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CdSe quantum dot-decorated double walled carbon nanotubes: The effect of chemical moieties

Yoong Ahm Kim,^{1,a)} Hiroyuki Muramatsu,¹ Ki Chul Park,¹ Daisuke Shimamoto,¹ Yong Chae Jung,¹ Jin Hee Kim,¹ Takuya Hayashi,¹ Yasunori Saito,¹ Morinobu Endo,¹ Mauricio Terrones,² and Mildred S. Dresselhaus³

¹*Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano-shi 380-8553, Japan*

²*Advanced Materials Department, IPICYT, Camino a la Presa San José 2055, Col. Lomas 4a. Sección, San Luis Potosí 78216, Mexico*

³*Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307, USA*

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We report that fluorine atoms on the outer tubes of double walled carbon nanotubes (DWNTs) are more effective for nucleating and growing CdSe nanoparticles than oxygen-containing functional groups. The CdSe particles with an average size of 5–7 nm grow through infiltration into an interstitial space created by four to five thin bundled DWNTs. We envisage that DWNTs will replace single and multiwalled carbon nanotubes in a wide range of applications because chemical moieties could be introduced selectively on the outer tubes while the optical and physical properties of the inner tubes remain almost unchanged. © 2008 American Institute of Physics.

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In recent years, carbon nanotubes¹ and semiconducting nanoparticles² (or quantum dots) exhibiting quantum confinement effects have been under active investigation due to both their unique physicochemical properties and their widespread potential for applications. To date, various attempts to attach quantum dots to one-dimensional carbon nanotubes [i.e., single walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs)] have been reported due to their potential applications in electronic, optical, and biomedical devices.^{3–8} In order to attach quantum dots to carbon nanotubes, the hydrophobic surface of the tube should be modified by the introduction of chemical moieties. In the case of SWNTs, the commonly used oxidative method is known to be very effective for creating specific binding sites with regard to quantum dots, while this process gives rise to a substantial deterioration in the electrical and optical properties of SWNTs through the breaking of C=C double bonds.³ Here we suggest double walled carbon nanotubes (DWNTs) as the preferable substitute for loading quantum dots: The covalently modified outer tubes of DWNTs provide effective anchoring sites, while the small-sized inner tubes below 0.9 nm preserve their excitonic transitions between van Hove singularities (vHss) in the electronic density of states after experiencing chemical treatments.

DWNTs consist of two coaxial tubes and have certain advantages over SWNTs for various specific applications due to their superior mechanical properties and structural and thermal stabilities.⁹ Moreover, we have reported on the selective functionalization of the outer tube of the DWNTs without any structural and optical changes to the inner tubes.^{10,11} In this study, we demonstrate the homogeneous decoration of nanosized CdSe quantum dots on oxidized and fluorinated DWNTs. With the aid of optical spectroscopy, we proved that homogeneously distributed fluorine atoms grafted to the outer surface of the DWNT act as nucle-

ating and anchoring sites for the small-sized and homogeneous formation of CdSe quantum dots without significant changes in the optical response of the inner tubes of the DWNT.

In this study, we have used highly pure and crystalline DWNTs, prepared by the catalytic chemical vapor deposition method and the subsequent purification process.¹² In order to introduce oxygen-containing functional groups, a high-purity DWNT sample was acid treated by refluxing in nitric acid (HNO₃, 5 mol/l) for 3 h. As an alternative to surface modification, we have carried out an attachment of fluorine atoms to the DWNT sample as follows. As a pretreatment, the tubes were heated at 200 °C under vacuum for several hours in order to remove residual oxygen gas and moisture. The DWNTs were directly fluorinated by the introduction of fluorine gas (1 atm) into the reaction chamber at 200 °C for 5 h.

Then, we have self-assembled CdSe quantum dots on the DWNTs as follows. The acid-treated or fluorinated DWNTs and an aqueous solution of cadmium acetate (0.60 mmol/l, 5 ml) were added to distilled water (10 ml). The thus-prepared nanotube emulsions were subjected to ultrasonication (24 kHz, 110 W) for 1 h. Then, the suspension was refluxed overnight to prepare Cd-loaded DWNTs. In parallel, sodium hydrogen selenide (NaHSe) was prepared for the selenation of the Cd-loaded DWNTs. Selenium powder was dispersed in distilled water by ultrasonication. Then, sodium borohydride aqueous solution (6 ml of freshly prepared 3.0 mmol/l solution), which was further diluted with water (40 ml), was added dropwise to the Se dispersion in argon, and the reaction mixture was stirred for 2 h. The resulting NaHSe solution was added dropwise to the prepared suspension of Cd-loaded DWNTs, followed by refluxing for 3 h. Then, the suspension was filtered, washed well with distilled water, and dried at 60 °C to yield a paperlike black solid.

Finally, we have carried out a systematic characterization of the CdSe-decorated oxidized and fluorinated DWNTs using a field emission scanning electron microscope (FE-SEM) (JSM6335Fs), a transmission electron microscope (TEM) (JEOL2010FEF), a Raman spectroscopy (Kaiser

^{a)} Author to whom correspondence should be addressed. Tel.: +81-26-269-5212. FAX: +81-26-269-5208. Electronic mail: yak@endomoribu.shinshu-u.ac.jp.

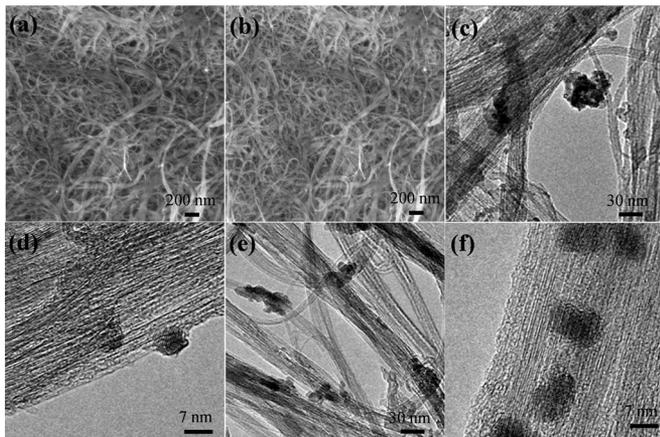


FIG. 1. FE-SEM and TEM images of CdSe-decorated [(a), (c), and (d)] oxidized and [(b), (e), and (f)] fluorinated DWNTs, respectively.

Hololab) with an excitation laser wavelength of 523 nm, an x-ray photoelectron spectroscopy (XPS) (MultiLab2000 spectrometer) with a Mg $K\alpha$ x-ray source of 1253.6 eV, and an uv-vis absorption spectroscopy (Solidspec-3700, Shimadzu).

The morphological features of decorated CdSe on the oxidized and fluorinated DWNTs were evaluated using FE-SEM and TEM observations. There is no distinctive change in the bundled features of DWNTs via chemical oxidation and fluorination [Figs. 1(a) and 1(b)]. Small-sized CdSe nanoparticles with an average size of 7 nm are attached on the outer surface of the acid-treated bundled DWNTs [Fig. 1(d)] and entrapped within the fluorinated bundled DWNTs [Fig. 1(f)]. CdSe particles are not spherical but are relatively deformed squares, indicating that they are strongly bound to DWNTs. We expect that CdSe nanoparticles grow through the infiltration of interstitial spaces created by four to five thin DWNTs. In addition, the high density of CdSe particles in the fluorinated tubes compared to that of oxidized tubes [Figs. 1(c) and 1(e)] suggests that the fluorine atoms on the outer tubes of the DWNT act as anchoring site for CdSe growth. We can expect two possible reasons for these: (a) Small and reactive fluorine gas molecules could easily penetrate into the central part of the bundled DWNT while wet-based chemical treatment leads to the partial introduction of oxygen-containing functional groups onto the outer surface of the bundled DWNT. (b) The high electronegativity of F atoms makes the fluorinated DWNTs very sensitive to chemical attack. As a result, homogeneously introduced fluorine atoms within the bundled DWNTs could provide a large density of anchoring sites for the nucleation and growth of CdSe nanoparticles.

In order to understand the effect of the infiltrated CdSe particles within the bundled DWNTs, we have measured Raman spectra at 532 nm excitation (Fig. 2). In the low frequency range, we could see the radial breathing mode (RBM) for the outer (below 200 cm^{-1}) and inner tubes (above 200 cm^{-1}) of the DWNT, which could be assigned to the E_{11}^M inner tubes and the E_{33}^S outer tubes according to the electronic transition energies for different tubes using the extended tight-binding model. The strongest mode at 1592 cm^{-1} is identified with the G^+ contribution, while the peak at 1575 cm^{-1} is the G^- feature associated with semiconducting nanotubes. No distinctive change in the Raman

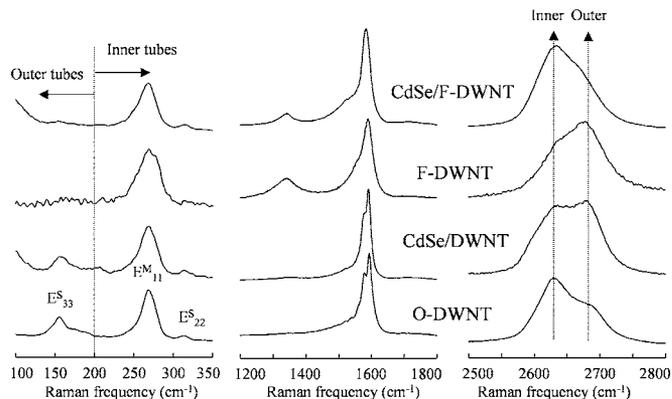


FIG. 2. Raman spectra of oxidized and fluorinated DWNTs, and CdSe-decorated DWNTs with an excitation laser wavelength of 532 nm. $E_{ii}^{S(M)}$ indicates the ν Hs transition energy between the i th levels of the semiconducting (metallic) tubes.

spectra of the acid-treated DWNTs suggests that the introduction of oxygen-containing functional groups did not cause any large variation in the structural integrity. However, F-DWNT and CdSe/F-DWNT samples exhibited a completely depressed RBM intensity at 150 cm^{-1} , an intensified D band, and substantial metallic tails for the G^- peaks since the selectively introduced fluorine atoms to the outer tube induce a depressed resonance effect in the semiconducting outer tubes¹⁰ and thus give rise to the dominant Raman spectra from the metallic inner tubes. Interestingly, we could see a distinctively changed G' band, which is the second harmonic of the disorder-induced D band,¹³ in the region of $2600\text{--}2700\text{ cm}^{-1}$. The G' band involves a scattering process consisting of the two intervalley phonons with almost opposite wavevectors. For the G' band of DWNTs, two groups^{14,15} have assigned the Raman lines at 2630 cm^{-1} to the small diameter inner tubes and the Raman line at 2677 cm^{-1} to the large diameter outer tubes based on the correlation of the frequency of the G' band and tube diameter.¹³ Very recently, Cardenas and Gromov¹⁶ suggested that a wide and splitted G' band for highly solubilized SWNT solutions is due to the simultaneous resonance of the incident and the scattered light while Kim *et al.*¹⁷ reported the intensity of the G' band on the metallicity of SWNTs. Based on the above studies, we can assume two possible factors on the reversed line shape of the G' band upon the CdSe decoration process. First, we have to consider adjacent tube-tube interactions within the bundled DWNTs because the covalently introduced chemical moieties on the outer tubes of the DWNT as well as the infiltration process of CdSe nanoparticles within the bundled DWNTs could enlarge the interstitial spacing and thus weaken the tube-tube interaction. Second, the selectively decorated CdSe particles on the outer tubes of the DWNT preferentially modify the electronic structure of the outer tube involving the metallicity of constituent tubes. As a result, two factors alter the interaction between the inner and outer tubes and finally perturb the resonance Raman scattering processes selectively.

We have carried out XPS measurements to analyze the chemical state of the CdSe particles grown within the bundled DWNTs (Fig. 3). For acid-treated DWNTs, an intense peak at 284.9 eV is assigned to the C-C 1s excitation, while the two peaks at 286.1 and 289.5 eV were assigned to -C-OH and -C=O and to COOH, respectively. However,

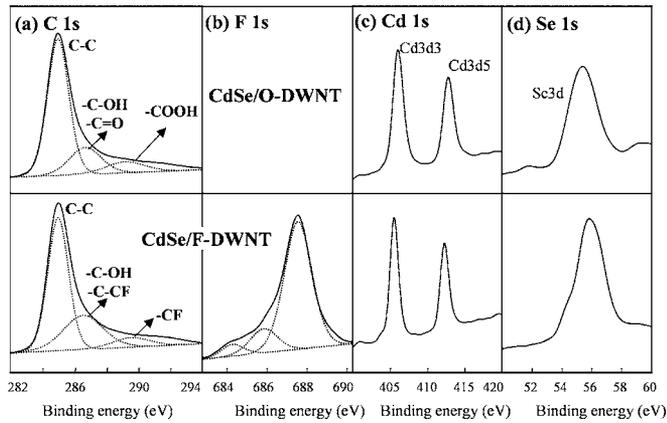


FIG. 3. (a) C 1s, (b) F 1s, (c) Cd 1s, and (d) Se 1s spectra of CdSe-decorated oxidized and fluorinated DWNTs.

fluorination induced a more intense peak at 286.1 eV due to the added amount of $-C-CF$, which is supported by the appearance of three peaks in the F 1s XPS spectra [Fig. 3(b)]. As a result, the bonding nature of fluorine in DWNTs exhibited three different types of C-F interactions. In addition, the chemically attached fluorine atoms on the DWNT sample induce a downshifted and sharper Cd 1s peak [Fig. 3(c)] and an upshifted Se 1s peak [Fig. 3(d)] because of the large screening effect of fluorine atoms, which have high electronegativity. This result also supports the observation that fluorine atoms are more effective for growing CdSe particles than oxygen-containing functional groups.

Finally, to confirm the modified electronic structure of DWNTs by their decoration with CdSe quantum dots, we have measured the UV absorption spectra for the homogeneously dispersed DWNT suspensions with the help of sodium dodecylbenzene sulfonate (Fig. 4). The high-purity DWNTs exhibited well-resolved sharp absorption peaks due to their strong excitonic transitions, thus indicating that nanotubes are individually isolated. When considering the diameter distribution of our DWNTs (inner diameter = 0.6–0.9 nm, outer diameter = 1.4–2.0 nm), the intensified peaks at 900–1300 nm could be assigned to E_{22}^S of the outer tubes and to E_{11}^S of the inner tubes. However, the broadened and weakened absorption peaks at 900–1300 nm in the CdSe-loaded oxidized and fluorinated DWNT suspensions indicate the preservation of the bundle structure, possibly

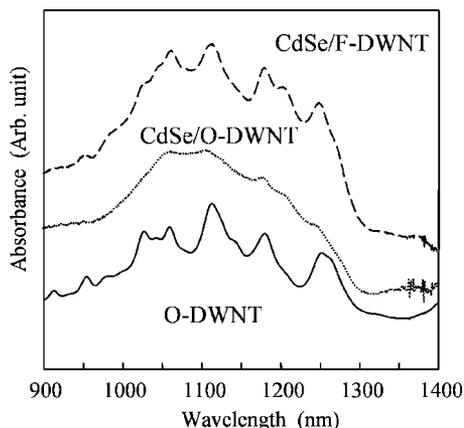


FIG. 4. UV absorption spectra of oxidized, CdSe-decorated oxidized, and fluorinated DWNTs.

due to the infiltrated CdSe particles (with an average size of 5–7 nm) within the DWNT bundle, which is well consistent with TEM observations. In other words, the self-grown CdSe nanoparticles within the DWNT bundle strongly prevent the dispersion of tubes in distilled water.

Here we have demonstrated that the chemically modified outer tubes of the DWNTs provide effective sites for CdSe nanoparticles without any altered optical properties of the inner tube. It is found that the fluorine atoms on DWNTs were more effective for anchoring and growing CdSe nanoparticles than oxygen-containing functional groups due to the weaker bonding nature of the C-F interaction. Our hybrid structure consisting of chemically modified DWNTs and nanosized CdSe quantum dots could find their use in electronic and optical devices because the inner tubes of the DWNT exhibit their intrinsic optical and physical properties after experiencing the acid-treatment, fluorination, and CdSe decoration processes.

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