ZnO-Coated Carbon Nanotubes: Inter-Diffusion of Carboxyl Groups and Enhanced Photocurrent Generation

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1. Introduction

Metal oxides prepared by atomic layer deposition (ALD) at low temperatures are always nonstoichiometric and defects can be classified into n- and p-types. For example, ZnO contains excess metal ions and an electron deficiency, owing to oxygen vacancies inducing optical transitions in the visible regime.[1] Recent studies have shown that carbon nanotubes (CNTs), which are one-dimensional conductors made of rounded graphene sheets, can be coated with oxides, and the resultant composites display interesting effects, including enhanced photocatalysis at visible wavelengths and the creation of large coercivity in low magnetic fields.[2, 3] Deposition of oxides onto CNTs, however, is challenged by interfacial issues. First, conjugated surfaces are governed by dispersive forces and can barely interact with oxides; second, epitaxial growth of oxides on a curved template is difficult and coatings lack a well-defined structure. Accordingly, CNTs are often chemically etched to create roughness, and peak shifts in the binding-energy spectra confirm interactions of oxygenated groups with cations.[4] In this work, ALD is employed to produce ZnO nanoparticles (NPs) on oxygenated CNTs, and we find that the coating induces diffusion of carboxyl groups into oxygen vacancies during prolonged deposition cycles (DCs). Elemental analyses confirm the presence of C=O in the oxide lattice, and this doping results in a reduced electron deficiency and the quenching of oxygen vacancies related to light emissions in the visible regime. The oxide coatings, however, remain optically active at ultraviolet (UV) wavelengths, and emissions through near-band-edge (NBE) transitions are verified through the photoluminescence (PL) profiles at low and room temperature. Upon photoexcitation, fully coated nanotubes exhibit an increased photocurrent ($I_{ph}$), and the quantum efficiency ($\eta$) is promoted by 22% relative to bare nanotubes.

2. Results and Discussion

Figure 1 shows XRD profiles of the coated CNTs and reflections at $2\theta = 31.5, 34, \text{ and } 36^{\circ}$, which correspond to the (100), (002), and (101) planes of wurtzite ZnO. We found that at DC$_{50}$ the full width at half maximum of the (101) profile approximates 0.6$\sigma$ ($\sigma$ = the standard deviation, ± 10%), which then increases to 0.8$\sigma$ at DC$_{100}$ and 4.1$\sigma$ at DC$_{150}$; this is indicative of DC being proportional to the NP size.

Interestingly, ZnCO$_3$ is also present and reflections can be seen at $2\theta = 38.7, 42.8, \text{ and } 53.8^{\circ}$, which, according to the Joint Committee on Powder Diffraction Standard Card (No. 79-0206), ZnO is a defect-governed oxide and emits light at both visible and UV regimes. This work employs atomic layer deposition to produce oxide particles on oxygenated carbon nanotubes, and the composites only show emission profiles at short wavelengths. The quenching of defect-related emissions at long wavelengths is verified, owing to carboxyl diffusion into oxygen vacancies, and doping is supported by ZnCO$_3$ formation in oxide lattice. Fully coated nanotubes display an increased photocurrent and the quantum efficiency increases by 22% relative to the bare nanotubes.

Figure 1. XRD profiles of DC$_{50}$ (dark), DC$_{100}$ (red), and DC$_{150}$ (blue).

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come from the crystallographic planes of (110), (113), and (018), respectively. TEM supports the XRD data, and fully coated CNTs are only detected at DC 100 and DC 150 (Figure 2 a), at which the average NP size is estimated to be 60–80% greater than at DC 50 (Figure S1). It is worth mentioning that low-temperature ALD-created oxide structures are often found to be ill-defined and an improved degree of crystallization relies on heat treatment. High-resolution TEM indicates that the coatings are well crystallized and the wurtzite structure is further verified by selected-area electron diffraction (Figure 2 b). The TEM beam spot was then converged to 10 nm and intentionally focused onto the oxides for 30 s. We found that the NPs remained coated and bombardments carried out on DC 50, DC 100, and DC 150 gave a similar result, which is indicative of sufficient binding at the oxide/CNT interfaces.

Figure 3 a shows XPS spectra of the coated CNTs at low energy, and the profiles were fitted with the Lorentzian model to highlight the energy contributions from various groups (Figure 3 b–d). The C 1s peak consists of three components arising from conjugated edges (C=–C), carboxyl (C=O), and carbonyl (C=O) (284–287.6 eV) groups, and individual contributions based on Beer’s law are found to be 22.3, 30.1, and 41.8% for DC 50 (Figure 3 b), 24.3, 46.7, and 20% for DC 100 (Figure 3 c), and 27.7, 35.6, and 21.4% for DC 150 (Figure 3 d). The increased contribution of C=O to the C 1s peak at DC 150 again verifies ZnCO₃ formation in oxides and also implies carbonate formation through inter-diffusion of carboxyl, that is, Reactions (1) and (2):

\[
\text{Zn}^{2+} + \text{COO}^- + \text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} 
\]  
\[
\text{Zn}^{2+} + \text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + 2\text{H}_2\text{O} 
\]

First, inter-diffusion has been observed in SiO₂-coated CNTs. Second, carboxyl groups thermally detach at 200 °C, approximating the ALD temperature. Third, the asymmetric stretching mode of O=C=O (288–289 eV) becomes strong at DC 150, supporting Reaction (2) (Figure 3 b–d). Fourth, the O 1s state (530.6 eV, line 1, Figure 4 a), from both ZnO and C=O, slightly shifts to high energy as the DC increases (531.3 eV, line 2, Figure 4 a), which is indicative of the reduced electron deficiency upon anionic diffusion into oxygen vacancies [i.e. Reaction (1)]. Note that the Zn2p₁/₂ and Zn2p₃/₂ peaks also shift and lie, respectively, on 1022.5 and 1045.8 eV for DC 50, 1022.8 and 1046 eV for DC 100, and 1023.2 and 1046.5 eV for DC 150 (Figure 4 b). Fifth, Raman and infrared spectra confirm that the pyrolysis produced CNTs that are defective in nature (I⁺/Iₐ ≈ 1), and breaking of the hexagonal symmetry is attributed to oxygenation of carboxyl and carbonyl groups (Figure 5). The pure oxide exhibits PL at 370–400 nm and 440–700 nm; the former comes from NBE transitions and involves neutral donor-bound excitons (FX A) and free excitons (FX B). The latter appears as a broad band and is created by oxygen vacancies known as F⁺ centers. Sixth, Figure 4 c shows cathodoluminescence spectra of DC 150-prepared oxides on CNTs and Si wafers; the samples produced at DC 50 and DC 100 give similar profiles (Figure S2). For coated CNTs, the room-temperature spectra are dominated by a single peak in the UV region (dark), and the
The disappearance of the light emission in the visible regime again verifies ZnO coating at low F\(^+\) concentration. The peak then splits into four distinguishable features (red) at 20 K, including FX\(_A\) (369 nm = 3.36 eV), FX\(_B\) (374 nm = 3.32 eV), and longitudinal optical phonons (LO, 382 nm = 3.246 eV and 389 nm = 3.187 eV).\(^{[10]}\)

The coated wafer shows a similar profile at 300 K (blue), but the peak intensity is up to 40% lower than that on the coated CNTs, which is indicative of the finite-sized NPs. At 20 K, defect-related emissions emerge and are located at 405, 420, 465, 540, and 570 nm (green). Figure 4d shows the elemental mapping; the highlighted C (red) and Zn (blue) profiles are produced at an energy count of 50000 ± 5%. First, the C-rich region is elongated and surrounded by metal, confirming the ZnO-coated CNT structure. Second, C dispersion in the Zn region supports ZnCO\(_3\) formation in the oxides. According to the XRD data, both oxides and carbonates show individual reflections and the compound is absent. Therefore, ZnCO\(_3\) possibly forms as nanodomains in the oxide matrix and phase separation is further supported as discussed hereafter. First, the carbonate lattice constant is two-fold greater and cannot alloy with the oxide (ca. 3.2 and 1.6; Figure 6a). Second, carbonate formation does not induce a breaking of hexagonal symmetry (wurtzite cell) and the cell integrity is supported by the pres-

**Figure 4.** XPS spectra obtained from DC\(_{50}\) (dark), DC\(_{100}\) (red), and DC\(_{150}\) (blue) samples at a) 526–538 eV and b) 1020–1050 eV. c) PL profiles and d) elemental mapping of DC\(_{150}\).

**Figure 5.** Raman (top) and infrared spectra (lower) of bare CNTs.  

**Figure 6.** a) Simulated ZnCO\(_3\) (left) and ZnO structures (right). b) Simulated binary ZnCO\(_3\)/ZnO structures.
ence of LO phonons in the PL (Figure 4c). Third, FXA- and FXB-created emissions resemble the bulk phase, which is indicative of unaltered excitation edges. Fourth, the coatings are produced through two steps in sequence: 1) Zn deposition and 2) reaction of the deposited metal with water vapor. Accordingly, Zn$^{2+}$ may preferentially combine with COO· to form isolated domains in the oxides. Figure 6b displays ab initio simulations,[11] and the ZnCO$_3$ (113) and ZnO (101) crystallographic planes are highlighted according to the XRD data. We were, however, unable to determine the diffusion path from the CNT to the oxide, whereas the migration of carboxyl groups into ZnO (100) planes seems feasible. First, an interface forms at the ZnO (100) plane (arrow) and the oxygen atoms (red) marked as 1 and 2 come from the oxide and the carboxyl, respectively. Second, the large spacing between (100) planes facilitates the diffusion process at elevated temperature.

Figure 7 shows time-evolved resistance ($R$) profiles of green-laser-excited CNTs (Figure 7a), DC$_{50}$ (Figure 7b), and DC$_{150}$ (Figure 7c), the measurements were carried out in a vacuum (10$^{-3}$ Torr). For bare CNTs, $R$ decreases and increases at light-on and light-off; $I_{ph}$ was measured to be 104 $\mu$A. For DC$_{50}$, in contrast, $R$ increases at light-on and decreases at light-off (i.e. negative $I_{ph}$) and $I_{ph}$ reduction reaches one order of magnitude with respect to bare CNTs. The $I_{ph}$ in DC$_{150}$ again increases with optical excitation and is greater than that of bare CNTs by 23 $\mu$A. The UV-excited samples give similar results and the negative $I_{ph}$ value is also present in DC$_{150}$ (Figure S3). It is now understood that, for bare CNTs, optical excitation produces a photovoltaic effect and $I_{ph}$ is generated through the separation of electrons and holes at defect-created p–n barriers.[12] CNTs, however, do not show negative $I_{ph}$ values and optical gain is determined by the Schottky barrier at CNT/lead contacts.[13] Accordingly, the negative $I_{ph}$ here must come from trapping of photocarriers at oxides, and the processes can be described by using the band diagram proposed by Lin et al. (Figure 8a).[14] Upon illumination, electrons in both the CNTs and the oxides (DC$_{50}$) are excited to interfacial states and then they relax in the oxides (paths 1 and 2 in the insert) and CNTs (paths 3 and 4); the former is a nonthermal process and leads to negative $I_{ph}$ values. The latter is known as electron–hole compensation and does not contribute to $I_{ph}$.[14] Oxides become electrically connected as the CNTs are fully coated (DC$_{150}$) (Figure 8b) and photocarriers are collected at the leads, accounting for the increase in $I_{ph}$ observed in Figure 7c and Figure S3. We have calculated the $\eta$ according to Equation (I)

$$\eta = \left(\frac{I_{ph}}{q}\right) \times 100\%$$

where $q$ is the electron charge, $P_{inc}$ is the incident beam power, $h$ is Planck’s constant, and $v$ denotes the frequency of the incident beam.[15] Calculations confirm a positive $I_{ph}$ enhancement from oxide coating and $\eta$ is found to be 5.37 × 10$^{-3}$ for bare CNTs and 6.57 × 10$^{-3}$ for DC$_{150}$; the improvement being 22%.

3. Conclusions
Coating ZnO onto oxygenated CNTs induces the diffusion of carboxyl groups into oxygen vacancies and results in the quenching of defect-related emissions in the visible regime. The oxide coatings remain optically active at UV wavelengths, and emission through NBE transitions is detected at low and room temperatures. DC$_{150}$ exhibits a positive $I_{ph}$ enhancement and $\eta$ increases by 22% with respect to bare CNTs.
Experimental Section

CNT production and ZnO coating were carried out according to reported procedures. Briefly, a silicon wafer (30 x 30 mm) was first placed in an electrical furnace and repeatedly purged with N2 at 300 °C. Second, the furnace temperature was promoted to 850 °C and ferrocene was dissolved in xylene solution (0.02 g per 10 cm³.) and injected into a ceramic tube. This produced arrays of aligned multiwalled CNTs on a silicon substrate and the array height was 1 ± 0.01 mm. Third, the wafer-supported CNTs were transferred to an ALD reactor and subsequently heated at 200 °C. Fourth, diethyl-zinc and water were used as precursors and the deposition rate was controlled at 0.9 cycle / 1 cycle. Coatings were made at DC = 50, 100, and 150 and the coated CNTs were analyzed by using X-ray diffraction (XRD) with CuKα radiation (λ = 0.154 nm, Shimadzu-6000). The ZnO/CNT interfacial structure was probed by using a high-resolution transmission electron microscope (HRTEM, 200 keV, 0.19 nm point-to-point resolution, 0.1 nm lattice resolution, JEOL-3000FX, 300 keV) and the binding energy was measured with an X-ray photoelectron spectroscope (XPS, Al-Kα, 1486.6 eV, concentric hemispherical analyzer, ESCA system, VG Scientific Microlab-310F). The PL was recorded with a 2400 nm gating spectrometer at different temperatures and the peak intensity and position were calibrated with excited ZnSe. For photoelectric experiments, the two-terminal technique was employed to measure resistance (R) change at green laser (532 nm, 8W) and UV excitation (325 nm, 200 mW), and the Iph was obtained by using a power supply (Keithley-2400) at a bias voltage of 0.5 V.

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