Platinum Deposition on Carbon Nanotubes via Chemical Modification

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Received May 14, 1997. Revised Manuscript Received December 2, 1997

Carbon nanotubes can be functionalized by oxidation of HNO_3 or H_2SO_4−HNO_3. The latter shows a higher capability in producing a high density of surface functional groups. These groups can act as specific nucleation sites for a well-dispersed deposition of Pt clusters on the surface of carbon nanotubes. These modified carbon nanotube materials were investigated by TEM, XPS, and DRIFT. A deposition mechanism is tentatively proposed and discussed.

Introduction

Ever since the first reports of tubular structure and macroscopic production of carbon nanotubes,[1,2] many theoretical and experimental studies in recent years have been focused on their properties and potential applications.[3−9] As a new form in the carbon family, carbon nanotubes are usually concentric seamless tubules with a graphitic multilayer. As recent studies revealed, the unusual geometry, electrical conductivities, and mechanical characteristics may make carbon nanotubes suitable for applications ranging from forming tips of scanning probe microscopes (SPM),[10] in field-emitters,[11] as ultrahigh-strength engineering fibers[12,13] and quantum wires.[14] In view of the tubular morphology and unique electronic properties,[15,16] carbon nanotubes can also act as new supports for metal catalysts[2,17] and form new reinforced metal−nanofiber composites. For example, Ru has been deposited on the raw carbon nanotube, and the resultant material shows good catalytic behavior,[18] and the reinforcement of metal−matrix or fiber−matrix composites has been proposed.[19] However, carbon nanotubes formed in the electrode deposit prepared by arc-discharge method[2] are usually stacked on each other and inevitably accompanied by many carbon nanoparticles. In addition, since the surface of the carbon nanotube itself is rather inert, it is difficult to control the homogeneity of metal deposition on the surface by conventional methods. It is therefore important to explore a feasible technique whereby surface modification and then metal deposition on carbon nanotubes can take place and to investigate the details of the modification process. Herein we demonstrate a novel means to deposit and disperse platinum clusters on carbon nanotubes via a chemically specific nucleation mechanism.

Generation of functional groups on the surface of carbon nanotubes can be realized through chemical oxidation treatments. Such surface functionalization enhances the reactivity, improves the specificity and provides an avenue for further chemical modification of the carbon nanotubes, such as ion adsorption, metal deposition, and grafting reaction. Several oxidants, such as HNO_3, $KMnO_4$, OsO_4, and RuO_4, have been employed to oxidize carbon nanotube materials.[20−23] However, some of these reagents are known to open the tips of the tubules,[20] cause damages to the tubular structure,[22] or introduce contaminants.[23] Details of these oxidative processes are unknown. In this project,

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S0897-4756(97)00364-5 CCC: $15.00

we explore the use of a $H_2SO_4-HNO_3$ mixture and exploit its oxidizing and acidic effects in the metal deposition on these modified materials.

Experimental Section

An arc discharge of two pure graphite electrodes was conducted at 100 A, 22 V dc current in a 300 Torr He environment. After the evaporation of graphite anode (8 mm in diameter, 15 cm in length), a carbonaceous deposit containing mainly carbon nanotubes and nanoparticles was collected on the cathode.

This carbonaceous deposit (sample **A,** 0.5 g) serves as the starting carbon nanotube material. It was ground to fine powder and refluxed with a concentrated $H_2SO_4-HNO_3$ mixture (1:1 v/v, 40 mL) for 5 h to form a dark-brown suspension. The resultant mixture was diluted with distilled water (200 mL) and stirred for several hours. A black solid (0.36 g) was obtained after filtration, washed several times with distilled water, and dried in vacuo for 8 h. This $H_2SO_4-HNO_3$-treated solid material (sample **B**) serves as functionalized carbon nanotubes. It was mixed with a dilute aqueous solution of $PtCl_2$ and stirred for $^1/_2$ h under an Ar atmosphere. H_2 gas was passed through the solution for 15 min to facilitate reduction of Pt(II). The resultant Pt-deposited carbon nanotubes **C**, obtained after filtration, was dried in vacuo for 5 h. As a comparison, another sample of **A** (0.5 g) was treated similarly, but in concentrated nitric acid (40 mL), to give material **D** (0.46 g) and subsequently its Pt-deposited material **E**.

The resulting products were examined under a JEOL-100 CXII transmission electron microscope (TEM) at 100 kV accelerating voltage. X-ray photoelectron spectroscopy (XPS) analyses of the samples were performed on a VG ESCALAB MKII spectrometer using an Mg Kα X-ray source (1253.6 eV, 120 W) at a constant analyzer. The energy scale was internally calibrated by referencing the binding energy (E_b) of C_{1s} peak at 284.60 eV for contaminated carbon. Spectra at the O_{1s}, S_{2p}, and Pt_{4f} regions were recorded. Deconvolution of these spectra were carried out with a curve-fitting program VGX900 on a Pentium computer.[24] A Perkin-Elmer 2000 FTIR spectrometer equipped with a diffusion reflectance detector was applied to measure the diffusion reflectance infrared fourier transform (DRIFT) spectroscopy of the samples.

Results and Discussion

It has been described[1,2] that carbon nanotubes prepared by arc evaporation of graphite in an inert atmosphere are inevitably accompanied by some other forms of carbon, such as amorphous carbon and carbon nanoparticles. In our samples, it was found that the impurities are mainly carbon nanoparticles and a small amount of amorphous carbon. The carbon nanotubes, mostly ranging from 10 to 40 nm in diameter and up to several micrometers in length, are hollow tubular structure with highly graphitized multilayer wall. For future applications of carbon nanotubes, those impurities in the samples should be removed as much as possible.

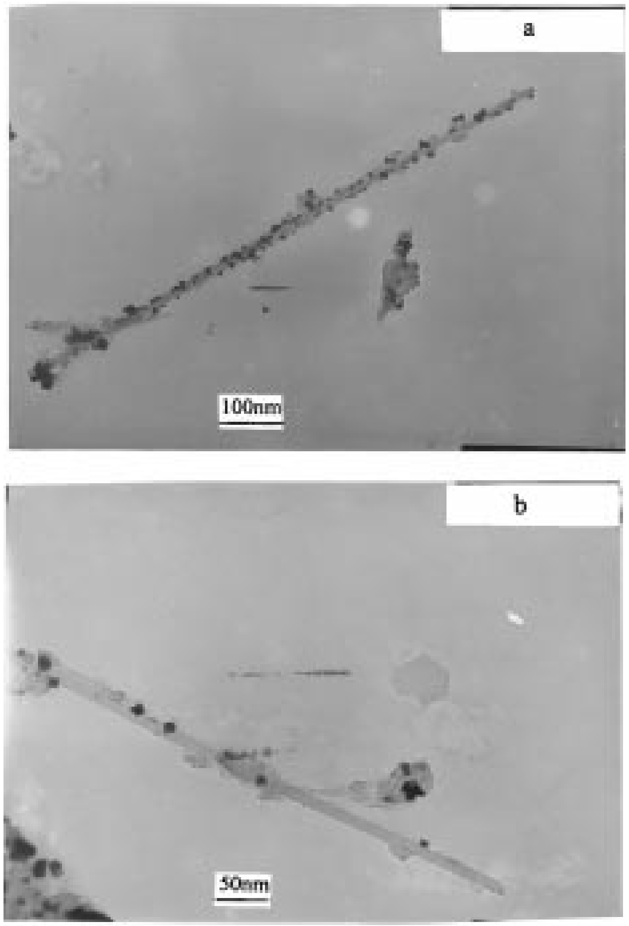

Figure 1. TEM micrographs of deposition of Pt clusters on functional carbon nanotubes after treatment with (a) a mixture of $H_2SO_4-HNO_3$ and (b) HNO_3.

As shown in Figure 1, the TEM studies of these modified carbon nanotubes indicate that deposition of well-dispersed Pt as small metal clusters on the surface of the functionalized carbon nanotubes **C** is achieved when treated with the $H_2SO_4-HNO_3$ mixture (Figure 1a). On the other hand, the HNO_3-treated sample **E** gives only some isolated patches of Pt clusters deposited on the carbon nanotubes (Figure 1b). The size of these Pt clusters in both cases is about 10−20 nm. In addition, from the TEM observations, many isolated carbon nanotubes can be seen in samples **B** and **C**, although some carbon nanoparticles are still visible. Comparatively, carbon nanotubes are found to coexist with more nanoparticles in samples **D** and **E**. This suggests that $H_2SO_4-HNO_3$ is more efficient than HNO_3 in the separation of nanotubes from the nanoparticles through oxidation and functionalization. The enrichment of carbon nanotubes after oxidative treatment shows that amorphous carbon and carbon nanoparticles are more reactive and more readily removed under the oxidation process. The higher reactivity of these impurities is consistent with the highly disordered structure of amorphous carbon with many active dangling atomic sites and some weak C−C bonds.[25] Carbon nanoparticles with a structural pattern of higher curvature are also expected to experience higher conformational strain[26,27] and hence higher reactivity, when compared with the carbon nanotubes.

Some surface functional groups such as hydroxyl and carboxyl groups on carbon fibers or carbon nanotubes

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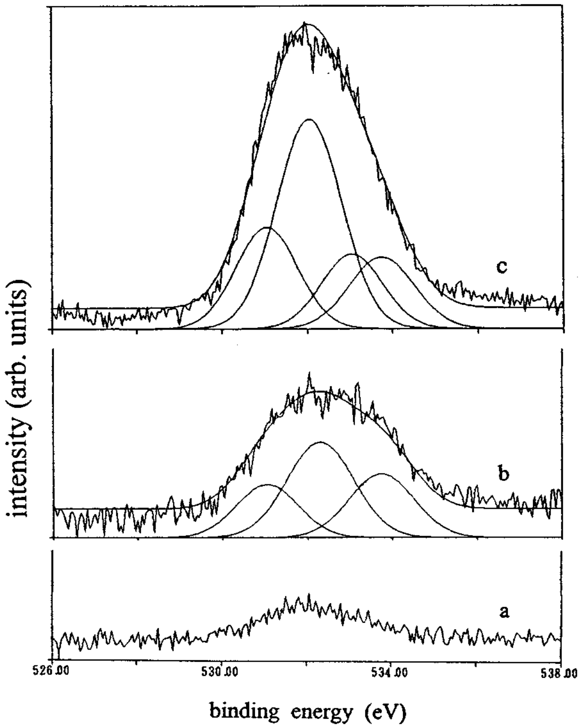

Figure 2. XPS spectra of oxygen-containing species on the surface of (a) the raw carbon nanotube material **A**, (b) HNO_3-treated carbon nanotubes **D**, (c) $H_2SO_4-HNO_3$- treated sample **B**, showing a higher density of O-containing groups in **B**.

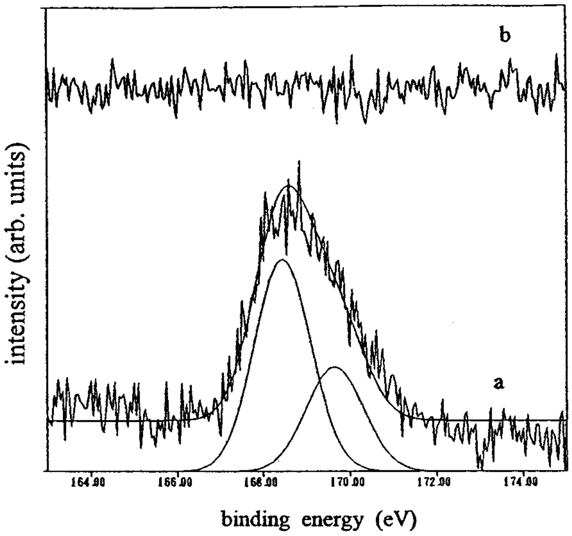

Figure 3. XPS spectra of the sulfur region (S_{2p}) of (a) the $H_2SO_4-HNO_3$-treated sample **B** and (b) Pt-deposited carbon nanotubes **C** modified from **B**, showing that the S-containing groups are removed as a result of hydrolysis.

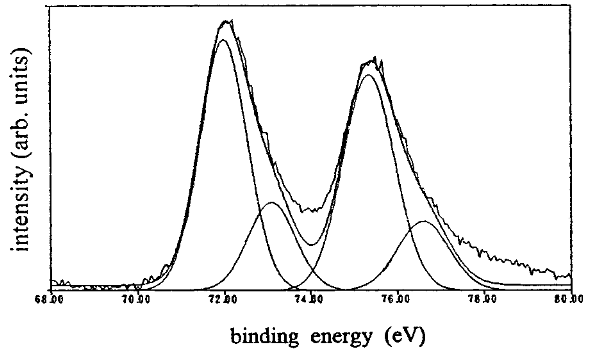

Figure 4. Pt_{4f} core level XPS spectrum of Pt-deposited carbon nanotubes **C**.

are known to be generated through oxidation.[21,28] To elucidate the surface states of these carbon nanotube materials after modification and to correlate the surface states with metal deposition, XPS and DRIFT analyses were applied. Our experimental results confirm the existence of the surface functional groups on these modified materials. The XPS studies clearly demonstrated that the carbon nanotubes treated with HNO_3 (**D**) and $H_2SO_4-HNO_3$ (**B**) give enhanced O_{1s} peaks compared with the untreated sample **A** (Figure 2). In sample **A**, only a small amount of oxygen is detected which can be considered as adsorbed oxygen species. These results imply that a high density of oxygen-containing species is produced on the surface of carbon nanotubes after oxidation. Furthermore, the ratio of the O_{1s} peak area in samples **B** and **D** is found to be about 2.7:1, indicating the higher efficiency of $H_2SO_4-HNO_3$ in the modification of the carbon nanotube surface. Referring to the XPS studies of surface-oxidized carbon fibers,[29,30] the present curve-fittings of the O_{1s} peaks suggest the presence of new and additional surface functional groups with the binding energy (E_b) at 533.00 eV in sample **B**. Other peaks attributed to phenol (532.05 eV), carbonyl (530.95 eV), and carboxyl (533.76 eV) groups can also be found both in **B** and **D**. It is interesting to note that a sulfur-containing species was found only in sample **B**, but not in **C** (Figure 3). Despite the use of HNO_3, there is no evidence for any stable nitrogen-containing groups on these modified carbon nanotubes. The presence of S peaks at 168.50 eV (S_{2p}) with a spin–orbit splitting of the $2p_{3/2}$ and $2p_{1/2}$ states of 1.18 eV (Figure 3a), together with the above curve-fitting results of the new O_{1s} peak at 533.00 eV, suggests the new surface S-containing species in **B** to be a sulfate group. A similar conclusion was drawn in the studies of C_{60} treated by $SO_3-H_2SO_4$.[31] The absence of sulfate on the surface of sample **C** implies that incorporation of Pt ions would promote the hydrolysis of sulfate, which enhances the specific nucleation sites for the anchoring of Pt^{2+}. Since S-containing species are usually considered as catalyst poisons, the elimination of sulfur in the conversion of **B** to **C** offers an advantage for these Pt-deposited carbon nanotubes in catalytic applications. The reducing effect of H_2 gas readily converts Pt^{2+} ions to Pt metal which is deposited on the carbon nanotubes. From the XPS analysis shown in Figure 4, two chemically different Pt entities can be identified in **C**. The spectrum gives broad bands that can be curve-fitted into two pairs of Pt_{4f} peaks at 71.84 and 73.05 eV, both of which have a spin–orbit splitting of the $4f_{7/2}$ and $4f_{5/2}$ states of ca. 3.33 eV. The use of XPS in distinguishing chemically inequivalent metal or ligand sites has been described.[32–34] The majority is present as metallic Pt (71.84 eV), and the minor peak (73.05 eV) can be

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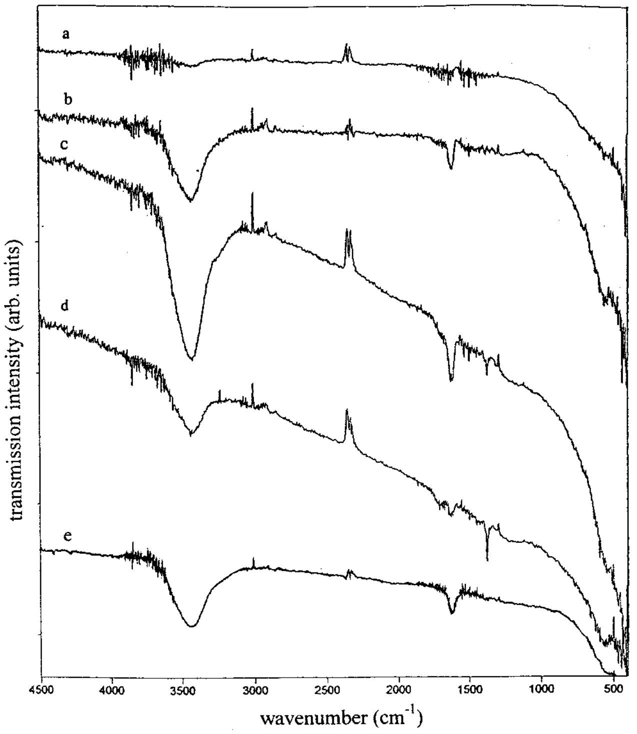

Figure 5. DRIFT spectra of (a) the raw carbon nanotube material **A**, (b) HNO_3-treated carbon nanotubes **D**, (c) $H_2SO_4-HNO_3$-treated sample **B**, (d) carbon nanotubes treated in $H_2SO_4-HNO_3$ with a higher ratio of H_2SO_4, and (e) Pt-deposited carbon nanotubes C.

assigned to the oxide species in an abundance ratio of ca. 85:15. The presence of a small amount of Pt oxides is responsible for the oxygen-containing species found on the chemically treated samples.

In collaboration with XPS analyses, DRIFT, a sensitive technique used in the detection of functional groups on material surfaces,[35] was employed to study the surface states of these modified carbon nanotubes. The results of DRIFT measurements support the conclusion drawn above. Figure 5 indicates that oxidation by HNO_3 or $H_2SO_4-HNO_3$ can produce some functional groups on the almost clean surface of the raw carbon nanotube material **A**. Compared to the spectrum of sample **D**, modified carbon nanotubes **B** oxidized by $H_2SO_4-HNO_3$ clearly show the presence of a new peak at ν 1380 cm^{-1} corresponding to the $-OSO_3H$ group besides the carbonyl and carboxyl groups at ν 1600–1700 cm^{-1} and the hydroxyl and phenolic bands at ν 3300–3500 cm^{-1}. Increasing the ratio of H_2SO_4 to HNO_3 intensifies the $-OSO_3H$ peak. This phenomenon supports the presence of sulfate found in the XPS study and confirms the role of H_2SO_4 in the modification process. Interestingly, when Pt is deposited on the surface of **B**, the $-OSO_3H$ peak disappears, indicating that the sulfate groups readily undergo hydrolysis during the process of Pt deposition. Meanwhile, in sample **B** much stronger absorption bands are found around ν 3300–3500 and 1600–1700 cm^{-1}, which implies a higher density of other surface functional groups, such as phenol, carbonyl, and carboxyl groups produced after $H_2SO_4-HNO_3$ treatment. It is also in good agreement with the XPS results. These surface functional groups provide active sites for interaction with metal ions. They hence contribute to a well-dispersed deposition of Pt clusters on the surface of carbon nanotubes.

Our studies show that the outer surface of carbon nanotubes can be modified with the surface functional groups, which can act as specific sites for metal nucleation. The detailed mechanism of the generation of various functional groups is not completely clear at present. It is reasonable to propose that the functionalization process is initiated by interaction of the oxidants with the reactive pentagons at the tips,[36,37] or some surface defects,[38] or with the amorphous carbon layer which is usually observed on the outermost surface under the high-resolution TEM images of carbon nanotubes.[39] It should be noted that the fine structure of carbon nanotubes is quite different from those of amorphous carbon and carbon nanoparticles. The main outer shell of the carbon nanotube is a highly oriented graphitized wall which is more stable and resistant to oxidation. In our experiments, the outer surface layer of carbon nanotubes of different diameters can be effectively modified and functionalized and their tubular structure is intact after a short period of oxidation. In addition, through this chemical modification method, the extent of Pt deposition on carbon nanotubes depends mainly on the surface states of the carbon nanotubes, especially the density of surface functional groups. The Pt deposition is not found to be sensitive to the diameter distribution of the carbon nanotubes. All these features allow us to propose a tentative mechanism of Pt deposition via the oxidation of $H_2SO_4-HNO_3$ under acidic conditions (Scheme 1).

As illustrated in Scheme 1, in reflux with a mixture of $H_2SO_4-HNO_3$, the surface graphitic layers of carbon nanotubes would react with the oxidants and produce a high density of various functional groups, such as carboxyl, carbonyl, and phenolic groups. In addition, cyclosulfate species could also form as intermediates, which convert to sulfate groups after hydrolysis in the acidic aqueous solution.[31] Upon introduction of Pt^{2+} ions into the system, these ions would interact with and attach to these surface functional groups by ion exchange or coordination reaction and serve as nucleation precursors. Upon reduction by hydrogen, Pt deposition as well-dispersed nanoclusters on the surface of these modified carbon nanotubes is envisaged.

With the presence of high-density surface functional groups, carbon nanotubes treated by $H_2SO_4-HNO_3$ (**B**) show much better dispersibility in water, ethanol, and other solvents compared with the raw nanotube material **A**. Sample **B** has lasting suspension behavior in water and disperse well in organic solvents. The raw

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Scheme 1

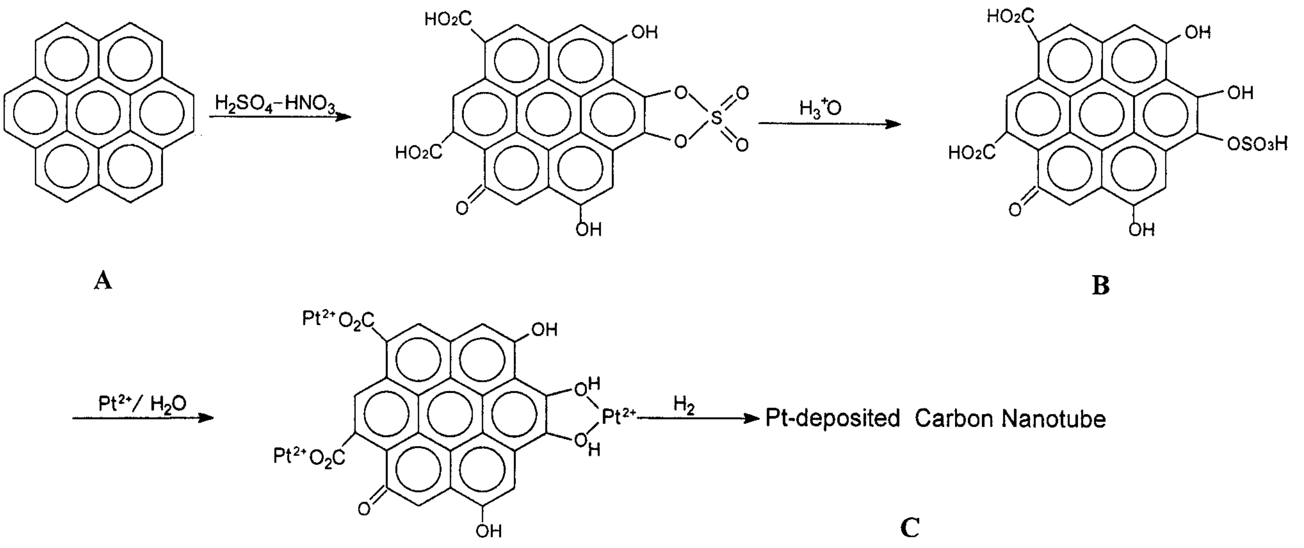

Table 1. Preparation, Properties, and Key Characterization Data of the Treated and Untreated Carbon Nanotube Materials

materials	preparation	properties and characteristics	characterization data
A	from pure graphite in helium gas by arc-discharge method	carbon nanotubes stacked onto each other, accompanied by nanoparticles and some amorphous carbon; a small amount of oxygen adsorbed on the surface; no functional groups detected	three carbon forms exist: nanotubes, nanoparticles and amorphous carbon; weak oxygen signal in XPS and no obvious functional groups in DRIFT
B	reflux of **A** with $H_2SO_4-HNO_3$ (1:1) in 5 h, hydrolyzed in distilled water and dried in vacuo for 8 h	mostly carbon nanotubes isolated, amorphous carbon removed but a small portion of carbon nanoparticles remained; surface of carbon nanotubes modified by a higher density of various surface functional groups (hydroxyl, carbonyl, carboxyl, and sulfate)	four strong O_{1s} peaks with E_b: 530.95, 532.05, 533.00, 533.76 eV; S_{2p} peak at 168.50 eV; DRIFT adsorption bands at ν 3300–3500, 1600–1700, and 1380 cm^{-1}
C	mix of **B** with $PtCl_2$ solution for $^1/_2$ h under Ar, reduced by H_2 gas for 15 min and dried in vacuo for 5 h	Pt nanoclusters dispersed well on the surface of carbon nanotubes; some surface functional groups remained but sulfate group removed	two components of Pt_{4f} with E_b: 71.84 and 73.05 eV, O_{1s} peak exists but no S_{2p} signal detected; DRIFT absorption bands at ν 3300–3500 and 1600–1700 cm^{-1}
D	reflux of **A** with HNO_3 in 5 h, hydrolyzed in distilled water and dried in vacuo for 8 h	mostly carbon nanotubes isolated but containing more carbon nanoparticles than **B**; some surface functional groups produced (hydroxyl, carbonyl, and carboxyl group)	medium O_{1s} peak including three components (E_b): 530.95, 532.05, 533.71 eV; DRIFT absorption bands at ν 3300–3500 and 1600–1700 cm^{-1}
E	mix of **D** with $PtCl_2$ solution for $^1/_2$ h under Ar, reduced by H_2 gas for 15 min and dried in vacuo for 5 h	some isolated patches of Pt nanoclusters deposited on the surface of carbon nanotubes; some surface functional groups remained	Pt_{4f} signal containing two components (E_b): 71.85 and 73.05 eV, O_{1s} peak exists; DRIFT absorption bands at ν 3300–3500 and 1600–1700 cm^{-1}

material **A**, on the contrary, displays poor dispersibility in all solvents. Such dispersibility is traced to the different surface states of these materials. Sample **B** shows a high density of various surface functional groups which can interact with the solvent molecules, while the raw nanotube material **A** has no surface functionality to support such an interaction. The rich surface functional groups and good dispersibility for sample **B** will provide a promising means to graft carbon nanotubes with other functional materials such as organic polymers to form other advanced composites.

For direct comparisons and easy reference, the treatments and characterization of the above materials are illustrated in Table 1. In summary, carbon nanotubes can be modified conveniently by the oxidation of HNO_3 or the $H_2SO_4-HNO_3$ mixture. The latter is significantly more effective in surface modification, leading to a well-dispersed Pt deposition on carbon nanotubes. The Pt-deposited nanotube materials are potentially useful in catalysis. Formation of Pt-deposited nanotube composites through a chemical modification method would be beneficial to the preparation and applications of new metal–nanofiber composites. Explorations of these work are in progress.

Acknowledgment. The authors acknowledge the National University of Singapore (NUS) for financial support (RP930631) and technical assistance from our departments. R.Y. thanks NUS for a research scholarship award.

CM970364Z