Size-Controlled in situ Synthesis of Metal Nanoparticles on Dendrimer-Modified Carbon Nanotubes

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Multiwalled carbon nanotubes (MWCNTs) were covalently modified with fourth-generation NH$_2$-terminated poly(amido amine) (G4-PAMAM) dendrimers, named CNT/DEN. The covalent linkages between CNT and dendrimers were identified by an infrared absorption spectrometry, and the weight content of G4-PAMAM dendrimers in CNT/DEN was determined to be about 40 wt % by a thermal gravimetric analysis. By simply tuning the metal ion-to-dendrimer terminal amine ratio, Au nanoparticles (NPs) with different sizes from 3 to 11 nm were in situ synthesized and deposited on the surface of CNT/DEN, as confirmed by a transmission electron microscopy (TEM) and an ultra violet–visible (UV–vis) absorption spectrometry. Furthermore, many metal NPs other than Au NPs, such as Ag, Cu, and Pt NPs, as well as binary NPs of Ag@Au, were synthesized in situ on CNT/DEN, which were identified with TEM and UV–vis spectrometry, as well as an energy-dispersion X-ray spectroscopy, yielding the water-dispersible and stable CNT/DEN/NPs.

Introduction

Carbon nanotubes (CNTs), known as a class of promising one-dimensional (1-D) nanomaterials, bear many fascinating properties, such as mechanical strength, chemical stability, and electrical conductivity, and possess possibilities of various potential applications as electronic devices, quantum wires, high-strength materials, biosensors, and catalyst supports.[1] To optimize the use of nanotubes in many of those applications, there is a need to introduce different functional building blocks to CNTs, especially onto the surface of CNTs. For example, the attachment of organic molecules onto CNTs improved greatly the solubility of CNTs and brought more extensive applicability in such fields as biomedicine and catalysis.[2]

Meanwhile, zero-dimensional metal nanoparticles (NPs) have been attracting considerable attention of chemists, physical scientists, engineers, and even biologists due to their unique photonic, electronic, magnetic, biologic, and catalytic properties, which are recognized to be dependent strongly on their sizes and shapes.[3] As a result, size-control of NPs is always of special interest, and a handful of organic molecules has been adopted as protectors or stabilizers to control the sizes of metal NPs.[4] In particular, well-defined polymers known as dendrimers (DEN) have shown promising properties to control the shape, size, stability, and solubility of metal nanoparticles because of their uniform compositions and structures.[5] Then various kinds of nanoparticles have been produced by using dendrimers as templetes or protectors, some of which showed novel catalytic properties.[6]

Recently, it was realized that combination of CNTs with metal NPs generates a new family of novel materials with more advanced properties and applications than the pristine precursors. As a result, hybrid materials of CNTs with metal NPs have attracted great attention due to their promising applications as electronics, catalysts, and biosensors.[7] Methods developed to produce CNT/NP hybrids can be roughly divided into two categories: one is synthesis and deposition of NPs onto CNTs by physical adsorption, electrodeposition, or spontaneous reduction,[8] and the other is polymer-mediated deposition of presynthesized NPs on functionalized CNTs by electrostatic interaction or self-assembly, which made the composites more compatible with solvents and thus more useful in catalysis and biomedicine.[9] However, the in situ synthesis of metal NPs on functionalized CNTs in order to control the particle sizes has never been reported.

In the present work, we report that multiwalled carbon nanotubes (MWCNTs) modified by fourth-generation poly-(amido amine) (G4-PAMAM) dendrimer (CNT/DEN) could be used to synthesize Au NPs in situ, and the particle sizes could be concisely controlled by simply tuning the ratio of HAuCl$_4$ to the covalently bonded dendrimers on CNTs. Furthermore, this method could be successfully generalized to produce *in situ* other metal (Cu, Ag, Pt) NPs and binary metal (Ag@Au) NPs on the surface of CNT/DEN.

Experimental Section

MWCNTs were purchased from Wako Pure Chemical Industries, Ltd., and purified by refluxing in concentrated HNO$_3$ for 2 days, followed by filtration with a Millipore VC membrane (pore size = 0.1 μm). NH$_2$-terminated G4-PAMAM dendrimer (10 wt % in methanol) was a product from Aldrich. All metal salts, NaBH$_4$, and solvents were purchased from Wako and used as received except DMF, which was dehydrated upon refluxing over molecular sieves.

Instead of attaching presynthesized metal NPs onto CNTs,[8,9] here we chose to grow NPs in situ on the surface of MWCNTs through the intermediary of the covalently bonded dendrimers. As shown in Scheme 1, MWCNTs were sequentially treated with HNO$_3$/H$_2$SO$_4$ and thionyl chloride to introduce chloride acid groups onto CNTs.[2a] Subsequent amidation with G4-PAMAM dendrimers in anhydrous DMF yielded CNT/DEN, which was then subjected to produce CNT/DEN/NP by reducing

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Dendrimer-Modified Carbon Nanotubes

J. Phys. Chem. C, Vol. 111, No. 6, 2007 **2417**

SCHEME 1: Schematic Illustration of Modification of MWCNTs with G4-PAMAM Dendrimers and the in situ Synthesis of Metal NPs on CNT/DEN
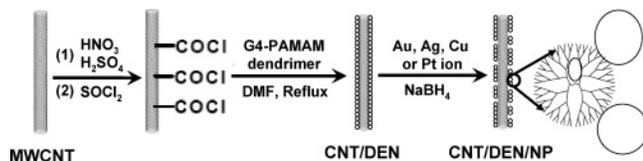
corresponding metal ions with $NaHB_4$ in aqueous dispersions of CNT/DEN.[5]

In a typical circuit of synthesis, 20 mg of MWCNT was refluxed in 20 cm³ HNO_3/H_2SO_4 (v/v = 3:1) for 24 h. After filtration and drying, the solid was dispersed in 20 cm³ $SOCl_2$ and refluxed for 24 h. Then $SOCl_2$ was distilled, the solid was redispersed in dehydrated DMF, and excess PAMAM dendrimers dissolved in dehydrated DMF were added dropwise under vigorous stirring. The mixture was refluxed for 12 h under nitrogen atmosphere, and then unreacted dendrimers were removed by filtering out through a Millipore GS membrane (pore size = 0.22 μm) and by washing at least 10 times with methanol. The product, denoted by CNE/DEN, is dispersible in water. Then the aqueous dispersion of CNT/DEN was subjected to synthesize various metal nanoparticles. For example, an aqueous $HAuCl_4$ solution at expected concentration was dropped into the dispersion of CNT/DEN in water under vigorous stirring, and 5 min later, fresh aqueous $NaBH_4$ solution was added dropwise at about 0 °C. The ratio of Au^{3+} ($HAuCl_4$) to amine terminal groups of dendrimers, which were used on the preparation of CNT/DEN, was denoted by M:D. After the reaction was completed (30 min later), the mixture was filtrated with a VC membrane (pore size = 0.22 μm) and the residuary solid was redispersed in water for further characterization. Two types of control samples were prepared by production of Au NPs on CNTs: (1) without dendrimer attachment and (2) with noncovalently bonded dendrimers under exactly same experimental conditions.

Transmission electron microscopic (TEM) images were obtained on a Hitachi H-7000 equipped with a charge-coupled device camera, operating at an accelerating voltage of 100 kV. The specimens for TEM were prepared by directly dropping the dispersions of corresponding products onto the carbon-coated copper grids, followed by air-drying. KBr pellets were prepared as specimens, and their infrared (IR) absorption spectra were recorded on a Bio-Rad FTS 575C instrument. Ultra violet−visible (UV−vis) absorption spectroscopic measurements were performed on a Shimadzu UV 2200 spectrometer with a 1-cm quartz cell. Thermal gravimetric analysis (TGA) measurements were done on a PETGA-7 instrument with a heating rate of 10 °C/min in the atmosphere. Energy-dispersion X-ray (EDX) microanalysis was carried out by using a field emission microscope (JEOL, JSM-6330F) equipped with a JEOL JED-2140 EDX microanalyzer and operated at an accelerating voltage of 10−20 kV.

Results and Discussion

The covalent linkages between MWCNTs and PAMAM dendrimers were confirmed by IR absorption spectrometry (Figure 1). Acid-treated CNTs (dashed line) displayed an IR band at 1765 cm⁻¹, which could be assigned to the C=O stretching mode of carboxylic acid. Besides, the absorption bands at 3445 and 1665 cm⁻¹ result from a trace of water in the sample.[10] In the spectrum of dendrimer-grafted CNTs (solid line), the absorption bands of dendrimers were found at 3277,
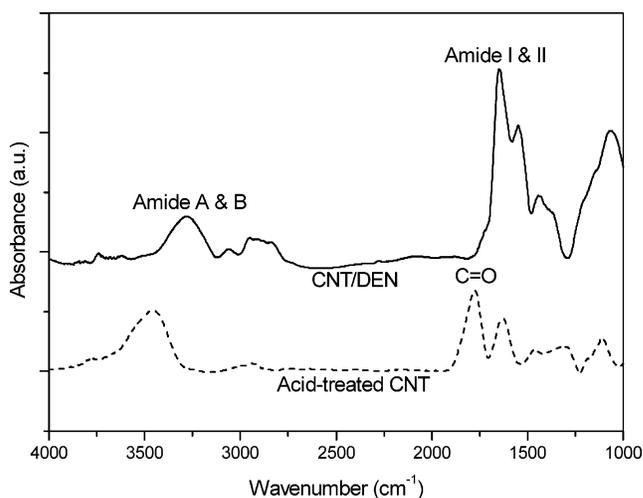

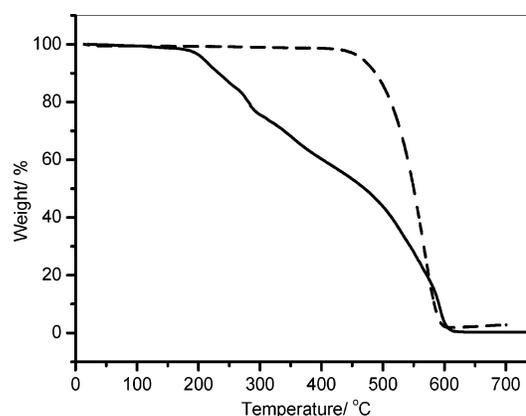**Figure 1.** IR absorption spectra of acid-treated CNT (dashed line) and CNT/DEN (solid line).

Figure 2. TGA curves of purified MWCNT (dashed line) and CNT/DEN (solid line).

3012, 1647, and 1549 cm⁻¹, ascribing to amides A and B and I and II, respectively.[5b] The results clearly proved that carboxylic groups on CNTs were completely converted into amide groups, confirming the successful attachment of PAMAM dendrimers onto carbon nanotubes through covalent bonds. Sano et al.[11] reported that shortened thionyl-treated CNTs reacted with G10 PAMAM dendrimers forming novel star-shaped patterns because of the higher reactivity of the end-caps than the sidewalls of CNTs. Here we presented the first spectroscopic evidence of covalent linkages of PAMAM dendrimers on whole surface of MWCNTs.

Weight content of dendrimers in CNT/DEN was determined by TGA. As shown in Figure 2, the purified MWCNT was burnt at the temperature range of 400−600 °C (dashed line). On the other hand, dendrimers were burnt up to 400 °C.[12] On a TGA curve of the CNT/DEN (solid line), the weight was about 60 wt % at 400 °C, which could be ascribed to the decomposition of covalently bonded dendrimers.[12] The rest was burnt at 600 °C due to the decomposition of CNTs. Therefore, from the weight loss in the TGA result, the weight content of covalently bonded dendrimers was evaluated to be about 40%.

It is known that well-defined dendrimers with unique structures and compositions could be used to control the size, shape, and solubility of metal NPs, and many successful results have been published.[5] In the present study, after attached to CNTs, G4-PAMAM dendrimers were used to fabricate Au NPs with controlled size, by simply varying the ratio M:D of Au^{3+} ($HAuCl_4$) to amine terminal groups of dendrimers. For four
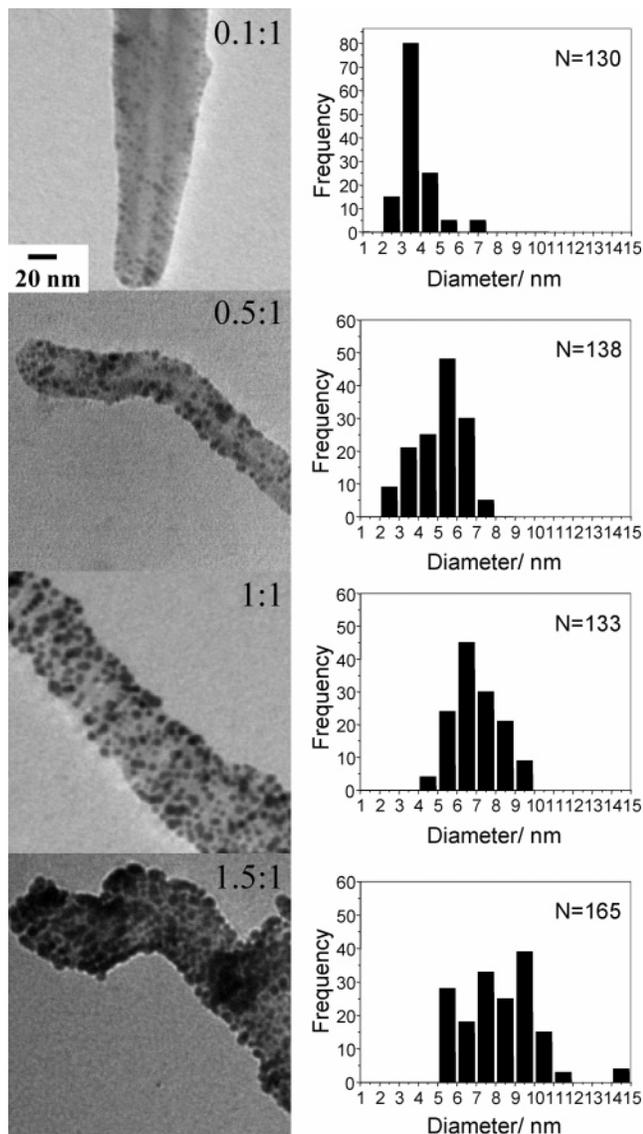
Figure 3. TEM images of CNE/DEN/Au at different M:D ratios and histograms of the Au particle size distribution in the CNT/DEN/Au structure. N in each histogram denotes the counted number of Au NPs. The magnification is the same for all TEM images, and M:D values are indicated in each TEM image.

different M:D values (0.1:1, 0.5:1, 1:1, and 1.5:1), TEM images of CNT/DEN/Au are shown in Figure 3, along with the histograms of size distribution on the right-hand of each TEM image. It was found that the sizes of Au NPs deposited on CNT/DEN increased with the increase in M:D values. This tendency is in consistency with the previous results for free dendrimers.[5b] Then it was confirmed that it is possible to control the sizes of Au NPs during the in situ synthesis process.

It was clear from Figure 3 that all Au NPs were confined on the surface of CNTs, indicating strong interaction between dendrimers and Au NPs. Two types of interactions between them are known: one is the encapsulation of NPs in dendrimers,[5a] and the other is the coordination of Nps outside dendrimers.[5b] When the M:D ratio was 0.1:1, the particle sizes were mainly in the range of 2−5 nm, with a great majority of 3 nm. Although the diameters of Au NPs are slightly smaller than that of G4-PAMAM dendrimers (4−5 nm),[13] the judgment of the type of interaction in this case is too speculative to determine from the present data. However, when the M:D ratio increased to 0.5:1, the sizes of Au NPs also increased: most particles were in the
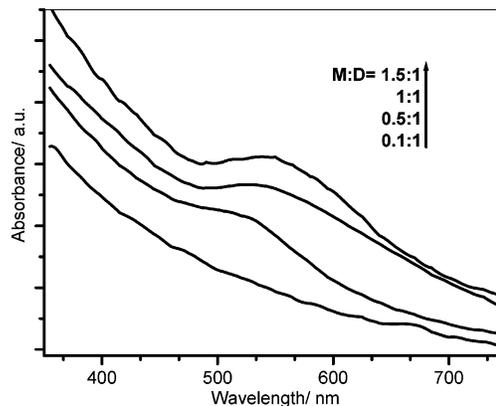

Figure 4. UV−vis Spectra of CNT/DEN/Au synthesized at different M:D ratios.

range of 3−7 nm, and very few populations of particles are larger than 7 nm in diameter, while only less than 10% of the NPs were smaller than 3 nm. Since most Au particles were larger than the dendrimer size, they seemed to coordinate outside the dendrimers. With the M:D ratio further increasing up to 1:1, the majority of the deposited Au NPs were larger than 5 nm, and only particles less than 4% were smaller than 5 nm, again meaning the coordination of Au NPs outside the dendrimers.[5b] However, when the M:D ratio was increased to 1.5:1, the particles were almost in the range of 5−11 nm, but some relatively large Au NPs with sizes between 20 and 30 nm coexisted on CNT/DEN (not included in the histogram). The formation of those larger Au NPs is due to the relatively lower ratio of dendrimers to Au ions, so that the imperfectly protected Au NPs grow up to larger ones. This tendency is consistent with the size variation of NPs in medium.[5b] These results indicate that PAMAM dendrimers attached on CNTs play a role as platforms for the preparation of metal NPs, matching with free dendrimers as protectors in medium. The platform is acting as a substrate for the nucleation of nanoparticles.

UV−vis spectrometry also disclosed the size change of Au particles depending on the M:D ratios, as shown in Figure 4. Because of the presence of CNTs, all spectra showed a monotonic increase toward low wavelength. The hybrid synthesized at M:D = 0.1:1 showed no characteristic absorption band in the wavelength shown, which is owing to the relatively small particle sizes (∼3 nm, quantum dot size). When the M:D value increased to 0.5:1, that is, the diameters of synthesized Au NPs were increased to 3−7 nm, a characteristic absorption band at 530 nm appeared in the UV−vis spectrum, which could be ascribed to the surface plasmon absorption of Au NPs. With further increasing of the M:D value to 1:1, the absorption band shifted to 545 nm, confirming the increasing of the particle sizes to 5−10 nm. As M:D increased to 1.5:1, the absorption spectrum showed a maximum centered at 560 nm along with a shoulder at 585 nm. Both bands can result from large particles of 5−11 nm and some aggregates with larger size of 15−30 nm, respectively.

Two types of control studies were examined. They are production procedures of Au NPs on CNTs (1) without dendrimer attachment and (2) with noncovalently bonded dendrimers (see Supporting Information S1). These are control systems of the procedure (3), which was adopted in the present work. Very few Au NPs were produced on CNTs on the procedure without dendrimers (see Supporting Information S2). When noncovalently bonded dendrimers coexisted, the production of NPs on CNTs was advanced, but the number of NPs was still less than on the surface of CNTs where dendrimers
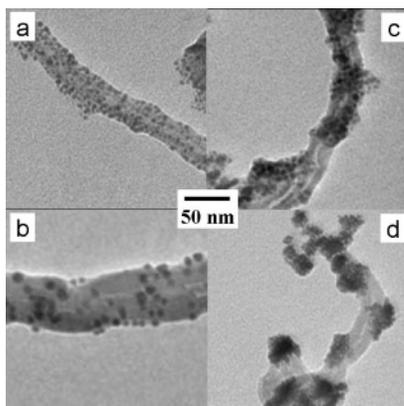
Dendrimer-Modified Carbon Nanotubes

J. Phys. Chem. C, Vol. 111, No. 6, 2007 **2419**

Figure 5. TEM pictures of CNT/DEN/NPs: (a) Au; (b) Ag; (c) Cu; (d) Pt.

Figure 6. UV−vis spectra of CNT/DEN/NPs in water.

were covalently bonded, as seen in comparison with Figure 5a and Supporting Information S2. These studies suggest that the dendrimer is playing an important role in the synthesis of NPs on CNTs. Namely covalent-bonding immobilized dendrimers on CNTs, and NPs were favorably fabricated on the dendrimer platforms. In addition, average diameters of NPs (10.5 nm from procedure (1); 11.9 nm from a procedure (2)) were larger than particles from procedure (3), since protection of NPs by dendrimers was no or less on former two procedures than on the latter. The tendency of effect of dendrimer content on particle size has been already reported.[5b]

The as-obtained CNT/DEN hybrids could also be subjected to synthesize in situ various other metal nanoparticles onto the surface of CNTs. In the present work, CNT/DEN/NPs consisting of Au, Ag, Cu, and Pt were produced at the M:D ratio of 1:1 by reducing the corresponding metal ions by $NaBH_4$. TEM images were shown in Figure 5, and additional TEM pictures can be found in Supporting Information (S3). It was clear that all metal nanoparticles were confined on the surface of CNTs, confirming the strong coordination between metal NPs and covalent-bonded dendrimers on CNTs. As a result, the CNT/DEN/NP hybrids were extremely stable: even after an 8-hours sonication in water, no obviously exfoliated NPs could be detected by TEM. However, control experiments, where dendrimers were simply mixed with acid-treated CNTs in water and then the corresponding metal ions were reduced in the aqueous solutions, showed very few NPs on CNT surfaces after sonication and filtration. This again supported the important role of dendrimers during the particle fixation.

The sizes and morphologies of different metal nanoparticles on CNT/DEN varied from metal to metal, owing to different coordination abilities with dendrimers and also different redox potentials of metal ions/metal NPs.[5b] As seen in Figure 5a, Au nanoparticles evenly coated the surface of CNT/DEN, and their diameters were in the range of 4−10 nm. However, fewer and slightly larger (5−15 nm) Ag NPs, as compared with Au NPs, were found on CNT/DEN (Figure 2b), because of the slower rate of reduction of Ag^+ and higher reactivity of Ag^0, as elucidated previously.[5b] Cu NPs with sizes of 3−9 nm tended to form some nanodomains along the carbon nanotubes (Figure 2c). In Figure 2d, Pt NPs covered only partly the surface of CNT/DEN, which was most probably owing to the weaker coordination ability of platinum with dendrimers. Furthermore, Pt NPs with sizes of 3−8 nm seem to aggregate together to form secondary nanoparticles with about 20−30 nm diameters.

CNT/DEN/NPs could be well dispersed in water, methanol, ethanol, and DMF, allowing the determination of their solution properties. Their electronic absorption spectra in water are
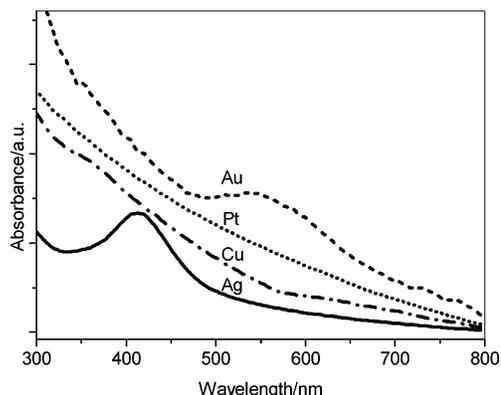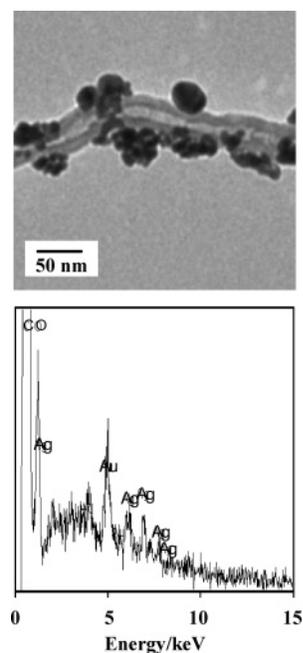

Figure 7. A TEM picture of CNT/DEN/Ag@Au and its EDX spectrum.

shown in Figure 6. On a monotonically changing spectrum of MWCNT, CNT/DEN/Au, and CNT/DEN/Ag showed characteristic surface plasmon bands at 550 and 410 nm of Au and Ag NPs, respectively. These results again verified the successful synthesis of metal NPs on CNTs.[5] However, the spectra of CNT/DEN/Cu and CNT/DEN/Pt had no obvious characteristic bands in 300 to 800 nm because of the smaller sizes (quantum dot sizes) of NPs, as demonstrated from TEM images.

The CNT/DEN/metal synthesis method proposed in the present work could also be applied to the preparation of binary metal NPs fixed on the surface of CNTs by metal displacement reaction.[5a] Experimentally, by dropping an aqueous $HAuCl_4$ solution into a dispersion of CNT/DEN/Ag, a material designated as CNT/DEN/Ag@Au was obtained. This reaction could be simply detected by visual observation and UV−vis spectrometry, since there was a significant color change from yellow to pink after the addition of $HAuCl_4$, and the characteristic surface-plasmon band of Ag NPs at 410 nm was shifted to 570 nm following the formation of Au NPs (Supporting Information S4). EDX spectroscopy and TEM provided direct evidence for the successful synthesis of binary NPs of Ag@Au on CNT/DEN, as seen in Figure 7. EDX results confirmed the existence of both Ag^0 and Au^0 in the final product. The particle sizes of Ag@Au NPs were mainly in the range of 10−30 nm, which

are much larger than the pristine Ag NPs (cf. Figure 5b), indicating that Ag NPs are encapsulated by Au NPs. Synthesis of other binary NPs on CNT/DEN is under investigation, as well as ternary metal NPs.

Potential advantages of the CNT/DEN/metal preparation are now described as follows: In the present work, dendrimers were immobilized on CNTs by covalent bonding. Such situation successfully produced abundant NPs on CNT through the intermediary of dendrimer platforms and concurrently controlled the size and amount of NPs on CNTs depending on the amount of dendrimers. The procedure developed in this work is applicable to nanoparticles of many metals and metal composites without any limitation. The present preparation technique is valuable for the production of metal nanoparticle shells coating on CNT. Metal nanoparticles in the shells will maintain and bring out characters of quantum dots or nanoparticles, different from metal tubes.

Conclusions

We have successfully modified MWCNTs with NH_2-terminated PAMAM dendrimers. By simply varying the ratio of Au^{3+} ($HAuCl_4$) to amine terminal groups of dendrimers, Au NPs with different sizes and size distributions were directly synthesized on CNT/DEN, and it was found that the sizes of Au NPs deposited on CNT/DEN increased with the increasing of M:D values. Furthermore, CNT/DEN is particularly suitable to be used to synthesize in situ metal nanoparticles on the surface of CNTs. This method is so versatile that metallic NPs of Au, Ag, Cu, and Pt, and even binary metallic NPs of Ag@Au, were produced and anchored on the surface of CNTs. Since water-soluble dendrimers were covalently bonded on CNTs, the hybrid materials obtained were dispersible in water and extremely stable, which are demanded on applications as biocompatible delivery agents, biosensors, and biocatalysts. This technique can be extended even to the SWCNTs without any limitation, and then further various applications will be developed.

Supporting Information Available: Scheme of different procedures for preparation of NPs on CNTs and TEM pictures of NPs on CNTs from different procedures were displayed. TEM pictures of purified MWCNTs, CNT/DEN, and CNT/DEN/NPs were taken, and UV−vis absorption spectra of $AgNO_3$, $HAuCl_4$, CNT/DEN/Ag, and CNT/DEN/Ag@Au were measured in water. These materials are available free of charge via Internet at http://pubs.acs.org.

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