce desorption or (b) the oxidation of the contact electrodes, changing the barrier between the electrodes and the SWNTs. Therefore, this phenomenon was named photoinduced conductivity. However, we could not observe any photoinduced conductivity behavior in our pristine SWNT device. This could be due to the different source of SWNTs and different electrode contacts of the FET devices. These slightly different conditions could easily vary the electrical properties of the SWNTs. Figure 5(b) shows the transport characteristics of the SWNTs@ZnO with and without UV light irradiation. As the electrical properties of ZnO-coated SWNTs were first measured by changing the gate voltage  $V_g$  from  $-5.0$  to  $5.0$  V, it was found that some of the ZnO-coated SWNTs exhibit distinct p-type characteristics and the other tubes show metallic behavior. In contrast, only in the case where ZnO was coated on the semiconducting SWNTs



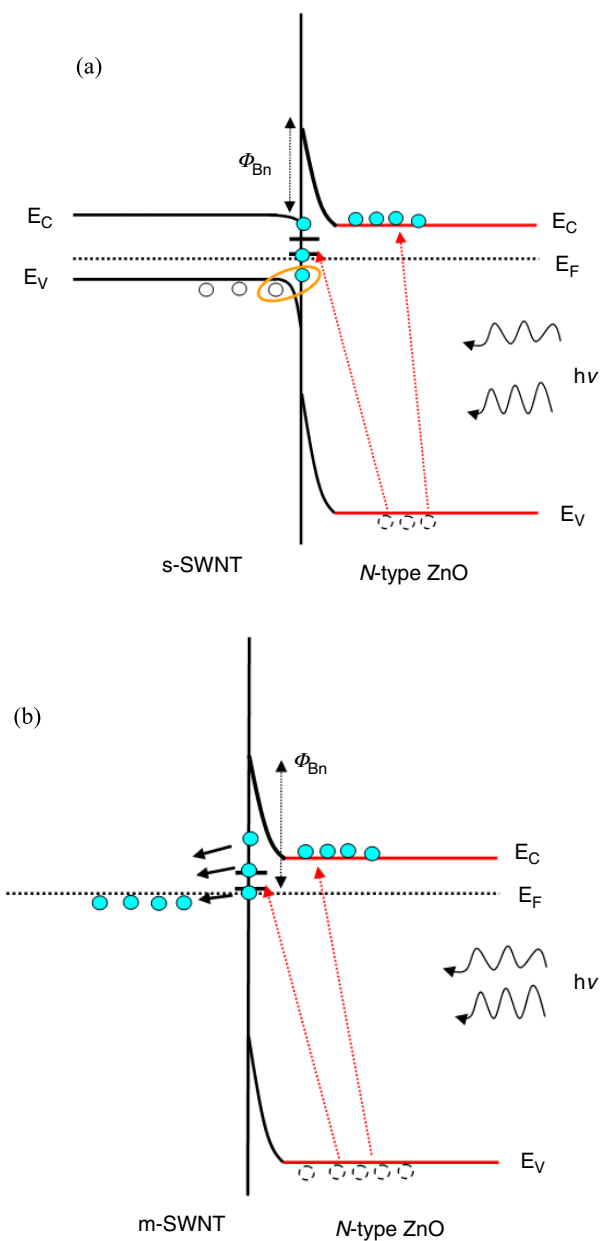
**Figure 4.** (a) A wide-angle XPS spectrum of pristine and ZnO-coated SWNTs. (b) Gaussian decomposition of the C 1s spectra from pristine (inset) and ZnO-coated SWNTs. (c) Zn 2p spectrum of SWNTs@ZnO.

can we observe a significant decrease in the conductance, of about 70%, while irradiating the device with the UV light. It is known that ZnO is a very sensitive photoexcited material when being irradiated with a short-wavelength light (less than



**Figure 5.** Gate dependence of conductance in SWNT transistors without (a) and with (b) ZnO coating in air under UV illumination. The nanotube diameter is (a) 1.8 nm and (b) 7.2 nm, measured by AFM topography (inset).

400 nm). Thus, we suggest that the reduction of conductance on the ZnO-coated nanotubes is a non-thermal process and it corresponds to an electron–hole (e–h) compensation. A schematic energy band diagram is given in figure 6(a) for the photoinduced mechanism in the presence of SWNTs@ZnO composite. In this diagram,  $\Phi_{\text{ZnO}}$  is the work function of n-type ZnO (about 4.5 eV),  $E_{\text{g-ZnO}}$  is the band gap of ZnO (3.3 eV). Also,  $\Phi_{\text{SWNT}}$  is the work function of the s-SWNT (4.8–5.1 eV),  $E_{\text{g-SWNT}}$  is the band gap of an SWNT ( $\sim 0.5$  eV) [30]. Because of large band mismatch in this system, the barrier height becomes large and electrons will be blocked in the ZnO region. The barrier height can be represented as  $\Phi_{\text{Bn}} = (\Phi_{\text{ZnO}} - \Phi_{\text{SWNT}})$ , and was calculated as 0.7 eV. The trapping at surface states drastically affects the transport in a high surface-to-volume ratio material structure. Upon illumination with photon energy larger than the semiconductor band gap ( $E_{\text{g}}$ ), electrons are not only excited into the conduction band but are also easily trapped at the surface states to compensate the hole carriers in the SWNTs. This hole-compensating mechanism through electron trapping in ZnO surface states causes the drastic decrease of the source–drain current,  $I_{\text{sd}}$ . If the UV light is turned off, the e–h compensation behavior will disappear and then the current increases. Moreover, if the SWNTs are



**Figure 6.** Energy bands for ZnO coated on (a) semiconducting and (b) metallic SWNTs after UV irradiation.

metallic (m-SWNTs), the band diagram of m-SWNTs@ZnO will be modeled as shown in figure 6(b). Electrons from ZnO will be injected into SWNTs during the UV irradiation. However, no change was observed in the  $I$ - $V$  characteristics of this system during the injection of electrons since the metallic SWNTs have a large current ( $\mu\text{A}$ ) and thus cover the injection of electrons. These unique and controllable properties could be applied in photon-controlled electronic devices.

#### 4. Conclusion

We have presented a new method to uniformly coat a ZnO nanolayer on SWNTs by aqueous phase processing. The

successful coating of the SWNTs has been confirmed by TEM and XPS analysis. The Raman measurement of SWNT@ZnO nanotubes confirms that the ZnO-coated layer would restrict the RBM vibration of SWNTs and make the peak shift towards lower frequencies. Transport measurements point out that the hole carriers in s-SWNTs could be described by electrons attributed to the ZnO layer under UV excitation but electrical property of m-SWNTs would not be changed by the ZnO-coated layer. The results presented in this study can pave the way towards the design of one-dimensional nanostructures with new possibilities in multifunctional nanodevices.

#### Acknowledgments

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