Nanoprecise Spontaneous Coating of Carbon Nanotubes with a Europium Hydroxide Layer

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A protocol for ultrathin nanoprecise coating of individual multiwall carbon nanotubes with amorphous europium hydroxide was developed. The nanocoated carbon nanotubes were successfully prepared by in situ deposition of europium hydroxide in the aqueous suspension by means of dative bonds to oxygen containing groups on the surface of a multiwall carbon nanotube. The coating layer was found to be very uniform, and its thickness was controlled by time of deposition with nanometer precision. The products were characterized by high-resolution transmission electron microscopy (HR-TEM), TEM/energy-dispersive X-ray spectroscopy (TEM/EDS), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and conductivity and current–voltage measurements. The ultrathin europium hydroxide could electrically insulate individual multiwall carbon nanotubes.

Introduction

The composite materials based on carbon nanotubes and inorganic oxides/hydroxides have attracted a great amount of interest because they are expected to create advanced functional material with superior characteristics. Precise coated carbon nanotubes were fabricated for insulated AFM tips,[1] for nanoelectrodes,[2] for nanowiring of nanoelectronic devices,[3,4] and to control their bioaffinity.[5]

The unique optical, chemical, and electronic properties of lanthanides make them very useful in a wide spectrum of applications, such as phosphors, catalysts, and laser materials. The luminescence of Eu(III) is of particular interest because it is a well-known red light emitter.[6,7]

Fabrication of thin-film-coated carbon nanotubes with thickness control to nanometer precision is an important technology that is expected to lead to a wide variety of nanotechnology applications. Coating of multiwall carbon nanotubes with a nanometer-thick layer of polymers[8] and ceramic oxides has recently been described.[9] Particularly interesting is coupling properties of carbon nanotubes (CNT) with lanthanides such as europium. There is only one article in the literature describing the coating of MWCNT with europium oxide via supercritical fluid coating with $Eu(NO_3)_3$ and consequent thermal decomposition.[10] However, because of the fact that Eu_2O_3 (like all Ln_2O_3) adsorbs water from the environment to form insoluble europium hydroxide,[11] it would be highly beneficial to create well-defined coating of CNT with europium hydroxide, which has a stable composition up to 250 °C (when it begins to dehydrate).[12] Here, we describe the preparation and characterization of unprecedently uniform nanocoating on individual multiwall carbon nanotubes (MWCNT) with europium hydroxide in thicknesses ranging from 7 to 18 nm via soft chemistry by spontaneous deposition of europium hydroxide on the surface of multiwall carbon nanotubes. Transmission electron microscopy equipped with energy-dispersive X-ray spectroscopy along with scanning electron microscopy, X-ray photoelectron spectroscopy, and conductivity and photoluminescence measurements were used to characterize the nanocoated MWCNT.

Experimental Section

Materials. Multiwall carbon nanotubes (MWCNT; length, 7 μm; o.d. 90 nm; MWCNT content >90%; metal catalyst (Fe) content,

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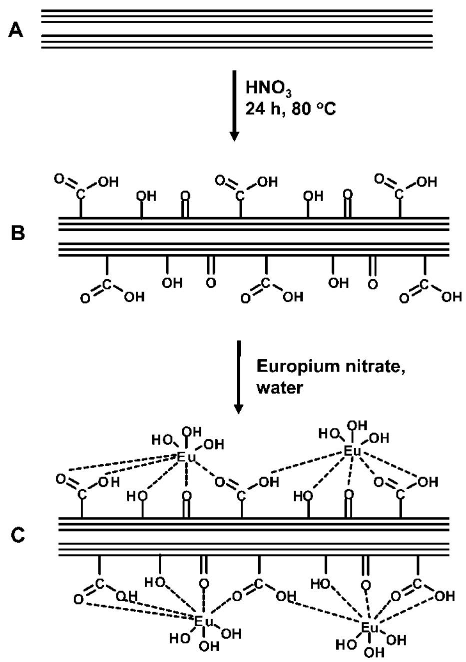
<0.1% (w/w)) and europium nitrate were purchased from Sigma-Aldrich (Japan).

Apparatus. Scanning electron microscope (SEM) (field emission type, Hitachi S-4800) was used to study the morphology of f-MWCNT and europium-hydroxide-coated MWCNT samples. JEM 2100F field-emission transmission electron microscope (JEOL, Japan) working at 200 kV was employed to acquire HR-TEM images in a scanning TEM mode (spot size, 0.7 nm; 200 kV). TEM/EDS spectra were collected using the above-described JEM 2100F equipped with an energy-dispersive X-ray spectrometer with an ultrathin window (JEOL, Japan). Laser microscope/profilometer (Lasertec VL2000, Japan) was used to obtain information on the thickness of f-MWCNT and europium-hydroxide-coated MWCNT films. X-ray photoelectron spectroscopy was performed in UHV chamber equipped with a hemispherical energy analyzer Phoibos 150 with a nine-channel charged particle detector and a dual (Al/Mg) X-ray source. In our experiments, we used the Al source (Al Kα line, 1486.6 eV) operating at 12.5 kV and 20 mA. Typical background pressure during the measurements was about 3×10^{-8} Pa. For analysis, the samples were pressed into silicon substrate (Goodfellow, 99.999% purity). Besides the overall wide spectrum, photoelectron peaks of Eu 3d core levels were recorded in detail. After subtraction of a Shirley background,[13] the Eu 3d peaks were fitted using mixed Gaussian–Lorentzian component profiles. Photoluminescence spectra were measured using a Hitachi F-4500 (Japan) fluorescence spectrophotometer. The values of the resistance were obtained using a four-point-probe sheet-resistance measurement system (RT-70/RG-7B) manufactured by Napson Corporation (Japan). This system has a probe head in which four tungsten carbide electrodes get lined with a distance of 0.5 mm. The upper limit of the applied voltage of the RT-70/RG-7B system is 1.0 V and the lowest current is 1.0 μA. Current–voltage experiments were performed using a μAutolabIII (Ecochemie) connected to a personal computer.

Coating. Multiwall carbon nanotubes were functionalized in concentrated nitric acid (6 M) 80 °C for 24 h.[14,15] The acid/MWCNT mixture was subsequently washed with distilled water and centrifuged several times until the aqueous solution reached neutral pH. Subsequently, oxygen-containing group functionalized multiwall carbon nanotubes were filtered through a 0.2 μm membrane (Nuclepore Track-Etch Membrane, Whatman) and left to dry in the air. The europium hydroxide coating step involved dispersion of f-MWCNT in the 0.1 mM europium nitrate (concentration of carbon nanotubes of 0.5 mg mL^{-1}; typically 2 mg of f-MWCNT in 4 mL of 0.1 mM europium nitrate) followed by 5 min of ultrasonication. This mixture was stirred by magnetic steering (at 550 rpm) for 1–34 days and finally filtered through a 0.2 μm Nuclepore membrane, thoroughly washed with distilled water, and left to dry in the air.

Current–Voltage Measurements. For nanowire film *I*–*V* measurements, nanoscale material (1.5 mg of f-MWCNT or europium-hydroxide-coated MWCNT) was dispersed in distilled water (3 mL) and filtered through a 0.2 μm Teflon membrane (Nuclepore Track-Etch Membrane, Whatman, U.K.). Such films were vaccuum-dried, and their thicknesses were measured with a laser profilometer. Electrical contact was achieved with conducting silver epoxy (D-550, Fujikura Kasei, Japan). Current–voltage curves were obtained by a linear sweep at a rate of 50 mV s^{-1}. The displayed data are average from 5 measurements.

Scheme 1. Schematic of Europium Hydroxide Coating of MWCNT: MWCNT (A) Was Refluxed in HNO_3 To Give Oxygen-Containing Groups at the Defect Sites of the Outer Graphene Layer (B); Such A Functionalized Carbon Nanotube Was Subsequently Coated with Europium Hydroxide (C)



TEM/EDS Spectra. For TEM measurements, 1 μL of a 0.5 mg mL^{-1} dispersion of europium-hydroxide-coated CNT was dropped on a copper TEM grid and left to dry in air. Note that Cu- and Cr-related peaks in TEM/EDS spectra originate from the specimen holder.

Results and Discussion

The dilute aqueous solution of europium nitrate slowly hydrolyzes and the resulting insoluble[16] europium hydroxide forms dative bonds to oxygen-containing groups (carboxyl, carbonyl, and hydroxyl) on the surface of functionalized multiwall carbon nanotubes. Gradually, europium hydroxide precipitates from solution, bonds to the surface of the multiwall carbon nanotubes, and forms ultrathin europium hydroxide films that completely coat the carbon nanotubes. We illustrate the coating process in Scheme 1. The MWCNTs (Scheme 1A) were first functionalized by refluxing them in 6 M nitric acid at 80 °C for 24 h to give surface-oxygen-containing groups (carboxyl, carbonyl, and hydroxyl) at the defect sites of the outer graphene layer of the nanotubes (Scheme 1B).[12,13] Subsequently, distilled-water-washed and dried carboxylic-acid-functionalized multiwall carbon nanotubes (f-MWCNT) were dispersed in water (0.5 mg mL^{-1}) containing europium nitrate (typically 0.1 mM). Europium nitrate hydrolyzed and a nanometer-thick layer of europium hydroxide spontaneously deposited on the surface of f-MWCNT to form europium-hydroxide-coated MWCNT during a period of several days (Scheme 1 C).

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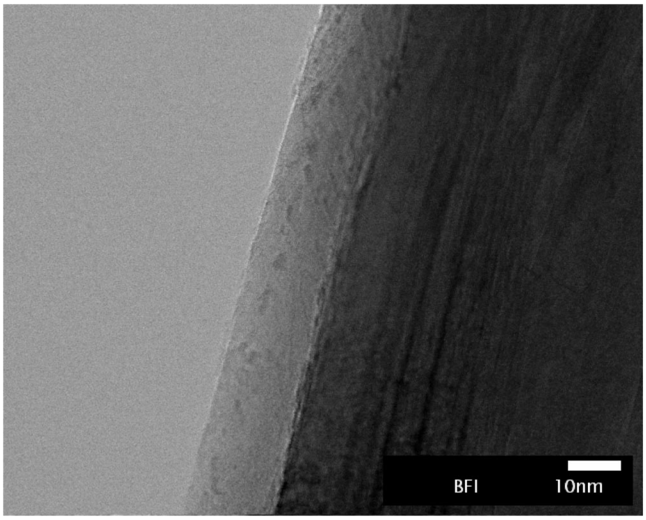

Figure 1. Transmission electron microscope image of europium-hydroxide-coated MWCNT. Detailed view of europium hydroxide at the side of one europium-hydroxide-coated MWCNT. Coating time, 15 days.

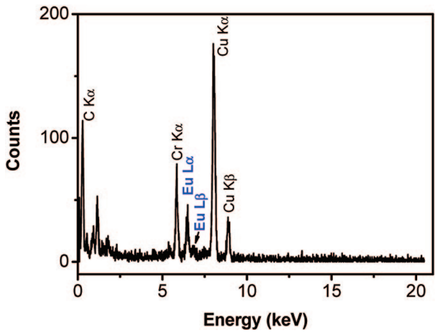

Figure 2. Transmission electron microscopy/energy-dispersive X-ray spectroscopy of segment of europium hydroxide coated MWCNT presented in Figure 1.

In Figure 1, we show a typical TEM image of a europium-hydroxide-coated multiwall carbon nanotube obtained after 15 days. The image reveals the coaxial structure of the resulting europium-hydroxide-coated MWCNT, where MWCNT is encapsulated by a nanometer-thick layer of europium hydroxide. The higher contrast of MWCNT (compared to the europium-hydroxide-coated layer) is due to more electron scattering on MWCNT lattice, whereas the low contrast of europium hydroxide layer is due to its amorphous structure. The surface of the resulting europium-hydroxide-coated MWCNT nanowires appears to be very smooth; the thickness is about 12 nm, with a variation in thickness of 1.2 nm for the same nanotube. Such uniform coating presented in this work is a result of hydrolysis-induced adsorption of europium hydroxide.

The elemental composition of individual europium-hydroxide-coated MWCNT was analyzed by TEM/energy-dispersive X-ray spectroscopy (TEM/EDS). TEM/EDS analysis of section of nanotube depicted in Figure 1 is shown in Figure 2, which reveals a strong presence of europium, as indicated by characteristic elemental emissions of Eu Lα and Eu Lβ lines.

To confirm the presence of europium hydroxide coating of MWCNT and gain insight in to its valence stages, we performed X-ray photoelectron spectroscopy (XPS) measurements on europium-hydroxide-coated MWCNT. Eu can be either divalent or trivalent depending on its chemical environment. Because of the electron configuration of Eu, we can observe splitting of the Eu 3d core level into two components, caused by the occurrence of $4f^6$ and $4f^7$ final-state configurations.[19] Figure 3 presents the detailed 3d XPS spectra of Eu in europium-hydroxide-coated MWCNT (solid line), which shows a double peak feature of spin-orbit split components. The doublet with the Eu $3d_{3/2}$ and Eu $3d_{5/2}$ peak components at energy levels of 1166.7 and 1136.3 eV, respectively, was assigned to the Eu(III) species[17,18], which well-correspond to values measured on pure europium nitrate (not shown). The doublet with energies of 1156.5 and 1126.4 eV was identified as the Eu $3d_{3/2}$ and Eu $3d_{5/2}$ peak components, respectively, attributed to the Eu(II).[19,20] Careful curve fitting allows us to quantitatively differentiate two stages of europium in europium hydroxide coating, Eu(III) and Eu(II). The ratio of Eu(III) and Eu(II) was found to be 41.15/58.85. Because the XPS profile leads to Eu(III) and Eu(II) compounds, europium hydroxide could in fact be mixed-valence compound $Eu(OH)_{2.5}$ (analogous to $EuF_{2.5}$[20]). We want to recall here that the Eu 3d electrons have a limited escape depth because of their small energy. Consequently, the 3d spectrum of the europium hydroxide coating is highly surface sensitive (about 1–2 nm).[20]

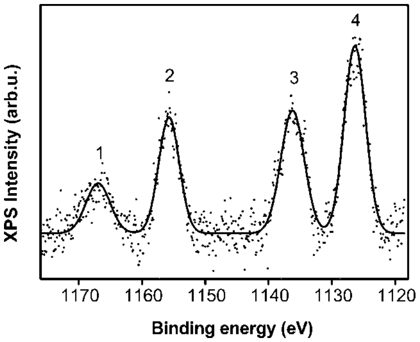

Figure 3. X-ray photoelectron spectra of europium-hydroxide-coated MWCNT. Peak 1, Eu $3d_{3/2}$ related to Eu(III); peak 2, Eu $3d_{3/2}$ related to Eu(II); peak 3, Eu $3d_{5/2}$ related to Eu(III); peak 4, Eu $3d_{5/2}$ related to Eu(II) of europium hydroxide layer. Coating time, 34 days.

Figure 4 shows the influence of the europium hydroxide deposition time upon the thickness of the europium hydroxide coating on MWCNT. When the coating time is short (1 day), the europium hydroxide was scattered over the surface of nanotube. Slow deposition of europium hydroxide takes first place on oxygen-containing group defect sites. However, the europium hydroxide coating of MWCNT at such a short coating time was not uniform. Because the surface of the carbon nanotube after treatment with strong mineral acid at high temperature is decorated with a high density of oxygen groups containing defects,[21,22]

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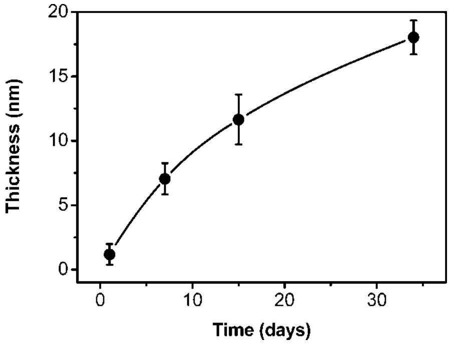

Figure 4. Influence of adsorption time upon thickness of europium hydroxide layer.

prolonged deposition of europium hydroxide on f-MWCNT results in uniform coating. When coating time reached 7 days, the europium hydroxide layer formed uniformly with an average thickness of 7.1 nm (RSD of 8%, $n = 5$); all observed MWCNTs in the sample were covered by an ultrathin europium hydroxide coating. A further increase in coating time to 15 or 34 days resulted in an increase in the europium hydroxide layer thickness to 11.6 and 18.0 nm, with similar variations in the europium hydroxide layer thickness (the error bars in Figure 4 indicate the variation in thickness between different MWCNTs).

Figure S-1 (see the Supporting Information) shows the photoluminescence (PL) spectra of europium-hydroxide-coated MWCNT at room temperature (after f-MWCNT blank subtraction). An excitation peak is observed at 593 nm, which arises from transition within the 4f shell of europium, and the strong emission spectrum originates from the $^5D_0 \rightarrow {}^7F_1$ Eu^{3+} electronic transition.[23]

Scanning electron microscopy (SEM) images demonstrate that the uniform europium-hydroxide-layer-coated MWCNTs do not aggregate. The morphology of the f-MWCNT sample (Figure 5A) is very similar to morphology of the europium-hydroxide-coated MWCNT sample (Figure 5B).

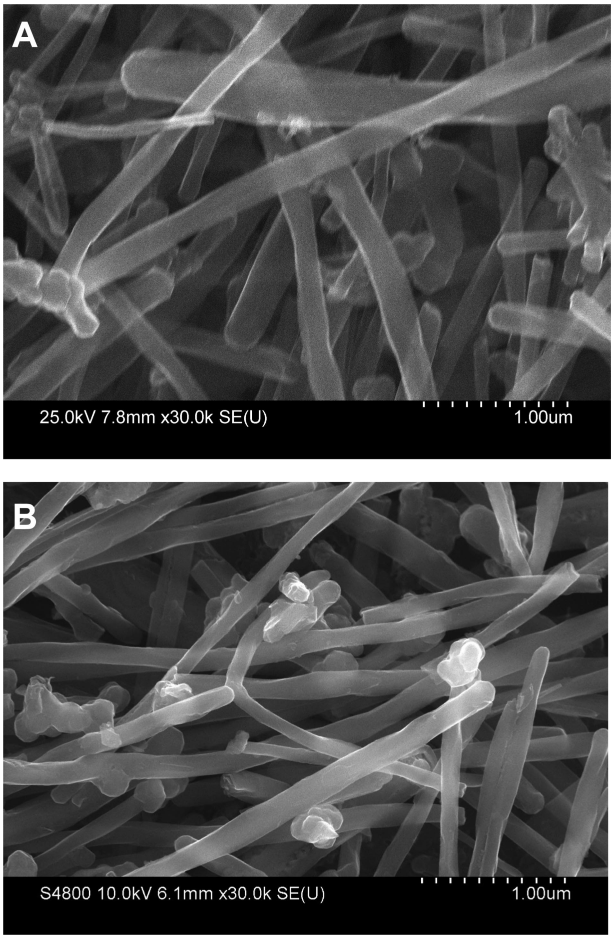

Figure 5. Scanning electron microscopy images of (A) functionalized f-MWCNT, and (B) europium hydroxide coated MWCNT at 30.000 × magnification. Other conditions as in Figure 3.

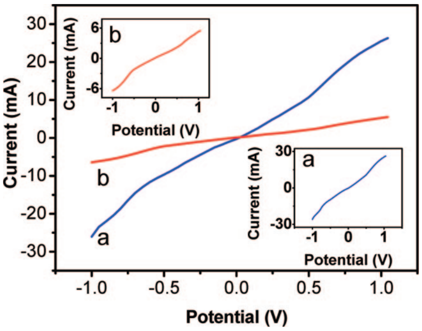

Figure 6. Current–voltage curves of (a) f-MWCNT and (b) europium-hydroxide-coated MWCNT films. Also shown are insets of *I*–*V* characteristics for f-MWCNT and europium-hydroxide-coated MWCNT separately. Other conditions as in Figure 3.

We measured the electric conductivity of the f-MWCNT film and the europium-hydroxide-coated MWCNT film. The films were formed by dispersing 1.5 mg of f-MWCNT or europium-hydroxide-coated MWCNT in 3 mL of distilled water and filtering this suspension through a 0.2 μm Teflon membrane. Such films were vaccuum-dried. The resistance of f-MWCNT film was 2.25 ± 0.19 kΩ sqr^{-1} ($n = 13$; film thickness of 5.22 μm),[8] and the resistance of the europium-hydroxide-coated MWCNT film was found to be 246.87 ± 25.06 kΩ sqr^{-1} ($n = 13$; film thickness of 5.13 μm). Because SEM confirms that the f-MWCNT and europium-hydroxide-coated MWCNT films have similar morphology, the resistivity of europium-hydroxide-coated MWCNT film being about 2 order of magnitude higher than that of the f-MWCNT film can be attributed to the insulating properties of the europium hydroxide layer. Figure 6 displays the current–voltage (*I*–*V*) traces of f-MWCNT (A) and europium-hydroxide-coated MWCNT (B) films ($n = 5$; thickness of films as in conductivity measurements). The slopes of the *I*–*V* characteristics are significantly different; the slope of the *I*–*V* curve of the f-MWCNT film displays a value of 23.8 mA V^{-1}, whereas the slope of the *I*–*V* curve of the europium-hydroxide-coated MWCNT film shows a value of 5.44 mA V^{-1}. Such a difference reflects the fact that the europium hydroxide coating layer effectively insulates multiwall carbon nanotubes.

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Conclusions

We have described a chemical approach to facilitating an ultrathin coating of europium hydroxide on multiwall carbon nanotubes. The europium hydroxide layer forms spontaneously on walls of MWCNT, and its thickness can be controlled by adsorption time. The europium-hydroxide-coated MWCNT has dramatically different electronic properties compared to f-MWCNT. The europium hydroxide coating effectively prevents electron transfer between the individual carbon nanotubes. This coating technique opens doors for many applications, ranging from chemical sensing to electronics.

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Supporting Information Available: Photoluminescence spectra of europium-hydroxide-coated MWCNT (PDF). This materal is available free of charge via the Internet at http://pubs.acs.org.

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