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### Advantages of immobilization of Pt nanoparticles protected by dendrimers on multiwalled carbon nanotubes<sup>†</sup>

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Pt nanoparticles (PtNPs) were synthesized in the presence of a NH<sub>2</sub>-terminated fourth generation poly(amido amine) (PAMAM) dendrimer as a stabilizer at different molar ratios (M:D) of metal precursor to amine terminal group of dendrimer. Subsequently, PtNPs protected by dendrimers (DENPtNPs) were covalently immobilized on multiwalled carbon nanotubes (MWCNTs) by using a condensing agent for amide bond formation between acid-treated MWCNTs and DENPtNPs and the product CNT/DENPtNPs were characterized. PtNPs on MWCNTs increased quantitatively in content with M: D and dispersed with same aspect as the dispersion of DENPtNPs in water: PtNPs homogeneously dispersed at low M: D ratio and slightly aggregated at high ratio. The decomposition of CNT/DENPtNPs occurred at the lower temperature owing to the catalytic effect of PtNPs. A near-infrared absorption band around 2083 nm, which is extremely weak for MWCNTs, was intensified and D, D' and G Raman bands were slightly downshifted when DENPtNPs were attached. These phenomena can be attributed to the electron transfer from DENPtNPs to MWCNTs. Remarkable advantage is apparent from the enhanced electrochemical behavior of CNT/DENPtNPs loaded on gold electrode. PtNPs promoted the electron transfer of MWCNTs and dendrimers contributed to uptake of redox materials.

### 1. Introduction

In the past decade, nanohybrid materials of carbon nanotubes with metal or metal oxide nanoparticles have received extensive attention.<sup>1–9</sup> According to their unique and promising properties, these nanohybrid materials have been used in many applications as gas sensors,<sup>2,9</sup> supercapacitor electrodes,<sup>6</sup> catalyst supports,<sup>1</sup> and antimicrobial therapies.<sup>7</sup> Since the size, shape and size distribution of particles play an important role in applications, such as catalysis, different techniques have been developed for synthesis of metal nanoparticles with controlled size and shape.<sup>10</sup> Using dendrimers as stabilizers or protectors is one of the most effective ways to produce homogeneous metal nanoparticles.<sup>11–14</sup> There have been some reports using dendrimers as a binder to attach the metal and metal oxide nanoparticles on the surface of carbon nanotubes.<sup>3,4,8</sup>

Dendrimers which encapsulate Au nanoparticles have been adhered on the surface of mutiwalled carbon nanotubes (MWCNTs) *via* electrostatic attraction between the positively charged dendrimers and the negatively charged surface of MWCNTs.<sup>8</sup> On the other hand, covalently functionalized dendrimers on MWCNTs as scaffolds have been utilized for *in situ* immobilization of metal and metal oxide nanoparticles on them.<sup>3,4</sup> Thus, this procedure should provide a promising methodology for the hybridization of metal nanoparticles on carbon materials. However, the *in situ* synthesized metal nanoparticles were inhomogeneously distributed on the MWCNTs modified with dendrimers. Therefore, a procedure to accomplish a uniform and chemically-bound attachment of nanoparticles must be developed.

In the present work, Pt nanoparticles (PtNPs) protected by poly(amido amine) (PAMAM) dendrimers, DENPtNPs, were synthesized at the condition where the ratios of metal precursor to amine terminal group of PAMAM dendrimer were optimized so as to provide the stably dispersed PtNPs. Then DENPtNPs were covalently immobilized on the MWCNTs. The distribution of DENPtNPs and the content of Pt on the nanohybrid materials consisting of MWCNTs were investigated and evaluated. Moreover, advantages of coexistence of PtNPs and dendrimers on MWCNTs are discussed. This procedure could provide a sufficiently homogeneous distribution and chemically stable immobilization of metal nanoparticles on MWCNTs.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: AFM images of PAMAM dendrimer and DENPtNPs, UV-VIS absorption spectra of PtCl<sub>6</sub><sup>2–</sup>/dendrimer complexes and DENPtNPs, and deconvolution of Raman G and D' bands. See DOI: 10.1039/c2cp41364g

MWCNT and NaBH<sub>4</sub> were purchased from Wako Pure Chemical Industries Ltd. Amine-terminated fourth-generation PAMAM dendrimer (10 wt% in methanol), Na<sub>2</sub>PtCl<sub>6</sub>, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDAC) and 4-mercaptobenzoic acid (MBA) (97%) were products from Aldrich Chemical Co. Sulfuric acid (98%), nitric acid (60%) and ethyl alcohol were commercial products. Potassium ferricyanide (99%) (K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O) was purchased from ACROS organics. Ultra-pure water was used throughout the entire experiment.

Synthesis of DENPtNPs was carried out as follows: A 0.2 wt% solution of PAMAM dendrimer was prepared by diluting a 10 wt% methanol solution of the dendrimer with water. Then 1 cm<sup>3</sup> of an aqueous Na<sub>2</sub>PtCl<sub>6</sub> solution was added into 19 cm<sup>3</sup> of the 0.2 wt% dendrimer solution. The solution of  $[PtCl_6]^{2-}$  dendrimer complex was stirred for 3 days and the pH of the solution was adjusted to be 4. Then 1 cm<sup>3</sup> of an aqueous 0.3 M NaOH solution of NaBH<sub>4</sub> was added to the complex solution. The concentrations of Na<sub>2</sub>PtCl<sub>6</sub> and NaBH<sub>4</sub> (of a 10-fold mole of Na<sub>2</sub>PtCl<sub>6</sub>) were varied along different ratios of Na<sub>2</sub>PtCl<sub>6</sub> to PAMAM dendrimer (see the text). The color of the solution immediately turned from light yellow to brown, indicating the formation of DENPtNPs.

DENPtNPs were immobilized on acid-treated MWCNTs as follows: MWCNTs were purified by refluxing in concentrated HNO<sub>3</sub> for 1 day as previously reported.<sup>3</sup> The purified MWNTs were then treated with HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (3:1  $\nu/\nu$ ) for 2 days to load carboxylic acid groups on the surface of MWCNTs. 20 mg of the acid-treated MWCNTs were dispersed in 5 cm<sup>3</sup> of a DENPtNPs solution and the mixture was stirred for 1 h at room temperature. Subsequently, EDAC was added to the mixture and vigorously stirred at room temperature for 2 days to allow amide formation. The dispersion was then filtered using a Millipore membrane (PTFE, pore size = 0.2 µm) and the filtered residue was rinsed with water and dried overnight at 110 °C.

Transmission electron microscopic (TEM) images were taken using a Hitachi H-7000 equipped with a CCD camera and an electron diffraction (ED) attachment, operating at a voltage of 100 kV. High resolution transmission electron micrographs (HR-TEM) were obtained using a Philips Tecnai F20 G2 FEI-TEM. The specimens for TEM and HR-TEM were prepared by dropping sample solutions onto carbon-coated copper grids and allowing drying in air. Field emission-scanning electron microscopic (FE-SEM) observation of sample powders on the carbon tape was performed on a JEOL JSM-6500F, operated at a voltage of 20 kV. Atomic force microscopic (AFM) observation was performed in air using a Digital Instruments NanoScope III apparatus. Freshly-cleaved mica was used as a substrate. The sample solutions were dropped directly onto the mica surface, and then dried overnight in air. Nuclear magnetic resonance (NMR) spectra of samples in D<sub>2</sub>O were recorded on a Bruker Avance NMR spectrometer operating at 500.132 MHz for <sup>1</sup>H. Thermogravimetric analyses (TGA) of sample powders were performed using a TGA/TA instrument (Perkin Elmer, Q500) under an atmosphere of air with a heating rate of 10  $^{\circ}$ C min<sup>-1</sup>. IR spectra were recorded for powders on an FTIR spectrometer (Nicolet, Nexus 670) with an ATR mode. Raman spectra were

recorded on a Raman Microscope, Kaiser Optical Systems, with a laser at an excitation wavelength of 785 nm. The specimens for Raman measurement were fabricated on a glass microfiber filter (Whatman No.1) by vacuum-filtering and drying at 110 °C overnight. Ultraviolet-visible-near infrared (UV-VIS-NIR) absorption spectroscopic measurements were performed on a Jasco V-670 series UV spectrometer with a 1 mm quartz cell. The specimens for UV-VIS-NIR spectra were prepared by dispersing materials in ethanol under sonication.

Electrochemical functionality of CNT/DENPtNPs was examined with a Hokuto-Denko HZ-3000. Disposable electrochemically printed (DEP) chips (with a screen-printed circular gold (SPCG) working electrode, a carbon counter electrode and an Ag/AgCl reference electrode) were purchased from BioDevice Technology. A self-assembled monolayer (SAM) of MPA on a working electrode was prepared by immersing DEP chip into a 20 mM ethanol solution of MBA for 24 h at room temperature, rinsed and dried.<sup>15</sup> The chemical immobilization of CNT/ DENPtNPs on SAM-SPCG electrode was performed through amide bond formation by means of condensing reagent, EDAC.<sup>15</sup> The DEP chips were supported vertically in 2 cm<sup>3</sup> of a test solution to be immersed in the circular working electrode area. The data were evaluated from the measurement of 20th CV cycle between -0.2 and 0.5 V at a scan rate of 20 mV s<sup>-1</sup>. Electrical current density (mA cm<sup>-2</sup>) was calculated by normalizing electrical current (mA) on the working area  $(3.67 \text{ mm}^2)$  of the SPCG electrode.

#### 3. Results and discussion

## **3.1** Fabrication of Pt nanoparticles protected by dendrimers (DENPtNPs)

DENPtNPs were prepared at five different molar ratios of  $Na_2PtCl_6$  to amine terminal group of PAMAM dendrimer (M:D = 0.1:1, 0.2:1, 0.3:1, 0.4:1 and 0.5:1 at the constant dendrimer concentration (0.2 wt%)), and their TEM images are shown in Fig. 1. Well dispersed PtNPs can be visualized at <math>M:D = 0.1:1 and 0.2:1. Their particle sizes were in the range of 2–3 nm. However, when the M:D ratios were increased from 0.3:1 to 0.5:1, aggregation and precipitation of DENPtNPs in the solution were observed after undergoing the reduction reaction for one day. This is due to the reason that the concentration of the PAMAM dendrimer is not high enough to protect and stabilize the DENPtNPs in the solution. This result is comparable to the effect of dendrimer content on the size of Au nanoparticles.<sup>14</sup>

The electron diffraction pattern of DENPtNPs at the M:D ratio of 0.2:1 showed a series of spots, as seen in Fig. 1(A). The spots provide the direct evidence that PtNPs in DENPtNPs are crystalline, and then the calculated lattice constant is 3.92 Å, confirming a face-centered cubic (FCC) crystal structure.<sup>16</sup> Fig. 2 shows HR-TEM images of DENPtNPs at M:D = 0.2:1. PtNPs had an average size of 2–3 nm. In addition, each PtNP revealed a crystal array pattern, where the spacing between each array was 2.68 Å and the lattice constant calculated from the spacing between arrays was 3.79 Å. This value is consistent with the value calculated from the electron diffraction pattern described above.



**Fig. 1** TEM images and an electron diffraction pattern of (A) DENPtNPs and (B) CNT/DENPtNPs at different M : D ratios.

AFM has been widely used to investigate the morphology of nanoparticles deposited onto flat surfaces.<sup>17–19</sup> Supporting Information Fig. SI-1† shows AFM topographic images of PAMAM dendrimer and DENPtNPs at M: D = 0.1: 1-0.5: 1 (0.2:1 and 0.4:1 are not included). A typical image of PAMAM dendrimer reveals that a lot of small dendrimer



Fig. 2 An HR-TEM image of DENPtNPs at M: D = 0.2:1.

molecules deposited onto the mica surface. It can also be observed that DENPtNPs at M:D ratios = 0.1:1 and 0.2:1 appeared to be substantially uniform in size and well dispersed on the mica surface. However, large irregular aggregates of DENPtNPs at M:D ratios = 0.3:1 and above were observed and the aggregation of DENPtNPs increased with the M:Dratio. These observations are consistent with the TEM results described above.

In UV-VIS absorption spectra (Fig. SI-2(a)<sup> $\dagger$ </sup>), free PtCl<sub>6</sub><sup>2-</sup> ions revealed two strong absorption bands at 201 and 261 nm. After the PtCl<sub>6</sub><sup>2-</sup> ion was added into the PAMAM dendrimer solution, these absorption bands disappeared. Meanwhile an absorption band around 216 nm arose as a shoulder on an UV absorption band (below 200 nm) of the dendrimer and increased in its absorbance as the amount of  $PtCl_6^{2-}$  increased. This shoulder band corresponds to a charge transfer associated with complexation of ligand  $PtCl_6^{2-}$  and PAMAM dendrimer. After the reduction, the band around 216 nm significantly decreased in absorbance as seen in Fig. SI-2(b).† Alternatively a broad and weak absorption band appeared at a longer wavelength around 250 nm and increased in its absorbance with the amount of  $PtCl_6^{2-}$  or a M : D ratio, which is characteristic of zero valent metal particles with nanoscale dimensions.<sup>20</sup> These observations confirm that PtNPs were formed.

NMR spectroscopy is one of the powerful techniques to investigate the intermolecular interactions between functional groups of dendrimers and metal ions.<sup>21,22</sup> The complexation of PAMAM dendrimer and  $PtCl_6^{2-}$  was carried out at pH 4 but the pH of the reaction solution shifted to 10 after DENPtNPs were produced. Then the <sup>1</sup>H NMR spectra of these samples in D<sub>2</sub>O were measured and compared with the spectra of PAMAM dendrimer at pH 4 and 10, as shown in Fig. 3. For a complex of PAMAM dendrimer and  $PtCl_6^{2-}$  at pH 4 (Fig. 3(b)), the triplet near 3.5 ppm is attributed to the protons of methylene groups (C/c) adjacent to amide group. The resonances from the NCH<sub>2</sub> type methylene groups (A/a and d) appeared as broad triplets near 3.35 and 3.6 ppm, respectively. A broad triplet at 3.1 ppm is assigned to the protons of methylene group (D) adjacent to the terminal NH<sub>2</sub>. The remaining broad triplet near 2.8 ppm is attributed to methylene groups (B/b)



**Fig. 3** <sup>1</sup>H NMR spectra of PAMAM dendrimers in  $D_2O$ : (a) PAMAM dendrimer at pH 4, (b) complex of PAMAM dendrimer with  $PtCl_6^{2-}$  at M : D = 0.2:1 and pH 4, (c) DENPtNPs at M : D = 0.2:1 and pH 10, (d) G4 PAMAM dendrimer at pH 10.

adjacent to C=O of amide group. No proton signals of protonated primary and tertiary amines appeared due to the exchange of proton with deuterium. These features of the <sup>1</sup>H NMR spectrum at pH 4 were very similar to those of the corresponding PAMAM dendrimer at an acidic condition (Fig. 3(a)),<sup>22</sup> although the slight broadening of the signals of all dendrimer protons was observed due to the influence of PtCl<sub>6</sub><sup>2-</sup> in the dendrimer cavity on the proton motion of PAMAM dendrimer. These results mean that the encapsulated PtCl<sub>6</sub><sup>2-</sup> has no strong influence to the dendrimer structure and no effective interaction except electrostatic interaction with dendrimer and the occupation of dendrimer cavity.

After the complex of PAMAM dendrimer and PtCl<sub>6</sub><sup>2-</sup> was reduced, the <sup>1</sup>H NMR spectrum (Fig. 3(c)) of DENPtNPs displayed a significant shift to lower field for all proton signals in comparison with the spectrum before the reduction.

The <sup>1</sup>H NMR spectrum of DENPtNPs is also different from PAMAM dendrimer at pH 10 (Fig. 3(d)).<sup>22</sup> In particular, the chemical shifts of A/a, B/b and C/c seem to be the superposition of sharp and broad signals. These changes in chemical shifts and the signal shapes of the <sup>1</sup>H NMR spectra indicate the restriction of proton motion in the interior or exterior of the dendrimer. These might be due to the encapsulation of PtNPs within PAMAM dendrimers, which was confirmed even by the UV-VIS absorption spectra described above.

#### 3.2 Immobilization of DENPtNPs on MWCNTs

DENPtNPs were chemically bonded to MWCNTs by means of EDAC as a condensing agent for amide bonding between carboxylic acid group on acid-treated MWCNTs and amine peripheral group on the DENPtNPs (Scheme 1). The covalent bonding of DENPtNPs on the surface of MWCNTs was confirmed by IR absorption spectroscopy, as shown in Fig. 4. Acid-treated MWCNTs exhibited IR absorption bands around 1685 and 1520 cm<sup>-1</sup> attributed to the C=O and COO<sup>-</sup> stretching vibration modes, respectively, of carboxyl group. However, the intensity of these bands significantly decreased after the immobilization reaction of DENPtNPs but, instead, the spectrum of CNT/DENPtNPs exhibited new absorption bands at 1635 and 1517 cm<sup>-1</sup> which are attributed to the amide I and amide II vibration modes, respectively, of the amide bond.<sup>3</sup> Thus these results strongly indicate the covalent immobilization of DENPtNPs on MWCNTs through the amide linkage. The immobilized hybrids are abbreviated as CNT/DENPtNPs hereafter.

The immobilization and distribution of DENPtNPs on MWCNTs were confirmed by TEM and SEM. TEM images of CNT/DENPtNPs at five different M:D ratios are shown in Fig. 1(B). It was clearly seen that PtNPs were successfully immobilized on MWCNTs. The distribution of DENPtNPs on the MWCNTs was dependent on the M:D: At M:D ratios of 0.1:1 and 0.2:1, DENPtNPs were homogeneously attached on the surface of MWCNTs. On the other hand, aggregated DENPtNPs tend to be seen, as the M:D ratio increased from 0.3:1 to 0.5:1. It is apparent from the comparison of Fig. 1(A) and (B) that such aggregates are the indigenous



MWCNT-COOH

CNT/DEN(PtNP)s

Scheme 1 Schematic representation for covalent bonding of DENPtNPs on MWCNTs.



Fig. 4 IR absorption spectra of acid-treated MWCNT and CNT/ DENPtNPs at M: D = 0.2:1.



Fig. 5 FE-SEM images of CNT/DENPtNPs at M: D = 0.1:1 and 0.4:1.

state of PtNPs but not formed during the immobilization, indicating the conservation of dispersibility of nanoparticles in solutions.

The surface morphology of CNT/DENPtNPs were observed by FE-SEM, as representatively presented in Fig. 5. The hybrid at M:D = 0.1:1 (and 0.2:1) displayed a rather smooth surface, while a smaller amount of PtNPs was homogeneously immobilized on the surface of MWCNTs as seen in Fig. 1(B). Meanwhile, the surface of CNT/DENPtNPs at M:D = 0.4:1(also 0.3:1 and 0.5:1) was relatively rough, and PtNPs seemed rather localized on the surface of MWCNTs in line with the TEM image in Fig. 1(B).

#### 3.3 Characterization of CNT/DENPtNPs

The thermal stability of CNT/DENPtNPs was investigated by TGA under air atmosphere. Fig. 6(a) shows the TGA results of acid-treated MWCNT and CNT/DENPtNPs. Acid-treated MWCNT was decomposed at 650 °C, but the degradation temperature of CNT/DENPtNPs decreased from 567 to 528 °C



**Fig. 6** (a) TGA results of acid-treated MWCNT and CNT/ DENPtNPs and (b) plots of degradation temperature and Pt content of CNT/DENPtNPs against M:D.

with increasing M : D from 0.1:1 to 0.5:1, as seen in Fig. 6(b). This is due to the reason that the presence of Pt nanoparticles could accelerate the degradation of MWCNTs so as to occur at the lower temperature in comparison with the MWCNT without PtNPs.<sup>23</sup> It has been reported that there is a lowering of the thermal stability of MWCNTs due to the presence of TiO<sub>2</sub>, which catalyzes carbon gasification and lowers the temperature of the maximum gasification occurring.<sup>24</sup>

The Pt content in CNT/DENPtNPs was also evaluated from TGA results as shown in Fig. 6(b). The wt% of PtNPs bound on MWCNT can be calculated as differential weight loss between MWCNTs and CNT/DENPtNPs at 800 °C, where MWCNTs are completely burned. It was found that the Pt content increased up to 10.2 wt% with M:D ratio.

UV-VIS-NIR spectroscopy is a powerful tool for probing the electron transfer within SWCNTs,<sup>25,26</sup> since optical absorption bands in the UV-VIS-NIR spectral regions are attributed to electronic transitions between valence and conduction bands. Thus the change in the electronic structure of the modified SWCNTs has been studied through the UV-VIS-NIR absorption spectra.<sup>27-29</sup> Moreover, the interaction between metal nanoparticles and single-walled carbon nanotubes (SWCNTs) has been investigated using UV-VIS-NIR absorption spectroscopy.<sup>26,30</sup> Meanwhile, the dispersion of the photochemically treated MWCNTs has been studied in the UV-VIS-NIR region (200-1400 nm).<sup>31</sup> The very weak absorption bands corresponding to van Hove singularities were observed around 1000-1400 nm. It was suggested that these absorption bands come from the semiconducting innermost tubes of MWCNTs but not from isolated SWCNTs. However, very few papers



**Fig. 7** UV-VIS-NIR absorption spectra of acid-treated MWCNTs, CNT/DEN and CNT/DENPtNPs at different M : D. Inset indicates a plot of absorbance ratio of a 2083 nm band *vs.* a 263 nm band.

have reported the electronic structure of the MWCNTs in the absence and presence of metal nanoparticles in the NIR region above 1400 nm.

In the present work, the interaction between DENPtNPs and MWCNTs was investigated in the UV-VIS-NIR region of 200–2200 nm. As seen in Fig. 7, absorption spectra of acid-treated MWCNTs, CNT/DEN and CNT/DENPtNPs displayed a strong absorption band at 263 nm, which comes from the surface  $\pi$  plasmon of carbon nanotubes.<sup>25,32</sup> In addition, absorption spectra of MWCNTs revealed a very weak absorption band around 2083 nm, which is slightly intensified after dendrimers were immobilized and significantly increased in intensity with M : D after DENPtNPs were attached: The intensity ratio of a 2083 nm band *vs.* a 263 nm band increased with M : D, as seen in Fig. 7(inset).

It has been reported that the magnitude of the  $S_{11}$  band (around 1900 nm) in the UV-VIS-NIR absorption spectra varied with addition of electrons to or removal of electrons from the semiconducting SWCNTs.<sup>26</sup> Thus, in the present work, the appearance of the absorption band around 2083 nm might come from the semiconducting component of MWCNTs, since the change in the intensity of this band was observed after dendrimers and PtNPs were attached on the MWCNTs. In addition, the increase in the intensity of this band could be due to the charge transfer from PAMAM dendrimers and PtNPs to MWCNTs, that is, exactly to the semiconducting innermost tubes of MWCNTs, although little is actually known about the electronic structure of the MWCNTs in the UV-VIS-NIR region of 1500–2200 nm.

Raman spectroscopy is a valuable tool for structural characterization that has been used to evaluate the functionalization of carbon nanotubes.<sup>28,33</sup> The chemical treatment on carbon nanotubes disrupts the continuous delocalization of electrons along the graphene sheet of carbon nanotubes, which is observed through the change in the position and intensity of Raman bands.<sup>34</sup> Fig. 8 shows Raman spectra of acid-treated MWCNT and CNT/DENPtNPs at an excitation wavelength of 785 nm. Raman D, G and D' bands<sup>9,35</sup> were observed in common at 1317, 1583 and 1613 cm<sup>-1</sup>, respectively. The D and G bands correspond to sp<sup>3</sup> and sp<sup>2</sup> carbon stretching modes, respectively, and the D' band is also attributed to an sp<sup>3</sup> carbon mode but observed only in the MWCNTs.<sup>36,37</sup>

Since G and D' bands are overlapping, these bands can be deconvoluted into two component bands as shown in Fig. SI-3. $\dagger$ 



Fig. 8 Raman spectra of acid-treated MWCNT and CNT/DENPtNPs at different M:D.

Fig. 9 shows the relation of Raman shift, band intensity and intensity ratio of the deconvoluted bands to M: D. Raman D, D' and G bands of CNT/DENPtNPs slightly shifted the lower wavenumber with M:D, as seen in Fig. 9(a). It has been reported that the effect of charge transfer appears in the Raman G band through downshift of the phonon frequency of G band, when the chemical species interacting with MWCNTs are donors, and vice versa.<sup>30</sup> In addition, the interaction of carbon nanotubes with electron-donating molecules such as aniline causes the downshift of the G band which contributes to charge transfer from aniline to carbon nanotubes.<sup>38-40</sup> However, the attachment of metal nanoparticles on carbon nanotubes also causes the change in the position and intensity of Raman G band due to the disturbance of the electronic properties of carbon nanotubes.<sup>26</sup> Therefore, the downshift of Raman bands of CNT/DENPtNPs could be attributed to electron transfer from electron-donating PAMAM dendrimer and also PtNPs to MWNCTs.

The intensity of D and D' bands significantly increased with M: D (Fig. 9(b)). This increase is attributed to the formation of sp<sup>3</sup> carbon after the functionalization by DENPtNPs on MWCNTs. It has been found that the selective electrodeposition of Ag nanoparticles on highly oriented pyrolytic graphite (HOPG) edges results in a selective enhancement of the defect modes of the graphite surface, leading to an intensity increase in the Raman D band.<sup>41</sup> It has also been reported that the increase in intensities of D and G bands for dendrimer-modified MWCNTs is due to the high degree of covalent functionalization of the dendrimer on the MWCNTs.<sup>38</sup> However, in the present case the intensity of the G band did not change with M:D (Fig. 9(b)). These results suggest that the immobilization of DENPtNPs induced structural defects on MWCNTs, thus giving rise to selective defect-induced enhancement effects on Raman D and D' bands.

The intensity ratios  $(I_D/I_G \text{ and } I_{D'}/I_G)$  of D and G bands and D' and G bands provide information about the degree of structural defect on the carbon nanotubes: The higher the  $I_D/I_G$  and  $I_{D'}/I_G$  ratios, the larger the degree of defect.<sup>42,43</sup> It has been reported that the increase in intensity ratio  $(I_D/I_G)$ is due to the increased amount of dendrimer functionalized on MWCNTs.<sup>37</sup> The intensity ratios  $(I_D/I_G \text{ and } I_{D'}/I_G)$  of D, G and D' bands of CNT/DENPtNPs were plotted as the function



**Fig. 9** (a) Raman shift of D, D' and G bands, (b) band intensity and (c) intensity ratio  $(I_D/I_G \text{ and } I_D'/I_G)$  of CNT/DENPtNPs as a function of M : D.

of M:D in Fig. 9(c). The  $I_D/I_G$  and  $I_{D'}/I_G$  ratios increased with M:D. Thus, it can be inferred that these increases are attributed to more defects owing to the larger degree of functionalization by DENPtNPs on MWCNTs.

The CNT/DENPtNPs-loaded SAM-SPCG electrode was prepared as described in the experimental section and supplied for the CV measurement which was carried out in a buffer solution of ferricyanide as a redox probe to investigate the electrochemical reactivity of the modified electrode.<sup>44,45</sup> CVs of bare SPCG, SAM-SPCG and CNT/DENPtNPs-loaded (at M:D = 0.2:1) SAM-SPCG electrodes in a 1.0 mM phosphate buffer (pH 7.4) solution of K<sub>4</sub>Fe(CN)<sub>6</sub> are shown in Fig. 10. Durability of the electrode could be evaluated from the measurement of 20 CV cycles: The CNT/DENPtNPs still retained their chemical immobilization on the SAM-SPCG electrode surface. These observations suggest that PAMAM



Fig. 10 Cyclic voltammograms of SPCG electrodes in a phosphate buffer solution (pH 7.4) of  $K_4$ Fe(CN)<sub>6</sub> (1.0 mM). (—) bare SPCG, (···) SAM-SPCG, (···) CNT/DENPtNPs-loaded (at M:D = 0.2:1) SAM-SPCG.

dendrimers in CNT/DENPtNPs act as strong chemical binders on the SAM-SPCG electrode surfaces. Three electrodes exhibited a pair of well-defined redox peaks, which was expected to be due to the electron transfer process of these electrodes, indicating a reversible process by  $[Fe(CN)_6]^{4-}$  in a solution phase.<sup>46</sup> However, potentials and current densities of redox peaks were different to each other between the electrodes. The potential interval  $\Delta Ep$ between anodic and cathodic peaks in an electrochemically reversible reaction relates to an electron transfer rate on the electrode, *i.e.*, the difference between potentials, *Epa* and *Epc*, of anodic and cathodic peaks.<sup>46</sup> The peak-to-peak intervals were about 143, 248 and 79 mV for bare SPCG, SAM-SPCG and CNT/DENPtNPs-loaded SAM-SPCG electrodes, respectively.

The SAM-SPCG electrode had a larger peak-to-peak interval and slightly lower current densities at redox peaks than the bare SPCG electrode, indicating that the MBA SAM acts as an insulating layer to effectively block the electron transfer between the redox species and the electrode surface.<sup>46–48</sup> Once CNT/ DENPtNPs were fabricated on the SAM-SPCG electrode, the potential interval significantly reduced to 79 mV and the current density obviously increased as compared with bare SPCG and SAM-SPCG electrodes. The SAM-modified Au electrode, on which the reduced graphene nanosheet film (GNF) was fabricated, revealed a pair of well-defined redox peaks with small potential interval (73 mV at 50 mV  $sec^{-1}$ ).<sup>46</sup> The present observation suggests a fast electron transfer process for  $[Fe(CN)_6]^{4-}$  on the CNT/DENPtNPs-loaded SAM-SPCG electrode as well as on the GNF/SAM Au electrode.

The shortening of the peak-to-peak interval and the enhancement of the redox current can be due to the promotion of the electron transfer between the redox species and the electrode loading CNT/DENPtNPs as electron transfer stations, where the large  $\pi$ -conjugated system within MWCNTs can behave as both an electron acceptor and an electron donor and the positive charges within PAMAM dendrimers can exert their uptake ability of negatively charged [Fe(CN)<sub>6</sub>]<sup>4-</sup> ions during redox process. Meanwhile, PtNPs in CNT/DENPtNPs can also help out to increase the electron transfer ability on the electrode surface<sup>49</sup> in addition to the electron transfer property of carbon nanotubes.<sup>48,50</sup> It can be inferred that each component in

CNT/DENPtNPs contributes to the promotion of the electron transfer between the redox ferricyanide solution and the modified electrode surface. Therefore, the electron transfer on the present electrode might proceed via two steps, the first between SPCG electrode and CNT/DENPtNPs and the second between CNT/DENPtNPs and redox species in the solution phase.

#### 4. Conclusions

DENPtNPs were synthesized by reduction of Pt precursor in the presence of a stabilizer, PAMAM dendrimer, and immobilized by chemical bonding on the surface of MWCNTs. On the surface of MWCNTs, DENPtNPs are homogeneously distributed at M:D = 0.1:1 and 0.2:1, but they tend to aggregate as the M:D ratio increases from 0.3:1 to 0.5:1. These behaviors reflect the dispersion characteristics of DENPtNPs themselves in solution. As the amount of Pt increases, the content of the PAMAM dendrimer becomes hardly adequate to stabilize the PtNPs, leading to the aggregation of DENPtNPs in the solution and on the surface of MWCNTs, as observed from TEM.

Hybridization is sometimes accomplished by noncovalent bonds such as hydrogen bonds, electrostatic interactions, coordination bonds and  $\pi-\pi$  stacking. However, hybrids constructed by noncovalent bonds might be affected by external conditions like temperature, pH and additives, and the attraction between component materials might be released from such hybrids, depending on a variation of conditions. Therefore, the hybridization of PtNPs on MWCNTs was performed using chemical (covalent) bond by mediation of dendrimer. Regardless of slight aggregation at high M:D, it should be noticed that the present procedure, that is, the chemical immobilization of pre-prepared DENPtNPs on MWCNTs, can offer preferable nanohybrid materials loading very stable and homogeneously distributed metal nanoparticles on the CNTs. The amount of Pt nanoparticles on MWCNTs seems rather low in the present work, since CNT/DENPtNPs were synthesized at only one ratio of MWCNTs with dendrimer. The increase in the amount of Pt nanoparticles on MWCNTs is possible by increasing the amount of DENPtNPs loading on CNTs. Otherwise, nitrogen-doping in CNTs before loading DENPtNPs should also be effective.<sup>51</sup>

The immobilization of DENPtNPs affects the thermal stability of MWCNTs, as the decomposition of CNT/DENPtNPs occur at the lower temperature owing to the catalytic effect of PtNPs. Although Pt content in CNT/DENPtNPs increases depending on M:D, the existence of DENPtNPs on MWCNTs has an effect on the electronic and chemical structures of the MWCNTs as observed from UV-VIS-NIR and Raman spectroscopy. The intensity of the absorption band around 2083 nm in the NIR region increases with M:D, and the positions of D, D' and G bands in Raman spectra shift to lower wavelengths. These phenomena are caused by the electron transfer from PAMAM dendrimers and/or Pt nanoparticles to MWCNTs. Meanwhile, the structural defect on the MWCNTs can be estimated from the increase in the intensity of D and D' bands or the intensity ratio  $(I_D/I_G \text{ and } I_{D'}/I_G)$  with M : D, since these values provide the information about the degree of defect of ordered structure on carbon nanotubes. Further characterization was carried

out for the potential applications of CNT/DENPtNPs for electrochemical sensing, after CNT/DENPtNPs were mounted on the working electrode. Carbon nanotubes enlarge the surface area of the working electrode and promote the electron transfer properties. PtNPs can also intensify the electron transfer ability in addition to catalytic performance, and dendrimers play a role in the uptake of the redox agent as well as the binder functionality. Thus, the CNT/DENPtNP-loaded electrode possesses high durability and reactivity.

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