X-ray Absorption Improvement of Single Wall Carbon Nanotube through Gadolinium Encapsulation

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Abstract. X-ray absorption improvement of single-wall carbon nanotube (SWCNT) through gadolinium (Gd) encapsulation has been studied. The liquid phase adsorption using ethanol has been performed for the doping treatment. The Gd-doped SWCNT (Gd@SWCNT) was characterized by nitrogen adsorption isotherms, Raman spectroscopy, Transmission electron microscopy (TEM), and thermal gravimetric analysis (TGA) techniques. A relatively high residual weight of Gd@SWCNT compared to non-doped SWCNT (n-SWCNT) indicated that Gd has been doped in the nanotube. Even though Gd nanoparticles could not be observed clearly by TEM image, however, a significant decrease of nitrogen uptakes at low pressure and RBM (Radial Breathing Mode) upshift of Raman spectra of Gd@SWCNT specimen suggest that the metal nanoparticles might be encapsulated in the internal tube spaces of the nanotube. It was found that Gd-doped in the SWCNT increased significantly mass attenuation coefficient of the nanotube.

1. Introduction

As the shortwave electromagnetic, X-rays having wave number ranging from 10\textsuperscript{-11} to 10\textsuperscript{-8} m not only provides benefits to human life but also give potential hazards such as cell mutation, chromosome damage, cancer, etc. Extensive studies have been carried out by many researchers\cite{1-5} for generating materials which are able to project electromagnetic radiation. For instances, sheet lead, concrete, and aluminum-foam have been produced for protecting against electromagnetic radiation. Generally, those materials are applied in such as reactor zone corresponding to electromagnetic radiation to overcome the radiation effect on human body. It is also possible to fabricate electromagnetic radiation protective materials which directly protect the human body from the radiation source such as clothes, gloves, shoes, etc.

Single-wall carbon nanotubes (SWCNTs) are projected to be one of the most promising candidate of the materials due to nanometric dimension, distinctive structure, extraordinary physical properties such as many-fold stronger than steel, harder than diamond, very lightweight, electrical conductivity higher than copper, thermal conductivity higher diamond and also it can easily be formed in bucky paper. Thus, SWCNT can be applied to generate new sustainable technology\cite{6} such as application as transistors and fuel cells\cite{7}, as well as for medical sciences\cite{8}. 

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Great efforts have been carried out by many researchers [9-12] for modifying structure of SWCNT in order to be applied in a wide variety of fields. Structural modification of SWCNT can be achieved through two ways, i.e., surface space [9] and internal tube space modifications [10-12].

Regarding the structural modification of carbon nanotubes (CNTs), it has been reported that the modified CNTs have been applied for electromagnetic shielding, particularly at high frequencies ranging in the GHz. In various types of CNT composites have been fabricated by mixing the tubes with metal powders [5]. These studies showed that CNTs could exhibit novel and outstanding electromagnetic effects [13]. It is noted that SWCNT has cylindrical nanotubules that can be nested, and the interaction of radiation with these nanotubules appears to be very different when compared to their interaction with planar or stacked graphene sheets [14]. Interestingly, Fujimori et al. [14] found that SWCNT possesses high shielding of X-ray radiation even higher than highly oriented pyrolytic graphite (HOPG). It is believed that the X-ray mass absorption coefficient does not depend on the nanostructure but on the component atoms. However, Fujikawa and Kaneko [15] theoretically showed that the established rule of X-ray absorption is valid within the approximation of the dipole moment transition and the higher order momentum transition depends on nanoscale structure. Hence, we need to continue fundamental studies on well-characterized nanocarbon. In this context, we studied improvement of X-ray absorption of SWCNT through gadolinium encapsulation. So far, improvement of X-ray absorption property of SWCNT through gadolinium encapsulation has never been studied.

In the case of X-ray absorption of gadolinium, experimental data exhibited that the metal has a specific mass absorption coefficient of 64.4 cm$^2$g$^{-1}$ using a monochromatic incident beam of Mo Kα [16]. Therefore, X-ray absorption of SWCNT which has a mass absorption coefficient of 0.515 cm$^2$g$^{-1}$ [17] is expected to increase significantly through the metal encapsulation method.

2. Method

2.1. Chemicals
Gd(NO$_3$)$_3$.6H$_2$O (99.9 at%), HNO$_3$ (60 wt%) HCl (36 wt%) and ethanol (99.5 wt%) were purchased from the Wako Chemical Co. The SWCNT synthesized by the arc-discharge method using 1.03 wt% of nickel and 0.26 wt% of yttrium was produced by Meijo-SO Co.Ltd.

2.2. Opening end cap and purifying of the SWCNT
Methods to open end cap and purify the SWCNT referred to our previous work [17]. Briefly, the SWCNT samples were thermally oxidized by air in order to obtain opened-end samples. The opened-end SWCNT was then chemically purified using sequential acid treatment technique. The sample denoted as $n$-SWCNT.

2.3. Doping of Gd(NO$_3$)$_3$.6H$_2$O solution into the SWCNT
Doping technique of Gd(NO$_3$)$_3$.6H$_2$O solution into the SWCNT has been conducted with the same as a doping technique of gold solution as published in our previous work [17]. Before the $n$-SWCNT was doped by gadolinium solution, the nanotube was evacuated at room temperature under 0.1 Pa for 24 h. The evacuated SWCNT of 5 mg was dipped in Gd(NO$_3$)$_3$.6H$_2$O solution of 10 ppm containing 99.5 wt% ethanol and dispersed ultrasonically by a 28 kHz ultrasound apparatus for 48 h at 298 K. It was then filtered through a Millipore porous filter (0.45 μm), rinsed with ethanol to 200 ml and dried at 383 K for 24 h. The obtained samples are denoted as Gd@SWCNT.

2.4. Characterization of non-doped SWCNT and Gd@SWCNT
Thermal gravimetric, as well as differential thermal analysis, were performed on TGA/DTA apparatus, RIGAKU Thermo plus TG 8120 under O$_2$-N$_2$ atmosphere. The gas flow and heating rates were 300 mL min$^{-1}$ and 3 K min$^{-1}$, respectively. The Raman spectrophotometer (RAMAN Renishaw in via Raman microscope) equipped with a red laser (energy 1.58 eV, wavelength 785 nm) was used. In order to obtain good reproducibility, samples were exposed for 3 min with triple accumulation and
spectra were taken at different places on the surface of each sample. Nanopore structure change of the samples preheated at 423 K, and $10^{-4}$ Pa for 2 h was determined by nitrogen adsorption at 77 K using a volumetric apparatus, Quantachrome-Autosorb-iQ2-MP.

2.5. X-ray absorption measurement
The samples were compressed by pelletizer at 10 MPa for 15 min in order to form a disc (tube-like shape) of 5 mm in diameter. Volumes of the samples (tube-like) were calculated by means tube volume formulation so that apparent densities of the compressed samples were obtained. The specimen densities of non-doped SWCNT and Gd@SWCNT were 1.03 and 0.97 g cm$^{-3}$, respectively. In the present work, measurement technique of X-ray absorption of the samples referred to work of Fujimori et al.[14] and our previous work [17].

3. Results and discussion

3.1 The effect of gadolinium encapsulation on the pore structure of the nanotube
The pore structure of the nanotube was examined by nitrogen adsorption isotherms. Nitrogen adsorption isotherms of gadolinium encapsulated SWCNT (Gd@SWCNT) and non-encapsulated SWCNT ($n$-SWCNT) at 77 K are presented in figures 1.

![Figure 1](image_url)

**Figure 1.** Linear (a) and logarithmic (b) plots of nitrogen adsorption isotherms at 77 K of the $n$-SWCNT (open circles)[17], and Gd@SWCNT (closed circles).

It can be seen that the metal doping remarkably decreases the nitrogen adsorption amount of about 75% at entire pressure range as shown in figure 1(a). It suggests that the metal was encapsulated in the internal tube space of the nanotube [18,19]. The nitrogen adsorption uptake at low pressure is associated with the internal tube space of the nanotube [18,19]. Thus, the small amounts of nitrogen adsorption uptake of Gd@SWCNT at low pressure as shown in figure 1(b) reveals supporting information that the internal tube spaces are filled with the metal particles.

The pore structural parameters of Gd@SWCNT and $n$-SWCNT are summarized in Table 1.

![Table 1](table_url)
as well as smaller surface area of the Gd@SWCNT suggest that the metal has successfully been encapsulated in the internal tube space of the nanotube [18,19].

Table 1. The pore structural parameters of Gd@SWCNT and n-SWCNT.

| Samples       | surface area (m²/g) | Micropore Volume (cm³/g) |
|---------------|---------------------|--------------------------|
| n-SWCNT       | 19.3±0.1³           | Natural                  |
| Gd@SWCNT      | 3.8±0.8³            | 99% enriched             |

The evidence of the metallic particles encapsulated in the internal wall of the nanotubes could also be confirmed by the relatively significant upshifts of the radial breathing mode (RBM) of Raman spectra. The Raman spectroscopy of n-SWCNT and Gd@SWCNT, in particular, RBMs are exhibited in figure 2. A detailed analysis of the RBM which usually appears at around 100-300 cm⁻¹ region reveals the information about encapsulation of metals into SWCNT in particular for determining the SWCNT diameter [20]. It is well-known that the RBM frequency of SWCNT is sensitive to chemical and physical factors as well as the tube diameter of the SWCNT. The relationship between RBM frequency and diameter of the nanotube is given in following equation (1) [20],

\[ \omega_{\text{RBM}} \ (\text{cm}^{-1}) = \frac{A}{i t} \ (\text{nm cm}^{-1}), \]  

where the \( A \) is constant of 248 cm⁻¹.

![Raman Spectra](image)

**Figure 2.** The RBMs of n-SWCNT (a)[17], and Gd@SWCNT (b) using laser energy of 1.58 eV.

Figure 2 indicates that the RBM peak-SWCNT appeared at 154 cm⁻¹ corresponds to the tubes diameter of 1.61 nm. After encapsulation treatment, the peaks slightly shift to a higher frequency that is observed at 157 cm⁻¹. This peak deals with the tube diameters of 1.58 nm.

The origin of this shifting might also be attributed either to an increase of C–C binding energy due to the charge transfer from the nanotube to the metals [10]. Besides, it is possible that the upshifts originate from van der Waals bond as a result of van der Waals interaction between non-hybridized \( p \) orbitals of carbon atoms in the nanotube and \( d \) orbitals of the metal as illustrated in Figure 3. If it is assumed that the non-hybridized \( p \) orbitals are \( p_z \) and that the \( d \) orbitals are \( d_z \) which each those
orbitals are occupied by an electron, they are then possible to interact each other through van der Waals attraction. The interaction might be lead to an increase of total binding energy of the nanotube. Consequently, the RBM frequencies of the nanotube went up after doping treatment due to an increase of the binding energy. Owing to the tube diameter is inversely proportional to $\omega_{\text{RBM}}$, it is reasonable. Therefore, the upshift of RBM frequency suggests that gadolinium particles have successfully been encapsulated in the internal tube spaces of the nanotube.

In addition, the metal doping shifted RBM of the nanotube to higher frequencies which point out hardening of RBM mode of carbon atoms in semiconducting nanotube[10]. The hardening is caused by the perturbation of radial flexibility of aromatic rings in the nanotube structure that leads to shrinking diameter of the tube[21]. This also implies that the metals have been encapsulated in the internal wall of the nanotube.

Figure 3. An illustration of interaction between the non-hybridized $p_z$ orbitals of carbon atoms in the nanotube and $d_z$ orbital of metals giving van der Waals interaction. Each the orbitals are occupied by an electron. CNT is the carbon nanotube which is represented by a benzene ring and M is the encapsulated metal.

Figure 4(a) and (b) show the TEM images of $n$-SWCNT and Gd@SWCNT, respectively. The SWCNT possess a well-ordered and strong bundle structure. Since the SWCNT has strong bundle structure, Gd nanoparticles encapsulated inside SWCNT could be observed clearly.

3.2. Mass attenuation coefficient of Gd-doped SWCNT
The X-ray absorption coefficients ($\mu$) of $n$-SWCNT (a) and Gd@SWCNT samples were determined from the Beer-Lambert law using monochromatic X-ray beam MoK$_\alpha$.

$$ \frac{I_o}{I} = e^{(\mu/\rho) t} \quad (2) $$

Figure 4. TEM images of $n$-SWCNT (a), and Gd-SWCNT (b)
Here $\rho$ and $t$ are the density of the material and the thickness of the specimen for X-ray penetration, respectively. The $(\mu/\rho)$ is the X-ray mass attenuation coefficient. The specimen density was used as the material density. The specimen for X-ray absorption experiment was prepared by compression of powdered the nanotube samples under 10 MPa for 15 min forming a disc. The specimen densities of $n$-SWCNT and Gd@SWCNT were 1.03, and 1.05 gcm$^{-3}$, respectively as shown in table 3. The observed $(\mu/\rho)$ of $n$-SWCNT and Gd@SWCNT were 0.518 and, 1.548 cm$^{-2}$g$^{-1}$, respectively (Table 3).

Owing to the Gd@SWCNT contains the metallic dopant and also the catalyst remains, it is necessary to take into account those compartments for evaluating mass attenuation coefficient of the nanotube after doping treatment. The $(\mu/\rho)$ of the mixed solid consisting of bi-components i and j can be expressed by the linear relation between the X-ray mass attenuation coefficients of the components i and j together with component fraction of $C_i$ and $C_j$ as described in equation (3), when the X-ray absorption property of the mixed solid follow the established law derived from dipole transition approximation.

$$(\mu/\rho) = (\mu/\rho)iC_i + (\mu/\rho)jC_j$$

(3)

If we have data on $C_i$ and $C_j$, $(\mu/\rho)$ can be calculated using the established $(\mu/\rho)$ values of the atoms components. In a similar case, this relation can be extended to a multicomponent-mixed solid by the introduction of the fraction of each component.

The metallic catalyst remained in the SWCNT and the metal particles doped in nanotube were quantitatively evaluated by thermal gravimetric analysis (TGA) while differential thermal analysis (DTA) was qualitatively used for predicting of metal oxides species, as SWCNT was synthesized using 1.03 wt % of nickel and 0.26 wt % of yttrium catalysts [22]. The residual weight after burning of the SWCNT sample provides the fraction of the components. Figure 5 shows TGA as well as DTA profiles of the $n$-SWCNT and Gd@SWCNT under the flow of air of 350 mL/min at 3K/min. The weight losses which appear at around 600 K should correspond to oxidation of carbonaceous. The sharp weight losses of $n$-SWCNT and Gd@SWCNT commencing at approximately 850 K stem from the oxidation of carbon materials. The weight losses of the samples become constant above 1100 K, giving the total weight of the metallic impurities. The residual weights of those specimens are summarized in Table 2. It is reasonable that when metal is oxidized with air (mixing of O$_2$/N$_2$), the metal oxides could be produced. Therefore, the residual weight of $n$-SWCNT should correspond to NiO and Y$_2$O$_3$ originated from the catalyst remains. Moreover, in the case of the Gd@SWCNT, the residual weight could stem from Gd$_2$O$_3$. Thus, the X-ray mass attenuation coefficient of Gd-doped SWCNT can be calculated by using the residual amount of Gd of 1.2 wt %.
Table 2. The residual weights of SWCNT before and after doping treatment

| Specimens      | Residual weights (wt %) |
|----------------|-------------------------|
| n-SWCNT        | 0.57\textsuperscript{[17]} |
| Gd@SWCNT       | 1.20                     |

Table 3. Mass attenuation coefficients (μ/ρ) and densities of the n-SWCNT and Gd@SWCNT

| Samples        | Density (g/cm\(^3\)) | Observed (cm\(^2\)/g) | Calculated (cm\(^2\)/g) |
|----------------|-----------------------|------------------------|--------------------------|
| n-SWCNT        | 1.03                  | 0.518                  | 0.515\textsuperscript{[17]} |
| Gd@SWCNT       | 1.05                  | 1.546                  | 1.20                     |

Table 3 compares the observed (μ/ρ) with the calculated one. The observed (μ/ρ) value of n-SWCNT of 0.518 cm\(^2\)/g, which are relatively close to (μ/ρ) of highly oriented pyrolytic graphite of 0.576 ± 0.005 cm\(^2\)/g\textsuperscript{[16]} is slightly higher than the calculated value. The (μ/ρ) observed value of Gd@SWCNT was approximately 1.3 times larger than the calculated (μ/ρ) derived from the sample dipole-moment transition approximation. Probably, the large observed value of metal-doped SWCNT stems from contributions of both nucleus charges of metal dopants and the remained catalyst in the nanotube. It is likely due to high nucleus charge of the dopants so that (μ/ρ) value of SWCNT increased after doping treatment.

The relatively high X-ray attenuation of the SWCNT is likely originated from the unique cylindrical nanotubules. Carbon atoms embedded in the hexagonal tubular concentric tube of different curvature, are not periodic. The exotic cylindrical of the nanotube induces a significant electron population fluctuation across the carbon tube wall\textsuperscript{[14]}. According to Grüneis et al. \textsuperscript{[23]} and Jiang et al.\textsuperscript{[24]} that such an electron fluctuation could lead to an enhanced X-ray absorption caused by an increase in the polarization factor. Accordingly, therefore, the presence of metal in the nanotube probably could enrich the electron population fluctuation in the nanotube wall, so that give the increase of X-ray attenuation.

4. Conclusions
We have demonstrated enhanced X-ray absorption property of Gd encapsulated SWCNT. We found that the mass attenuation coefficient of SWCNT increased significantly 2.3–fold due to Gd nanoparticles encapsulated in the nanotube. Production of Gd@SWCNT nano-composites would be promising and opening a new avenue for fabricating protective electromagnetic radiation materials.

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References
[1] Liu Z, Bai G, Huang Y, Ma Y, Du F, Li F, Guo T and Chen Y 2007 Carbon 45 821
[2] Ye Z, Deering WD, Krokhin A and Roberts J A 2006 J. Phys. Rev B 74 075425
[3] Yang Y, Gupta M C, Dudley K L and Lawrence R W 2005 Nano. Lett. 5 2131
[4] Higgibotham A L, Moloney P G, Waid M C, Duque J G, Kittrell C, Schmidt H K, Stephenson J, Arepalli S, Yowell L and Tour J M 2008 Compos. Sci. Tech 68 3087
[5] Wen F, Zhang F, and Liu Z 2011 J. Phys. Chem. C 115 14025
[6] Kumar M and Ando Y 2010 J. NanoSci. NanoTech 103 3739–3758
[7] Rutherford C, Jain D and Burke P 2009 Nat. Nanotech 4 811-819
[8] Hitoshi K, Katoh M, Suzuki T, Ando Yand Nadia M 2012 Biol. Pharm. Bull 35(4) 455-463
[9] Yu J G, Huang K-L, Liu, S-Q and Tang J C 2008 Physica E 40 689-692
[10] Eliseev A, Yashina LV, Brzhezinskaya MM, Chernysheva M V, Kharlamova M V, Verbitsky N I, Lukashin AV, Kiselev NA, Kuzmiksov AS, Zakalyuhin RM, Hutchison J L, Freitag B and Vinogradov A S 2010 Carbon 48 2708-2721
[11] Kobayashi K, Suenaga K, Saito T, Shinohara H and Iijima S 2010 Advanced Materials 22 3156-3160
[12] Kharlamova M V and Niu J 2012 Appl. Phys. A 109 25-29
[13] Imholt T J, Dyke C A, Hasslacher B, Perez J M, Price D W, Roberts J A, Scott A, Wadhawan J B, Ye Z and Tour J M 2003 Chem. Mater 15 3969
[14] Fujimori T, Tsuruoka S, Fujetsu B, Maruyama S, Tanioka A, Terrones M, Dresselhaus M S, Endo M and Kaneko K 2011 Mater. Express 1 (4) 273-277
[15] Fujikawa T and Kaneko K 2012 J. Electr. Spect. & Rel. Phen 185 509-511
[16] Hubbel J H and Seltzer S M 2004 NIST Standard Data Base 261 NIST Gaithersburg
[17] Alimin, Narsito, Kartini I, and Santosa S J 2015, Indonesia. J. Chem (Accepted)
[18] Ohba T, Matsumura T, Hata K, Yamura M, Iijima S, Kanoh H and Kaneko K 2007 J. Phys. Chem. C 111 15660-15663
[19] Hattori Y, Kaneko K and Ohba T 2013 Comprehensive Inorganic Chemistry II Vol 5 Oxford Elsevier p. 25-44
[20] Jorio A, Pimenta M A, Souza Filho, A G, Saito R., Dresselhaus G and Dresselhaus M S 2003 New Journal of Physics 5 139.1-139.17
[21] Gotovac S, Honda H, Hattori Y, Takahashi K, Kanoh H, Kaneko K 2007 Nano. Lett 7 (3) 583-587
[22] Al-zubaidi A, Inoue T, Matsushita T, Ishii Y, Hashimoto T and Kawasaki S 2012 J. Phys. Chem. C 116 7681-7686
[23] Grüneis A, Saito R, SamsonidzeGG, Kimura T, Pimenta M A, Jorio A, FilhoAGS, Dresselhaus G and Dresselhaus M S 2003 Phys. Rev. B 67 165402

[24] Jiang J, Saito R, Grüneis A, Dresselhaus G and Dresselhaus MS 2004 Chem. Phys. Lett. 392 383-389