

Gold Dendrimer Encapsulated Nanoparticles as Labeling Agents for Multiwalled Carbon Nanotubes

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We report immobilization of Au dendrimer encapsulated nanoparticles (DENS)¹ onto the surface of multiwalled carbon nanotubes (MWNTs). Clear differences in terms of aggregation of Au were observed depending on the hydrophilic or hydrophobic character of the MWNTs. Attachment to an insoluble, hydrophobic MWNT resulted in aggregation of the Au particles. Therefore, immobilization of Au DENSs onto the surface of the MWNTs requires that the latter be functionalized with carboxylic acid groups. This acidic functionalization leads to debundling of MWNTs and provides surface sites for interactions with amino groups present on the surface of the dendrimer. NMR spectroscopy and electron microscopy show that the structure of both dendrimers and the encapsulated nanoparticles, respectively, is preserved under our experimental conditions for the immobilization on the nanotube surface.

Poly(amidoamine) (PAMAM) dendrimers have been used to template monometallic,^{1–7} alloy,^{1,8,9} and core/shell^{1,8} bimetallic, nanoparticles containing up to a few hundred atoms. The synthesis of DENSs proceeds in two steps. First, metal ions are complexed to interior functional groups within the dendrimer. Second, chemical reduction of this precursor leads to particle formation. The nature of the chemical interactions between the AuCl₄[−] precursor and specific functional groups within the dendrimer has not been identified.^{10,11} Nevertheless, it has been found that there is a direct correlation between the metal-ion-to-

ABSTRACT In this paper, we report the functionalization of the surface of multiwalled carbon nanotubes (MWNTs) with Au dendrimer encapsulated nanoparticles (DENSs). The results show that, when pristine MWNTs having hydrophobic surfaces are exposed to DENSs, the dendrimers aggregate on the MWNT surface. However, when the MWNTs are oxidized in acid prior to exposure to DENSs, well-dispersed submonolayer coverages of Au nanoparticles are observed on the MWNT surface. This suggests that acid-induced debundling of the nanotubes is an essential prerequisite for attachment of nearly monodisperse DENSs. Electron microscopy and NMR spectroscopy confirm that the structures of the DENSs and dendrimers are retained after immobilization on the surface of acid-functionalized MWNTs.

KEYWORDS: dendrimer · gold nanoparticles · carbon nanotubes · nanomaterials

dendrimer ratio used in the synthesis and the size of gold DENSs.^{10,12–14} A variety of analytical methods, including electron microscopy,¹⁰ NMR,^{6,7} and selective catalysis experiments,^{15–17} have been used to show that DENSs reside within individual dendrimers. After reduction, the dendrimer serves as a protective agent to prevent aggregation of the nanoparticles which are hosted within the PAMAM cavities.^{6,7,18,19}

Multiwalled carbon nanotubes are concentrically rolled graphene sheets composed of carbon hexagons having highly strained regions at the tips where pentagons are present. Because of their desirable properties, these nanomaterials have played a leading role in fields such as nanomedicine,^{20–27} photophysics,^{28–31} and sensing.^{32,33} One of the main limitations of MWNTs is their poor solubility, which can be enhanced in polar solvents, such as dimethylformamide and water, by functionalizing their surfaces with polar groups.^{34,35} However, excessive functionalization damages

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the surface of CNTs and changes their physical properties. Dendrimers have previously been used as surface modifiers to improve the solubility of CNTs without damaging their carbon skeleton.^{28,36–40} Specifically, it has been found that attachment of PAMAM dendrimer-like fragments increases the solubility of MWNTs in water^{37,41} and of SWNTs in organic solvents, such as DMF or *o*-dichlorobenzene.²⁸ Likewise, the solubility of MWNTs^{38–40} and SWNTs^{38,39,42} is improved by immobilization of aryl-ether-type dendrimers, dendrimeric structures based on benzyl esters and amino polyesters.

Dendrimers have also been used to introduce new functionalities to CNTs. For example, there have been several examples in which dendrimers were used to immobilize metal and semiconductor nanoparticles on their surface.^{42–48} Specifically, groups led by Imae and Zhu, respectively, attached PAMAM dendrimers as templates to introduce metal and metal oxide nanoparticles on the surface of MWNTs.^{36,43,44} However, the metal nanoparticles were found to be too large to be fully encapsulated within individual dendrimers.^{43,44} This suggested the presence of small aggregates of DENs or larger nanoparticles, surrounded by multiple dendrimers, which are known as dendrimer-stabilized nanoparticles (DSNs).⁴⁹ Likewise, Stevenson and Vijayaraghavan showed that preformed Pt nanoparticles stabilized by dendrimers can be immobilized on nitrogen-doped MWNTs.⁴⁵ Finally, Newkome and co-workers synthesized CdS quantum dots encapsulated within amino polyester dendrons and tethered them to SWNTs.⁴²

The use of PAMAM dendrimer derivatives in nanomedicine^{41,47,50–55} has been extensively studied. For example, divergent growth of PAMAM dendrons on CNT surfaces has been reported for several applications, including light harvesting with chromophores²⁸ and biomedical applications such as gene transfer⁴¹ or antimicrobial therapy.⁴⁷ Presynthesized PAMAM dendrimers have also been immobilized on CNTs for applications to gene-transfer therapy.²¹

The key finding that emerges from this work is a procedure for attaching Au DENs to MWNTs that preserves the structure of both. Two important parameters are necessary to achieve these results. First, MWNTs must be at least partially soluble. For example, we have observed that the attachment of Au DENs onto pristine MWNTs (*p*-MWNTs), which are not soluble in water, leads to aggregation of the Au nanoparticles. Second, NMR spectroscopy shows that PAMAM dendrimers degrade when refluxed in water at 100 °C, and therefore elevated temperatures should be avoided during the immobilization process.

RESULTS AND DISCUSSION

Au DENs containing an average of ~200 atoms were encapsulated within sixth-generation, amine-terminated PAMAM dendrimers (G6-NH₂). These DENs, which we denote as G6-NH₂(Au₂₀₀), were synthesized

according to a previously reported procedure.⁵⁶ TEM (transmission electron microscopy) analysis of these materials (Figure S1a,b in Supporting Information) indicates they have a size distribution of 2.0 ± 0.5 nm, which is consistent with previous results from our group and with the theoretical size calculated for cuboctahedral nanoparticles containing 200 Au atoms (1.9 nm).¹³ UV–vis spectroscopic data (Figure S1c) indicate a monotonically decreasing absorbance toward higher wavelength and a very small plasmon band at 522 nm. These spectral properties are consistent with previous results and with Au DENs having diameters of ~2.0 nm.^{10,12,13}

The MWNTs used in the present study have average outer and inner diameters of 20–30 and 5–10 nm, respectively. One important objective of this study was to examine the attachment of Au DENs to MWNTs as a function of the MWNT surface properties (Figure 1). The materials illustrated in Figure 1 were characterized by TEM, energy-dispersive X-ray spectroscopy (EDS), thermogravimetric analysis (TGA), X-ray photoelectron (XPS) spectroscopy, and the Kaiser test (for determination of free primary amino groups). It was not possible to obtain UV–vis spectra of the MWNT/DEN composites due to a strong background arising from light scattering (Figure S2).

Two different synthetic approaches have been used to prepare MWNT/DEN composites. In the first procedure, Au DENs were stirred with underivatized *p*-MWNTs in 10/1 H₂O/DMF at 40 °C for 24 h (top of Figure 1). In the second procedure, the MWNT surface was oxidized prior to exposure to the DENs by treating the *p*-MWNTs with a solution of H₂SO₄/HNO₃ (3/1) in the presence of ultrasound (25 min with a sonic tip, 750 W) followed by sonication for 5 h in a water bath. This procedure has been shown to yield MWNTs functionalized on their surfaces with carboxylic acid groups (*c*-MWNTs).^{57–59} It also shortens the nanotubes and introduces edge sites. The composites were prepared by mixing *c*-MWNTs and Au DENs in 10/1 H₂O/DMF solutions at 40 °C for 24 h.

Figure 2a shows the dependence of the solubility on the chemical treatment of the MWNTs. The Au-*c*-MWNTs are rather soluble in water (~0.2 mg/mL), which is comparable to the findings of others.^{58,60} The other materials have significantly lower solubilities: Au-*p*-MWNT, ~0.04 mg/mL, and *c*-MWNTs, ~0.06 mg/mL. In the case of Au-*p*-MWNT, the increase in their solubility is originated by the presence of amino-terminated PAMAM dendrimers on their structure. It has previously been shown that primary amino groups of organic molecules interact with the carbon surface of *p*-MWNTs,^{61,62} giving rise to a slight improvement in their water solubility. The *p*-MWNTs are not soluble in water. The solubility of each material is related to its organizational structure in solution. Specifically, Figure S3a,b (Supporting Information) shows that *p*-MWNTs comprise en-

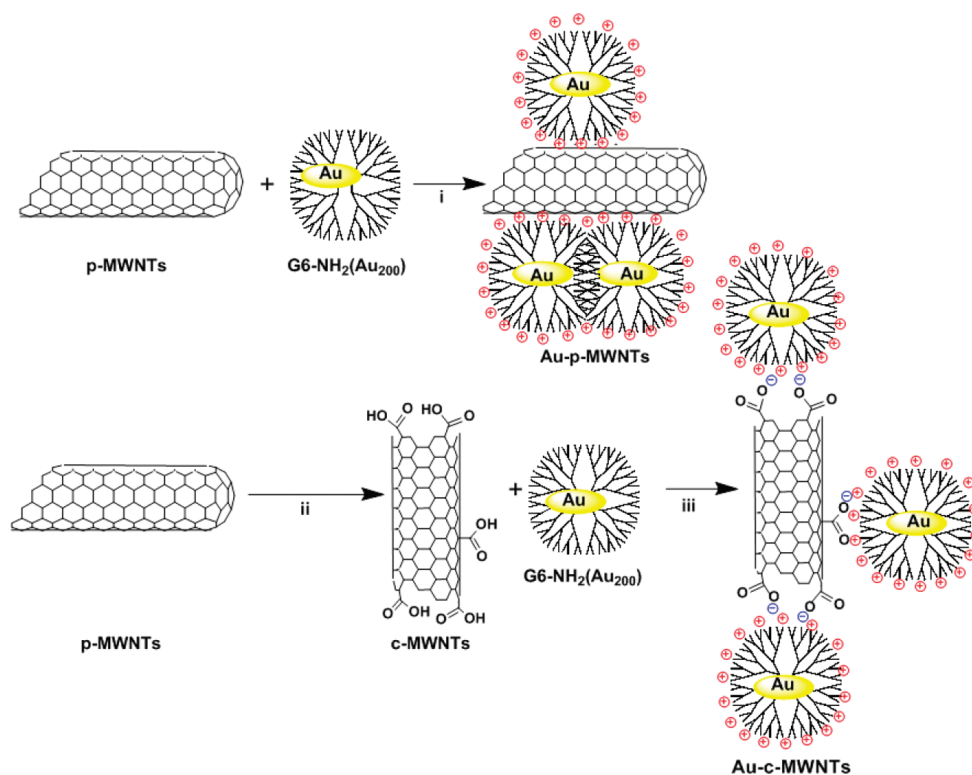


Figure 1. Reaction conditions: (i) water/DMF 10/1, 40 °C for 24 h; (ii) $\text{H}_2\text{SO}_4/\text{HNO}_3$ 3/1, sonication for 25 min in a sonic tip followed by sonication in a water bath for 5 h; (iii) water/DMF 10/1, 40 °C for 24 h.

tangled tubes that form bundles. In contrast, *c*-MWNTs are debundled due to the presence of polar groups on their surface (Figure S3c).

Figure 2b shows that Au DENs aggregate on the surface of *p*-MWNTs. Particle size distributions (Figure S3d) of the resulting aggregates reveal a bimodal distribution of nanoparticles. The average size of $\sim 30\%$ of the Au particles is centered at 3.5 ± 0.3 nm, and the remaining $\sim 70\%$ is centered at $5.4 \pm$

1.1 nm. We do not fully understand why the Au DENs aggregate on the *p*-MWNTs surfaces, but their weak adsorption could be accompanied by high mobility. Similar findings, involving weak adsorption on nondefective carbon surfaces, have previously been reported by Vijayaraghavan and Stevenson and our own group.^{45,63} Finally, ^1H NMR and pulsed-field gradient experiments, which are discussed later, indicate that the reaction conditions used for DEN im-

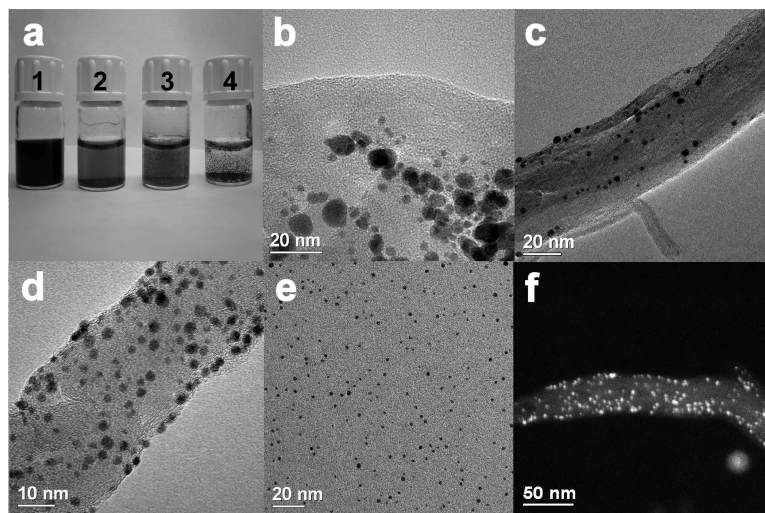


Figure 2. (a) Optical micrograph of vials containing aqueous solutions of MWNTs with and without DENs: **1**, Au-*c*-MWNTs (0.2 mg/mL); **2**, *c*-MWNTs (0.06 mg/mL); **3**, Au-*p*-MWNTs (0.04 mg/mL); **4**, *p*-MWNTs. TEM images of (b) Au-*p*-MWNTs; (c) and (d) Au-*c*-MWNTs. (e) TEM image of G6-NH₂(Au₂₀₀). (f) Representative high-angular annular dark-field STEM image of Au-*c*-MWNTs.

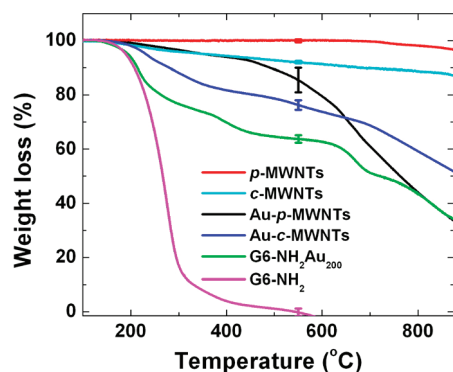


Figure 3. TGA of the dendrimers, Au DENs, and composites indicated in the legend. The measurements were performed under a N_2 atmosphere, and the heating rate was $10\text{ }^\circ\text{C}/\text{min}$.

mobilization need to be chosen with special care because they may lead to partial degradation of the dendrimers, and this could in turn lead to aggregation.^{43,44,49}

In contrast to the *p*-MWNTs, Au DENs are well-dispersed on acid-treated MWNTs (Figure 2c,d). Acid pretreatment of the MWNTs generates surface carboxylic acid groups,^{57,58} which enhances solubility and causes debundling of the individual nanotubes. We believe that a stronger adsorptive interaction between the positively charged dendrimers and the negatively charged MWNT surface leads to less surface mobility of the DENs and hence less aggregation. It is notable that the size of the Au DENs is the same before (2.0 ± 0.5 nm, Figure 2e and Supporting Information Figure S1a,b) and after (2.1 ± 0.5 nm, Figure S3f) electrostatic attachment to the acid-functionalized MWNT surface.

Figure 2f shows a STEM-HAADF (scanning transmission electron microscopy high-angular annular dark-field) image of the Au-*c*-MWNTs. The high nuclear density of the Au particles provides good contrast of the metal along the surface of the MWNT.⁶⁴ In future studies, this will facilitate the recognition of the MWNTs in the cellular media because cellular organelles have dimensions and electron contrast that are similar to MWNTs. Au DENs are suitable as biological markers as Baker and co-workers have recently shown.⁶⁵

XPS experiments confirm the presence of Au in the DEN-containing composites (Figure S4). The presence of Fe and Ni was determined by means of EDX experi-

ments (Figure S5). The latter two metals originate from the catalysts used to prepare the MWNTs.^{24,59}

Figure 3 shows the thermogravimetric analysis (TGA) of the dendrimers, Au DENs, and the DEN/MWNT composites. Weight losses were measured at $550\text{ }^\circ\text{C}$ because at this temperature metal-free PAMAM dendrimers are fully removed (purple line, Figure 3). These macromolecules are thermosensitive, and it has been reported that, in the presence of oxygen and metals, such as Pt, the decomposition is accelerated starting at temperatures as low as $75\text{ }^\circ\text{C}$.^{66–68} However, we cannot exclude the possibility of organic residue on the MWNT surface, even at $550\text{ }^\circ\text{C}$.⁶⁸ Importantly, no decomposition of the *p*-MWNTs is observed until $>700\text{ }^\circ\text{C}$ (red line, Figure 3).⁶⁹ Therefore, the measured weight loss from each sample can be attributed to loss of dendrimer attached to the MWNT surface. The highest weight loss value ($23.5 \pm 0.9\%$), which corresponds to $4.0 \pm 0.2\text{ }\mu\text{mol G6-NH}_2(\text{Au}_{200})/\text{g c-MWNT}$, is obtained for Au-*c*-MWNTs. Au-*p*-MWNTs samples exhibited a weight loss of just $9.6 \pm 4.5\%$, which corresponds to $1.6 \pm 0.8\text{ }\mu\text{mol G6-NH}_2(\text{Au}_{200})/\text{g p-MWNT}$. These results are in qualitative agreement with the TEM data, which revealed a higher surface concentration of Au DENs on Au-*c*-MWNTs.

Table 1 summarizes the results of the analytical techniques used to characterize the MWNTs and MWNT/DEN composites examined in this project. The results show that the uptake of Au DENs is substantially higher for *c*-MWNTs compared to the pristine nanotubes. For example, elemental analysis (EA) of Au-*c*-MWNT yields a total nitrogen content of $5.48 \pm 0.15\%$ $\text{g}_\text{N}/\text{g}_{\text{MWNT}}$. There are 1018 N atoms in each G6-NH₂ PAMAM dendrimer, thus the density of DENs is $3.8 \pm 0.1\text{ }\mu\text{mol G6-NH}_2(\text{Au}_{200})/\text{g c-MWNT}$. This value is in good agreement with the TGA results: $4.0 \pm 0.2\text{ }\mu\text{mol G6-NH}_2(\text{Au}_{200})/\text{g c-MWNT}$. We also performed on this sample the Kaiser test to prove the presence of free primary amino groups on the MWNT surface. This test is a qualitative analysis and is based on the reaction of ninhydrin with primary amines, which produces a characteristic dark blue compound.^{70,71} As expected, the test was positive in the materials containing PAMAM dendrimers, Au-*p*-MWNTs and Au-*c*-MWNTs. In contrast, *p*-MWNTs and *c*-MWNTs gave no color when exposed to ninhydrin.

The mild conditions ($40\text{ }^\circ\text{C}$, 24 h) used for immobilization of the DENs yielded a lower degree of functionalization ($\sim 4\text{ }\mu\text{mol G6-NH}_2(\text{Au}_{200})/\text{g c-MWNT}$) relative to

TABLE 1. TGA, Elemental Analysis of the MWNTs, and DEN/MWNT Composites Reported in This Work

sample	TGA (% weight loss)	EA ^a ($\mu\text{mol Au DEN/g MWNT}$)	solubility (mg/mL)	Au DEN size (nm)
<i>p</i> -MWNTs	0.1 ± 0.07		ns ^b	
<i>c</i> -MWNTs	8.3 ± 0.6		0.06	
Au- <i>p</i> -MWNTs	9.6 ± 4.5 (1.6 ± 0.8) ^c	1.2 ± 0.2	0.04	3.5 ± 0.3 ^d 5.4 ± 1.1 ^e
Au- <i>c</i> -MWNTs	23.5 ± 0.9 (4.0 ± 0.2) ^d	3.8 ± 0.1	0.20	2.1 ± 0.5

^aElemental analysis. ^bNot soluble. ^cWeight loss measured in $\mu\text{mol Au DEN/g MWNT}$. ^d70%. ^e30% of the sample population.

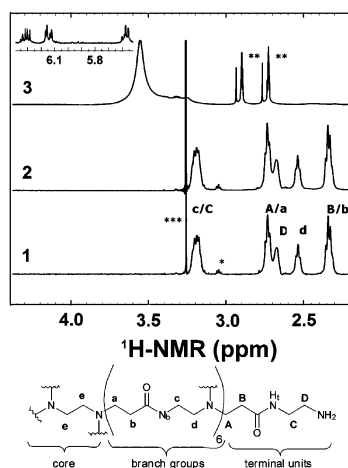


Figure 4. (Top) ^1H NMR spectra of G6-NH₂ recorded at 25 °C in D₂O (spectrum 1), at 40 °C for 24 h in D₂O (spectrum 2), and at reflux of DMF-*d*₇ for 48 h (spectrum 3). The intensity of the inset in spectrum 3 has been increased (2.5 times) for better visualization. (Bottom) Schematic representation of G6-NH₂ indicating the lettering scheme used to identify the methylene and nitrogen groups in the dendrimer. The peak marked with a single asterisk arises from impurities in the dendrimer solution. Peaks marked with a double asterisk correspond to the residual protons of the DMF-*d*₇ solvent. The peak marked with a triple asterisk comes from residual methanol present in the commercial dendrimer solution. Increasing the intensities of spectra 1 and 2 for a better visualization of all peaks results in an overlapping of the methanol peak with spectra 2 and 3.

other synthetic methods.^{43,44} However, to preserve the integrity of the dendrimers, the conditions used in our experiments were mild compared to others reported in the literature (e.g., DMF reflux, 2 days).^{43,44} Our low degree of functionalization is comparable with results previously reported for attachment of dendrimer-templated platinum particles also performed under mild conditions.⁴⁵ Specifically, it is known that PAMAM dendrimers are thermolabile, and that the retro-Michael reaction is favored at high temperatures.^{72–76}

Figure 4 shows NMR spectra of G6-NH₂ solutions in water and DMF at different temperatures. Spectrum 1 is a ^1H NMR spectrum obtained from an aqueous solution of G6-NH₂. The peak assignments were made using information obtained from complementary experiments, including ^1H – ^1H COSY, ^1H – ^{13}C HSQC, and ^1H – ^{13}C HMBC.⁷⁷ Spectrum 2 is identical to spectrum 1, except that it was obtained after heating the aqueous G6-NH₂ solution to 40 °C for 24 h. Comparison of spectra 1 and 2 using sodium acetate as an internal standard indicates that ~85% of the dendrimer remains unaltered by the heating. The increase in the signal of minor alkyl fragments at 3.05 ppm confirms some decomposition of the dendrimeric structure. As mentioned previously, this level of decomposition might be sufficient to lead to some nanoparticle aggregation on the *p*-MWNT surfaces. Spectrum 3 is the ^1H NMR spectrum of a G6-NH₂ solution after being heated at dimethylformamide-*d*₇ reflux for 48 h.^{43,44} After expo-

sure to these conditions, there is significant degradation of the dendrimer, which is signaled by the appearance of new olefin fragment peaks at 5–7 ppm and new alkyl group peaks at 3.1–3.5 ppm. When G6-NH₂ is heated to reflux in D₂O, similar results were extracted from the ^1H NMR experiment (Supporting Information Figure S6). New peaks assigned to olefins at 5–7 ppm and signals at lower chemical shifts (~2.6 ppm) were also detected. This is a consequence of some dendrimer degradation resulting from the heating process. These results confirm that low temperatures and short reaction times with MWNTs are necessary to preserve the structure of the PAMAM dendrimers, and therefore the encapsulated Au nanoparticles, during the immobilization process.

Pulsed-field gradient spin–echo (PFGSE) NMR experiments were also carried out to determine if particular reaction conditions induced dendrimer degradation. PFGSE NMR is a valuable tool for mixture analysis because it distinguishes different species depending on their diffusion coefficients and therefore on their hydrodynamic radii.⁷⁸ Figures S7–S9 in Supporting Information show the pseudo-2D DOSY plots for 100 μM D₂O solutions of G6-NH₂ at 25 °C (Figure S7), after being heated to 40 °C for 24 h (Figure S8), and after being heated at D₂O reflux for 24 h (Figure S9). Figure S8 shows that mainly all of the dendrimer molecules remain unaltered since only a couple of signals around 3.0 ppm appear with a similar diffusion coefficients to the dendrimer. However, in Figure S9, different new signals with higher diffusion coefficient than the dendrimer itself are observed around 2.6 ppm, confirming the degradation of the dendrimer at high temperature and the importance of choosing the right experimental conditions for the electrostatic attachment of Au DENs.

CONCLUSIONS

Mild reaction conditions during Au DEN attachment and high MWNT solubility are key factors for obtaining monodisperse Au nanoparticles fully distributed along the MWNT surface. We showed that an increase in the temperature during the dendrimer attachment results in decomposition of the PAMAM structure, very likely because of the occurrence of a retro-Michael reaction. The insolubility of nonfunctionalized carbon nanomaterials leads to a high local concentration of Au DENs on the entangled MWNT bundles, resulting in the presence of Au aggregates on the nanotube surface. The particle coverages obtained for MWNT/DEN composites at the lower temperatures used here are sufficient for the biomedical applications we envision. Specifically, experiments are presently being carried out in our laboratories to study the behavior of the MWNTs as carriers for drug delivery, gene transfer, and image contrast agents.

MATERIALS AND METHODS

Chemicals. G6-NH₂ was purchased as a 5 wt % methanol solution (Dendritech, Inc., Midland, MI). The methanol was removed under vacuum prior to use, and 18 M Ω · cm Milli-Q deionized water (Millipore) was added to obtain aqueous solutions of G6-NH₂ having the desired concentrations. MWNTs were purchased from Nanostructured & Amorphous Materials Inc., Houston, TX; Stock No. 1240XH, 95%, OD 20–30 nm). H₂AuCl₄, NaBH₄ (99.9%, Reagent Plus), anhydrous dimethylformamide, D₂O (99.98%), and deuterated dimethylformamide (DMF-*d*₇) (Sigma-Aldrich, Inc.) were used as received. All experiments were carried out in air unless specified otherwise.

Characterization. TEM experiments were performed using a FEI Tecnai G2 F20 transmission electron microscope, equipped with Schottky-type field emission gun, X-twin lenses, an EDAX energy-dispersive X-ray spectrometer (EDS), and a scanning TEM (STEM) unit with high-angle annular dark-field (HAADF) detector operating at 200 kV. Samples were prepared by sonication for 10 min and dropwise (8 μ L) addition of the sample onto a carbon-coated 400 mesh Cu grid (EM Sciences, Gibbstown, NJ) followed by solvent evaporation in air.

Thermogravimetric analyses were obtained using a TGA Q50 (TA Instruments) and recorded under N₂ by equilibrating at 100 °C followed by a ramp of 10 °C/min up to 1000 °C.

Elemental analyses were performed on a LECO CHNS-932 instrument.

XPS data were collected on a Kratos Axis Ultra DLD spectrometer using an Al K α X-ray source. The spectra were collected with a pass energy of 160 eV and a resolution of 1 eV for survey spectra and with a pass energy of 20 eV and a resolution 0.1 eV for high-resolution spectra. Dwell times were 1.00 s in all instances. Samples were prepared by dropping the sample solutions onto Si wafers and allowing to dry.

NMR experiments were carried out using a Varian, Unity Inova NMR spectrometer operating at 499.7722 MHz for ¹H and at 152.678 MHz for ¹³C. The spectrometer was equipped with a gradient amplifier and a four-nucleus 5 mm ¹H{¹³C-³¹P}PFG high-field indirect detection probe. A presaturation pulse sequence was used to minimize the water peak in the 1D experiment. All 1D ¹H experiments (presaturation) and 2D experiments (COSY, HMB, HSQC) were performed at 298 K using standard pulse sequences from the Varian library. Deuterated water (D₂O, 99.98%, Sigma-Aldrich, Inc.) and deuterated dimethylformamide (DMF-*d*₇, Sigma-Aldrich, Inc.) were used as solvent to perform the corresponding experiments of dendrimer stability. Sodium acetate (1.5 mM) was used as an internal standard and was added after cooling the solutions to 298 K.

Diffusion (PFGSE) experiments were performed at 298 K using the bipolar stimulated echo sequence with 32 increments in the gradient strength (2–95%), typically 64 averages per increment step, and 100 ms diffusion times. Pseudo-2D DOSY plots were processed with the standard Varian Software VNMR6.1C.

Peak assignments for G6-NH₂ were made using solutions containing 100 μ M dendrimer: ¹H NMR (499.772 MHz, D₂O) δ (ppm) 3.19 (br t, 504H, H_d), 3.15 (br t, 512H, H_c), 2.71 (t, 1016H, ³J_{H,H} = 5.0 Hz, H_{A/a}), 2.64 (br t, 512H, H_b), 2.52 (t, 504H, ³J_{H,H} = 5.0 Hz, H_d), 2.32 (br t, 1016H, H_{B/b}).

Synthesis of Au DENs. Twenty milliliters of 2.0 μ M G6-NH₂(Au₂₀₀) DENs were prepared according to a previous report.⁵⁶ Briefly, 0.8 mL of a freshly prepared, aqueous 10.0 mM H₂AuCl₄ solution was added to a 2.0 μ M (final concentration) aqueous G6-NH₂ solution (18.76 mL). The metal–dendrimer complex solution was stirred for less than 1 min before a 5-fold molar excess (0.04 mL) of freshly prepared, aqueous 1 M NaBH₄ dissolved in 0.3 M NaOH was added. The vial was then sealed. Reduction occurs almost immediately and is accompanied by a change in color from pale yellow to wine red.

Synthesis of Au-*p*-MWNTs. Twenty milligrams of *p*-MWNTs were suspended in 5 mL of DMF and sonicated in a sonic bath for 10 min. Dropwise addition of the 2.0 μ M Au DENs solution in water (2 \times 25 mL, pH 7.5) was then performed. The reaction mixture was heated at 40 °C for 1 day. Subsequently, it was filtered using a Millipore system (GTPP 0.2 μ m filter) and washed with methanol and water.

Synthesis of *c*-MWNTs. Five hundred milligrams of pristine MWNTs were sonicated (using a sonic tip) for 25 min in 125 mL of a 3/1 v/v mixture of concentrated H₂SO₄ and HNO₃, and then in a water bath for 5 h. The resulting suspension was diluted with water, filtered using Millipore system (GTPP 0.2 μ m filter), washed with water until the pH was \sim 6, and then rinsed with methanol and dried under vacuum at 298 K.

Synthesis of Au-*c*-MWNTs. Twenty milligrams of *c*-MWNTs were dispersed in 5 mL of DMF followed by dropwise addition of a 2.0 μ M aqueous solution of G6-NH₂(Au₂₀₀) (2 \times 25 mL, pH 7.5). The reaction mixture was heated at 40 °C for 1 day. Subsequently, it was filtered using a Millipore system (GTPP 0.2 μ m filter) and washed with methanol and water.

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Supporting Information Available: TEM micrographs, size distribution histograms, and UV–vis spectra of G6-NH₂(Au₂₀₀); UV–vis spectra of *p*-MWNTs, *c*-MWNTs, Au-*p*-MWNTs, and Au-*c*-MWNTs; TEM micrographs, EDX spectra, and size distribution histograms, and XPS spectra for MWNTs and MWNT/DEN composites; ¹H NMR spectra and pseudo-2D DOSY plots for G6-NH₂ after exposure to D₂O at different temperatures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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