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Single-Walled Carbon Nanotubes as a Molecular Heater for Thermoresponsive Polymer Gel Composite

Tsuyohiko Fujigaya and Naotoshi Nakashima
Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Japan

1. Introduction

The structural stiffness, effective optical absorption ranging from UV to IR region and efficient photothermal conversion of the carbon nanotubes (CNTs) are attractive feature as a molecular heater, which can be useful for therapy, actuator and so on. Dai et al. reported that the near-IR (NIR) irradiation to a living HeLa cell after uptaking a CNTs/DNA composite caused death of the cells (Kam, et al., 2005) due to the intense local heating triggered by the NIR irradiation. We have described that pulsed-NIR irradiation of CNTs wrapped by an anthracene-pendanted polymer allowed the dissociation of the polymer from the CNTs surface followed by aggregation of the CNTs, in which the CNTs act as a "molecular heater" that triggers removal of the polymer from the SWNT surface.(Narimatsu, et al., 2006)

On the other hand, thermoresponsive polymer gels, which show phase transitions, are of interests in wide areas of science and technology from the aspects of both fundamental (experimental and theory) and applications (Bohidar, et al., 2003). Poly(*N*-isopropylacrylamide) (PNIPAM) (Hirotsu, et al., 1987; Schild, 1992) and its derivatives are well-known thermoresponsive materials, which show a phase transition triggered by external stimuli such as the solvent composition, (Katayama, et al., 1984) pH, (Tanaka, et al., 1980) ionic strength, (Tanaka, et al., 1980) electric field (Tanaka, et al., 1982) and light. (Ishikawa, et al., 1993; Juodkazis, et al., 2000; Mamada, et al., 1990; Nayak & Lyon, 2004; Suzuki & Tanaka, 1990) Among the various light sources, NIR laser light is a fascinating stimulus especially from a biomedical point of view, because biomedical tissues have a slight absorption in the NIR region, (Weissleder, 2001) which enable remote stimulation of the NIR absorbent in the body from the outside.

The combination of CNTs with PNIPAM would expect to trigger the phase transition of PNIPAM with NIR irradiation through photothermal conversion of CNTs. In this article, we propose the utilization of single-walled carbon nanotubes (SWNTs) as a photon antenna that serves as an effective "molecular heater" around the NIR region.

2. Photoinduced phase transition of thermoresponsive gel

2.1 Preparation of the SWNTs/PNIPAM gel composite

SWNTs are hydrophobic materials with a high aspect ratio and are strongly bundled to each other, thus the dispersion of the SWNTs in organic and inorganic solvents is quite difficult to give an aggregation in the solvent as shown in Fig. 1a.(Nakashima & Fujigaya, 2007) Yodh et al.(Islam, et al., 2004) used a surfactant as a dispersant of the SWNTs in the preparation of a SWNT/PNIPAM gel in an aqueous solution, and examined liquid crystalline nature of the composite gel. However, the addition of anionic surfactants dramatically increases the transition temperatures (T_c) of the PNIPAM in an aqueous system.(Kokufuta, et al., 1993) To avoid such a problem, we introduced carboxylate groups onto the SWNTs surface by treating with strong acid to improve the dispersibility of the SWNTs in an aqueous system. The obtained acid-treated SWNTs were dispersed in deionized water with only mild shaking (Fig. 1b). The SWNT/PNIPAM composite gel preparations were carried out according to the typical procedure of PNIPAM gelation (Tanaka, 1978) in the absence of the SWNTs.

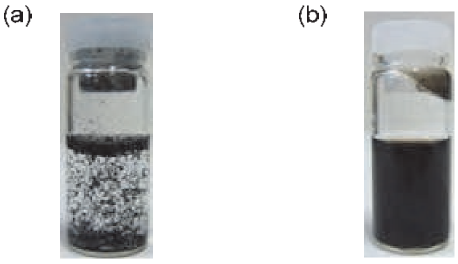

Fig. 1. SWNT dispersion solutions, (a) As-prepared SWNT dispersion in water. (b) Acid-treated SWNT dispersion in water.

The visible-NIR spectrum of the synthesized composite gel (Fig. 2a; inset) showed absorption over a wide range of the spectrum (solid line in Fig. 2a), while the gel without the SWNTs has no absorption in the visible-NIR region (dotted line in Fig. 2a). The composite gel was a transparent grey-color at temperatures below 23 °C, while upon heating in a temperature-controlled water bath, the gel changed to opaque at around 34.6 °C, suggesting that the transition temperature (T_c) of the SWNT/PNIPAM composite gel was virtually identical with that (T_c = 34.0 ˚C) of the SWNTs/PNIPAM gel (control sample). The phase transition of the PNIPAM gel was also investigated using UV-visible spectroscopy and differential scanning calorimetry (DSC). By plotting the absorbance at 600 nm, the transition temperature is determined to be ca. 33 °C (Fig. 2b). The T_c of the SWNTs/PNIPAM gel both upon heating and cooling were virtually identical to that of the gel without the SWNTs prepared as a control (Fig. 2c). In DSC, the endothermic peaks were appeared at around 35 °C for both the SWNT/PNIPAM and the PNIPAM gel (Fig. 2d), which agreed well with the results described above. It is clear that the SWNTs in the composite gel have virtually no effect on the phase transition temperature of the PNIPAM gel.

2.2 NIR irradiation to SWNTs/PNIPAM gel

We used the SWNTs as a “molecular heater” for the thermal phase transition of the composite gels. NIR laser irradiation experiments for the SWNT/PNIPAM gel and the PNIPAM gel were carried out for the gel tubes prepared and drawn from the capillary tube with inner diameter around 200 μm. As shown in Fig. 3a, upon irradiation with the NIR light centered at 1064 nm, the composite gel tube (initial diameter $d_0 \approx 240$ μm) containing the SWNTs become a smaller diameter ($d \approx 80$ μm) after 15 sec. As plotted in Fig. 3b that after turning off the irradiation, the shrunken gel gradually swells and becomes around 200 μm in diameter after about 67 sec. The further shrink-swell experiment upon ON/OFF irradiations was described in following session.

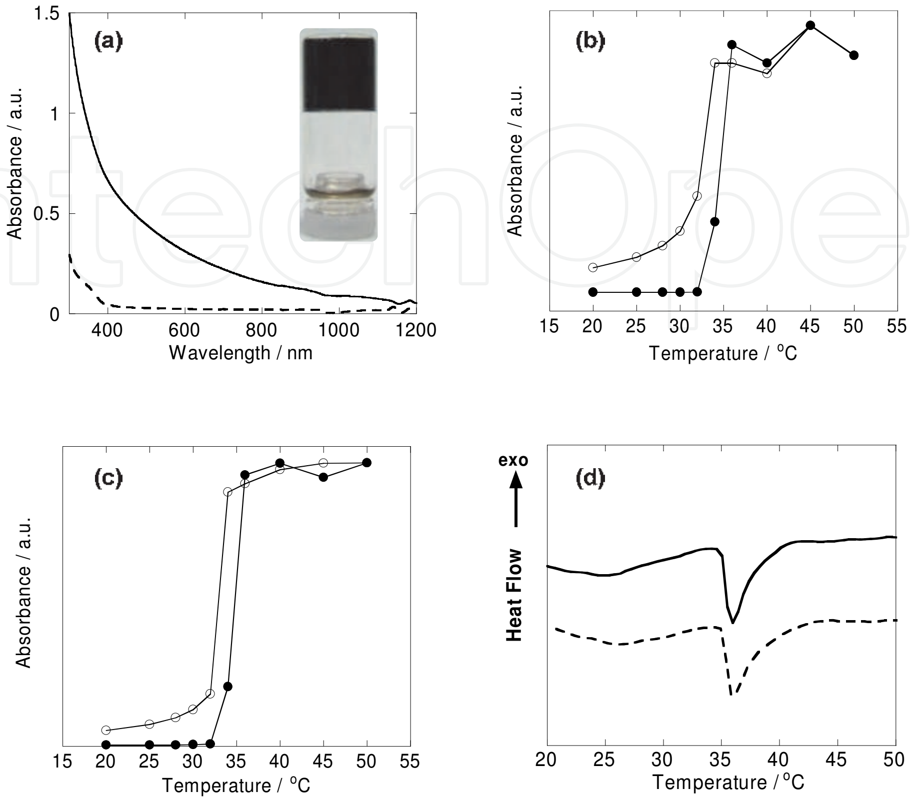

Fig. 2. Characterizations of a SWNT/PNIPAM gel, (a) Visible-NIR spectra of a SWNT/PNIPAM gel (solid line) and a PNIPAM gel (dotted line) at 20 °C. inset; photo of SWNT/PNIPAM gel (b) Temperature dependence of the optical absorption at 600 nm of a SWNT/PNIPAM gel was recorded for a heating process (solid circle) and a cooling process (open circle). (c) Temperature dependence of the optical absorption at 600 nm of a PNIPAM gel (controlled sample) upon heating process (solid circle) and a cooling process (open circle). (d) DSC curves of the gels of SWNT/PNIPAM gel (solid line) and PNIPAM gel (dotted line).

A stronger NIR laser power (> 1.2 W) has been reported to increase the temperature through the photothermal conversion of water.(Ishikawa, et al., 1996) However, this effect is excluded under our experimental conditions since the 210-mW NIR irradiation to the gel (controlled sample) prepared from the single component of PNIPAM showed no such volume phase transition even after the NIR-laser irradiation. It is conclusive that the NIR light irradiation to the SWNT/PNIPAM gel caused the phase transition of the PNIPAM gel via the photothermal conversion of the SWNTs. This contrasting result between the SWNT/PNIPAM gel and PNIPAM gel is the consequence of NIR absorption of the SWNT/PNIPAM gel at around 1064 nm (solid line in Fig. 2a), whereas the gel without the SWNTs has no absorption in the NIR region (dotted line in Fig. 2a). The proposed mechanism is that the local heating of the SWNTs due to the irradiation raises the temperature of the water around the irradiation spot in the gel over 35 °C, which induces the phase transition of the PNIPAM gel as discussed for the visible-light induced phase transition of the PNIPAM.(Suzuki & Tanaka, 1990) Here, the SWNTs act as a "molecular heater" to induce the phase transition of the PNIPAM in the composite gel.

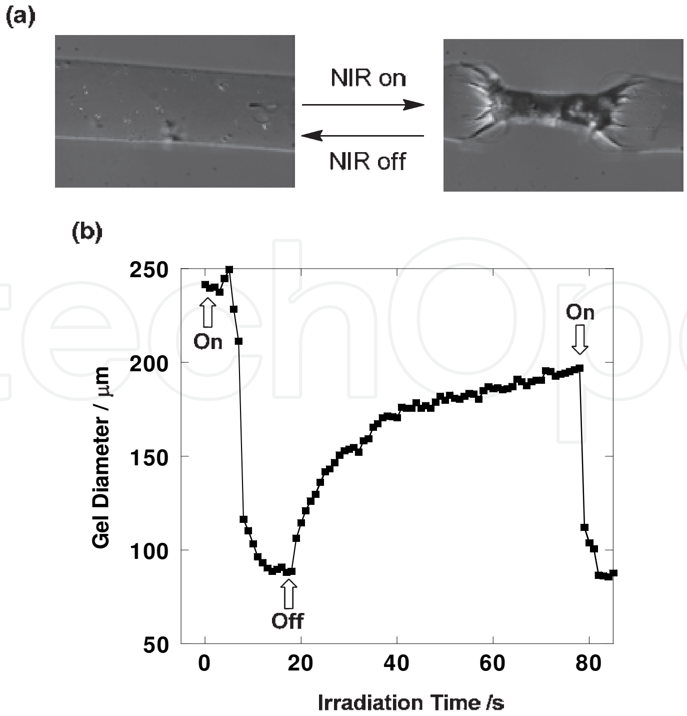

Fig. 3. NIR-induced phase transition, (a) NIR laser-driven volume change of a SWNT/PNIPAM gel shown by optical microscopic images. (b) Plot of the diameter of the SWNT/PNIPAM gel plotted as a function of time.

The response time of the volume change can be controlled by changing the concentration of the SWNTs as well as the power of the NIR laser light. The d/d_0 values obtained by the 210-mW or 390-mW irradiations of the composite gels synthesized using the different concentrations of the acid-treated SWNTs in water (2.0, 1.0, 0.5, 0.25, and 0.13 mg/mL) are plotted as a function of the irradiation time in Fig. 4a (210-mW irradiation) and Fig. 4b (390-mW irradiation). In the case of the 210-mW irradiation, the NIR-driven volume change in the gel samples synthesized at the concentrations of acid-treated aqueous SWNTs=2.0, 1.0, and 0.5 mg/mL almost finished in 4, 5, and 6 sec, respectively, whereas the gels synthesized from the lower concentration of the SWNTs = 0.25 and 0.13 mg/mL showed no phase transition.

On the other hand, at a 390-mW irradiation, the gels synthesized at the concentration of the SWNTs= 2.0, 1.0, 0.5, and 0.25 mg/mL shrunk within 2, 2, 5, and 12 sec, respectively, while the gel prepared at SWNTs=0.13 mg/mL showed no change. The absence of the phase transition observed for the gels from the SWNTs=0.25 and 0.13 mg/mL upon 210-mW irradiation and SWNTs=0.13 mg/mL upon 390-mW irradiation suggests the importance of the initial process, that is, the dark spot generated on the focal point enhances the absorption of the NIR light in that region, which accelerates the heating of the gels. The rate of this initial process varies with the concentration of the SWNTs as well as the NIR laser irradiation power. It is clear that the higher-powered light irradiation and the higher concentrations of the SWNTs in the gels render the composite gels a faster response. Of interest, for the gels especially with 2.0 and 1.0 mg/mL concentrations, we observed a bubble generation from the center of the irradiation spot upon the 390-mW irradiation. This phenomenon indicates that the temperature at the spots in the gels reached over 100 °C due to the photothermal conversion of the SWNTs. All the obtained results guarantee that the phase transition of the composite gels is triggered by photon absorption of the SWNTs in the NIR region.

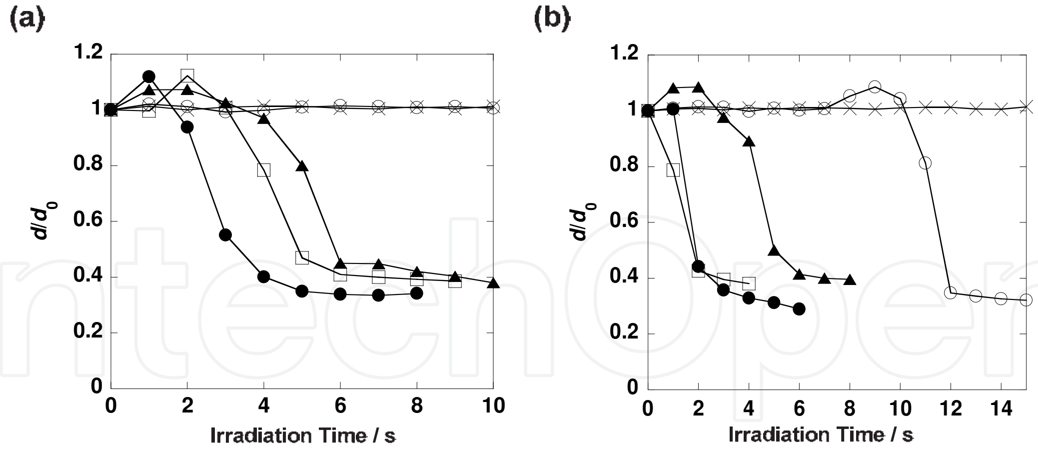

Fig. 4. Effect of SWNT concentration, The d/d$_0$ values of the composite gels synthesized using the different concentrations of acid-treated aqueous SWNTs = 2.0 (•), 1.0 (□), 0.5 (▲), 0.25 (○), and 0.13 (X) mg/mL on a (a) 210-mW and (b) 390-mW NIR laser irradiation plotted as a function of irradiation time.

2.3 Durability of SWNTs upon NIR irradiation

The SWNTs possess a robust structures arising from their rigid fused aromatic structures, and thus the SWNT-composite gels are expected to show high durability for the repeated ON/OFF-laser irradiation. We carried out an endurance test using the hybrid gel under optical micrograph monitoring, in which the tests were conducted by a programmed NIR laser operation repeated with ON irradiation for ca. 4 sec, followed by OFF irradiation for 55 sec to ensure the shrink-swell cycles (Fig. 5). Amazingly, no notable deterioration of the gel actuation was observed even after the 1200-cycle operation. As shown in Fig. 6, the Raman spectra of the gels before (dotted line) and after (solid line) the endurance test supports this durability, namely, both spectra exhibit virtually identical G/D (Graphite/Defect) ratios, which guarantee that the SWNTs remain structurally intact.

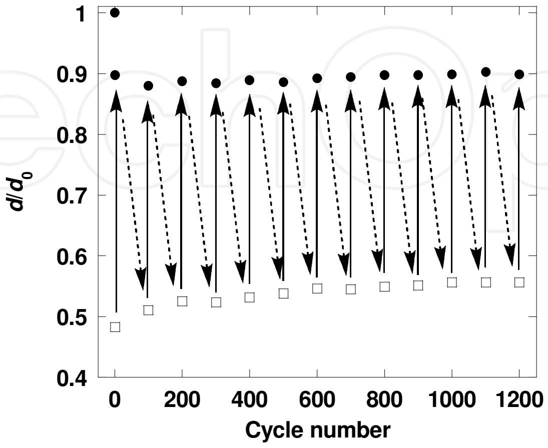

Fig. 5. Durability of the composite gel, The d/d$_0$ values of a SWNT/PNIPAM gel for ON (open square)/OFF (solid circle) switching of the NIR laser light irradiation plotted as a function of the cycle number. Data are collected every 100 cycles to avoid complication.

It is readily expected that the composite gel system can tolerate additional operations of more than 1200 cycles. We tested the gold nanorod (Au-NR)-mediated systems(Gorelikov, et al., 2004; Sershen, et al., 2005; Sershen, et al., 2000; Sershen, et al., 2001; Shiotani, et al., 2007) as another candidate for the NIR actuation of PNIPAM gels since Au-NR has an absorbance in the NIR region. The extinction coefficient of the Au-NR/PNIPAM mixture at 1064 nm is matched to that of the SWNT/PNIPAM mixture used in the endurance test for the fair comparison. Au-NR in the Au-NR/PNIPAM gel caused an aggregation of the particles after the 1200-cycle durability test, namely, we observed a blue shift in the peak that stemmed from the plasmon band of Au-NR at around 800 nm. It is evident that the SWNT/NIPAM gels have a stronger durability for the NIR irradiation.

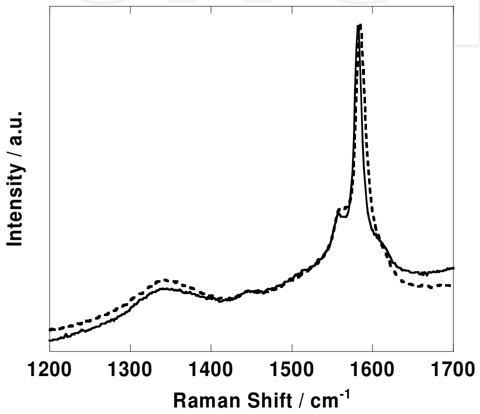

Fig. 6. Estimation of damage for SWNTs, Raman spectra of the gel before (dotted line) and after (solid line) the 1200-cycle irradiations.

3. Preparation and applications of SWNTs/PNIPAM gel using pristine SWNT (Fujigaya, et al., 2011)

3.1 Preparation of the SWNTs/PNIPAM gel composite

One of the goals of the study is to design and fabricate a NIR laser-driven drug-releasing system using isolated SWNTs as the material, in which the SWNTs having large surface areas embedded in a polymer gel serve as an efficient drug reservoir through physisorption of the molecules onto SWNTs. π-conjugating graphitic surface induces a molecular adsorption thorough many different interaction mode such as $\pi-\pi$, hydrophobic and van der Waals interactions. To realize an effective adsorption of the drug typically have a hydrophobic nature, employment of pristine SWNTs is essential since the surface of acid-treated SWNT possess many carboxylic group and turned to hydrophilic nature.

The preparation strategy of the composite gel are illustrated in Fig. 7. The composite gel composed of pristine SWNTs was prepared by the gelation of NIPAM in the presence of pristine SWNTs individually dissolved in an aqueous solution of the sodium dodecyl benzenesulfonic acid sodium salt (SDBS). SDBS was chosen as an SWNT dispersant since it is known to individually dissolve the SWNTs quite efficiently by encapsulating the SWNTs into the interior of the SDBS micelle in aqueous media.(McDonald, et al., 2006) The composite SWNT/PNIPAM gel was almost transparent similar with a PNIPAM gel without SWNT and slightly grey-colored due to the presence of a SWNTs. The mesh size of the SWNT/PNIPAM gel in aqueous media was determined by dynamic light scattering (DLS) to be around 10~20 nm (data not shown) which well agreed with previous reports.(Canal &

A. Peppas, 1989; Ishidao, et al., 1997) The observation of the intense photoluminescence (PL) signals from the composite gel guaranteed the isolation of the SWNTs even after the gelation since the PL signals are proved to be detected only from the individually isolated SWNTs (Fig. 8a).(O'Connell, et al., 2002)

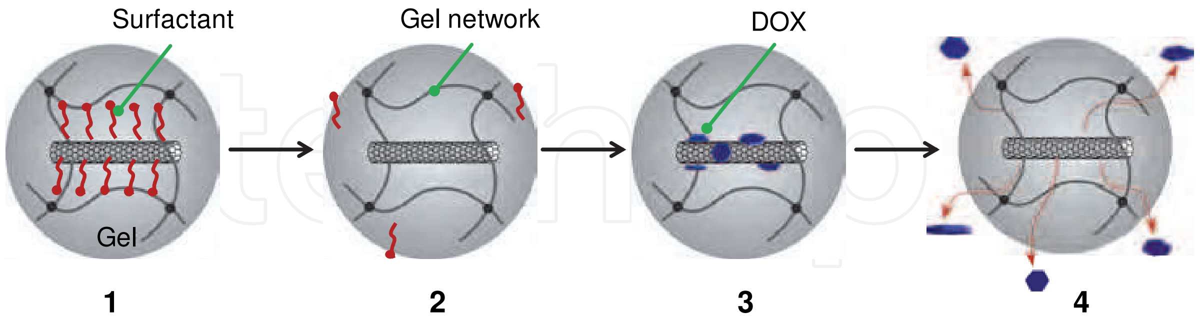

Fig. 7. Schematic illustration showing the strategy of this study. Stage **1**, Gelation carried out in an SDBS (dark blue) solution produces an SDBS-adsorbed SWNT in the gel. Stage **2**, SDBS on the SWNT surface are removed by dipping the gel in Milli-Q water. Stage **3**, The adsorption of drug molecules (red), occurs on the "vacant" SWNT surfaces through π-π and hydrophobic interactions. Stage **4**, The drug molecules on SWNT surfaces detach from the surfaces by a pH change or NIR laser irradiation by a photothermal conversion effect of the SWNTs.

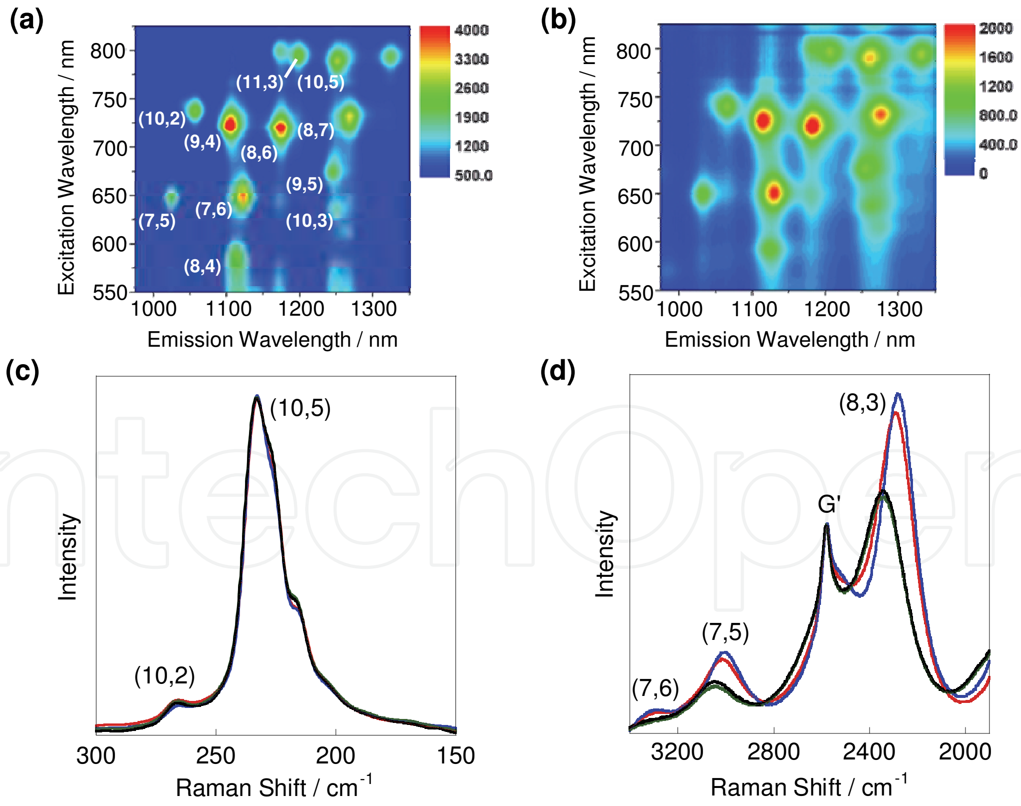

Fig. 8. Isolation of SWNTs in PNIPAM gel, (a,b) 2D PL mapping of the SWNT/PNIPAM gel before (a) and after (b) dipping in Milli-Q water for 72 h. (c,d) Raman spectra of the gel normalized at the (10,5) peak and G′ peak for c and d, respectively; the red, blue, green and black lines show the spectra after the immersion in water for 24, 48, and 72 h, respectively.

In order to remove the SDBS molecules from the surfaces of the SWNTs, the composite gel was immersed in a large amount of Milli-Q water for 72 h. The Raman spectra of the SWNTs in the composite gel were monitored during the immersion in water by measuring the radial breathing mode (RBM) (Fig. 8c) together with the PL signals(Jeng, et al., 2006; Moore, et al., 2003) (Fig. 8b). We recognized that the PL peak from the (8,3) SWNT bathochromically shifts from 2290 to 2350 cm^{-1} due to the increase in the micropolarity around the SWNTs as reported in the literature (Fig. 8d).(Jeng, et al., 2006; Moore, et al., 2003; Strano, et al., 2003) Such a clear shift as well as the decrease in the peak intensity after the immersion in water indicated that the SDBS molecules were removed from the SWNT surfaces and replaced by water molecules.(Strano, et al., 2003) In order to confirm the removal of the SDBS from the SWNT surfaces in the composite gel, we measured the X-ray photoelectron spectrum (XPS) of the SWNT/PNIPAM gel after drying, and found that the sulfur signal almost disappeared in the sample after the immersion in water (Fig. 9).

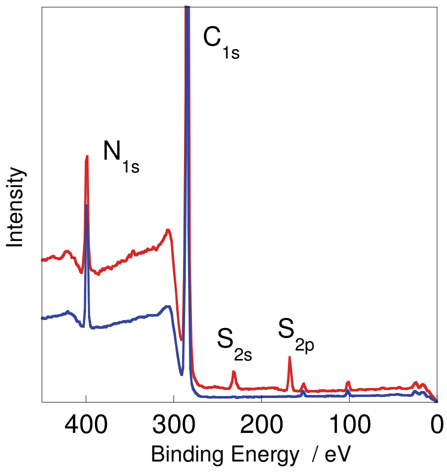

Fig. 9. X-ray photoelectron spectra, The spectra of SDBS/SWNT/PNIPAM gel before (red line) and after (blue line) immersion in deionized water.

Moreover, it is also important to emphasize that we observed a clear PL from the SWNTs in the gel after the immersion, whose PL-mapping (Fig. 8b) is virtually identical with that before the immersion (Fig. 8a). This suggests that the SWNTs remained in an isolated state even after the removal of the SDBS molecules. The Raman data also support this, namely, the intensities of the (10,2) RBM peak of the gel before and after immersion at around 267 cm^{-1}, which is known as an indicator for the evaluation of the degree of the SWNT aggregation,(Ericson & Pehrsson, 2005; Fujigaya, et al., 2009; Heller, et al., 2004; Kumatani & Warburton, 2008; Luo, et al., 2006; O'Connell, et al., 2004; Strano, et al., 2003) are virtually identical (Fig. 8c). The obtained results are in sharp contrast to those previously reported, in which the SWNTs aggregate after removal of the dispersants.(Chen, et al., 2008; Ikeda, et al., 2009; Ishibashi & Nakashima, 2006; Nobusawa, et al., 2008) We suggest that the SWNTs (~ 1 μm) penetrated the three-dimensional gel network structure having a 10~20-nm mesh to form the semi-interpenetrating network (semi-IPN) structure,(Gong, et al., 2003) and the formed structure serves to prevent further assembling (aggregation) of the SWNTs even in the absence of the dispersants. To our surprise, PL signals were also observed from the re-swelled gel after drying in a vacuum, indicating that the isolated state of the SWNTs in the gel is highly stable in the three-dimensional gel framework.

3.2 Preparation of SWNT-encapsulated PAAM and PDMAAM composite gels

We also prepared the polyacrylamide (PAAM)- and poly(*N*,*N*-dimethylacrylamide) (PDMAAM)-based composite gels in a way similar to the SWNT/PNIPAM gel to explore the effect of the side chain structures of the polymers. Fig. 10 displayed the PL mapping of the SWNT/PAAM (Fig. 10a and 10b) and SWNT/PDMAAM) (Fig. 10c and 10d) before and after the SDBS removal from the gels. Although no visible aggregation was observed for both gels, we observed a drastic PL quenching in the SWNT/PAAM composite gel (Fig. 10b). We also observed a similar deterioration in the PL signals for the SWNT/PDMAAM

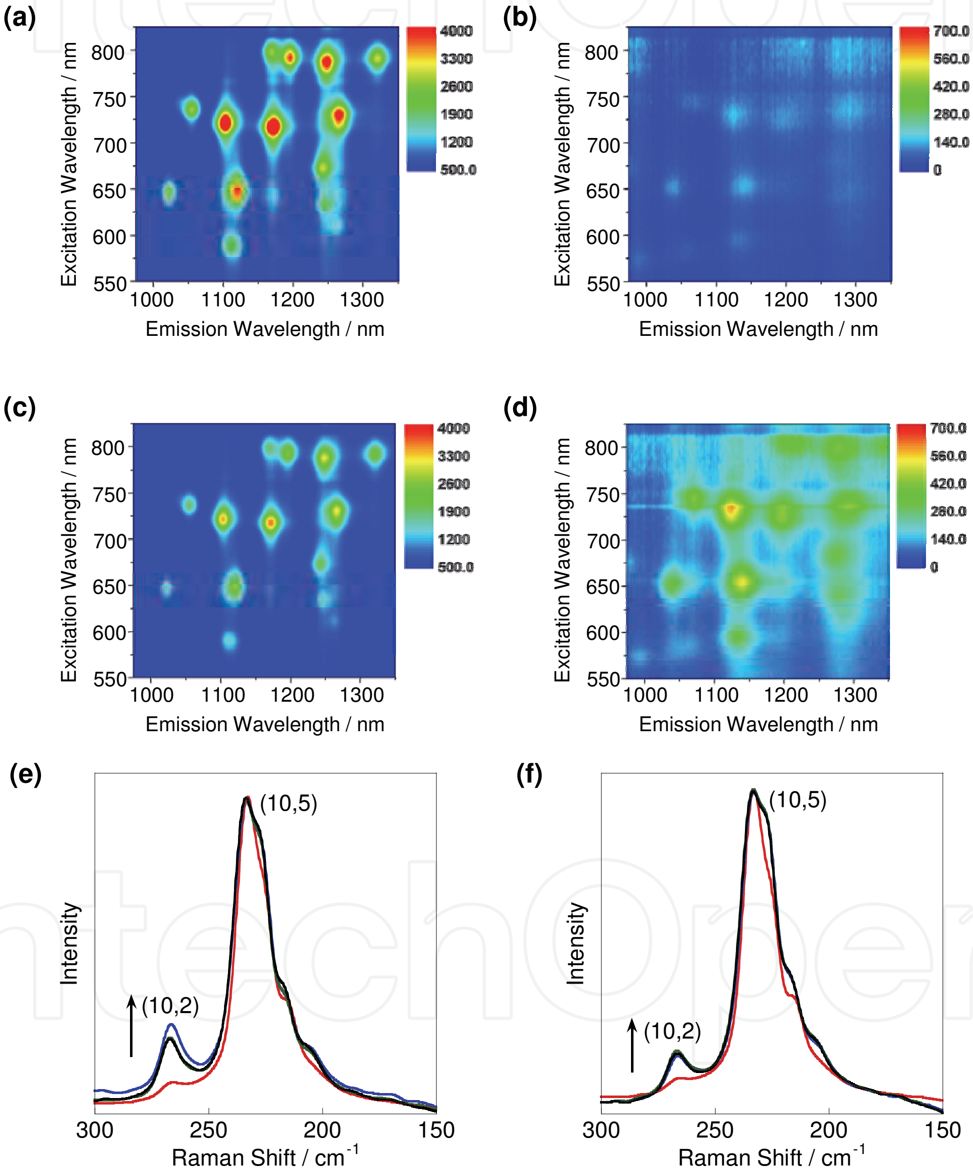

Fig. 10. Isolation of SWNTs in other gels, (a,b) 2D PL mapping of the SWNT/PAAM gel before (a) and after (b) dipping in Milli-Q water for 72 h. (c,d) 2D PL mapping of the SWNT/PDMAAM gel before (c) and after (d) dipping in Milli-Q water for 72 h. (e,f) Raman spectra of the SWNT/PAAM gel (e) and SWNT/PDMAAM gel (f) in the RBM region normalized at the (10,5) peak. The red lines show the initial spectra of the gels, and the blue, green and black lines are the spectra after the immersion for 24, 48, and 72 h, respectively.

gel (Fig. 10d), but the quenching degree is lower than that of the SWNT/PAAM composite gel. The Raman data agreed with the results, namely, we recognize larger (10,2) peaks in the RBM of the SWNT/PAAM after the removal (Fig. 10e) compared to that of the SWNT/PDMAAM (Fig. 10f). Considering the stable isolation of the SWNT in the PNIPAM gel, the CH-π interactions between the SWNTs and the polymer side chains are also considered to contribute to the SWNT isolation in the composite gels. The weaker CH-π interaction of the gel networks of PAAM and PDMAAM with the SWNTs allows to form small-sized bundled SWNTs, but the semi-IPN structure prevents to grow to visible-sized bundled SWNTs. Based on the chemical structures, it is readily expected that the intensities of such CH-π interactions are SWNT/PAAM < SWNT/PDMAAM < SWNT/PNIPAM, which is closely related the stable formation of the isolated SWNTs leading to a stronger PL intensity.

3.3 Drug holding and releasing from SWNT surface

Up to date, only several attempts for the stimuli responsive releasing of the physisorped molecules on SWNTs have been reported.(Ikeda, et al., 2009; Liu, et al., 2007; Nobusawa, et al., 2008) We showed a heat-driven desorption of pyrene-bearing vinyl monomer from SWNT surface.(Nakashima, et al., 2004) Dai et al. reported the detachment of doxorubicin hydrochloride (DOX) molecules from the SWNT surfaces upon lowering the pH of an aqueous media, which induces the increasing of hydrophilicity of the DOX due to the protonation.(Liu, et al., 2007) Redox active molecular detachment from SWNTs was performed with the Cu complex of the 2,2′-bipyridine derivative based on the geometry switching from the planner Cu^{II} complex to the tetrahedral Cu^{I} complex.(Nobusawa, et al., 2008) Light irradiation was also used as an external stimulus, in which the adsorbed malachite green unit (MG) was detached from the SWNT surfaces upon UV-driven ionization of MG.(Chen, et al., 2008)

All these previous studies, however, were carried out using SWNT dispersions and the detachment of the adsorbed molecules from the SWNT surfaces upon external stimuli resulted in the formation of insoluble SWNT aggregates.(Liu, et al., 2007) Additional sonication is required to dissolve the SWNT aggregates in solution. Thus, such irreversibility is inadequate especially *in vivo* application since the SWNT bundle possess a cytotoxic risk.(Wick, et al., 2007)

Dai et al. demonstrated the adsorption and pH responsive desorption of the DOX molecules, known as a cancer drug, on the SWNT surfaces dispersed in water with the aid of the lipid.(Liu, et al., 2007) In this study, we use the isolated SWNTs in the gels as the molecular reservoir to reach an efficient adsorption of the drug followed by a controlled release from the gels. Fig. 11a shows the absorption spectrum of the SWNT/PNIPAM gel before (red line) and after (blue line) dipping in a 1 mM DOX aqueous solution for 48 h. The DOX uptake after the dipping is evident since we see a clear peak around 490 nm due to the absorption of the DOX molecules. After the DOX uptake treatment, quenching of the PL intensity was observed for both the Raman (blue line in Fig. 11b) and PL spectrum (Fig. 11c), which might be induced by the adsorption of DOX molecules on the SWNT surfaces. In addition, the intensity of (10,2)SWNTs RBM peak around 270 cm^{-1} in the Raman spectrum increased slightly (Fig. 12), indicating the formation of the SWNT small bundles after the DOX uptake. This is in sharp contrast with the case without the gel, in which the DOX uptake caused visible aggregations of the SWNTs.(Liu, et al., 2007)

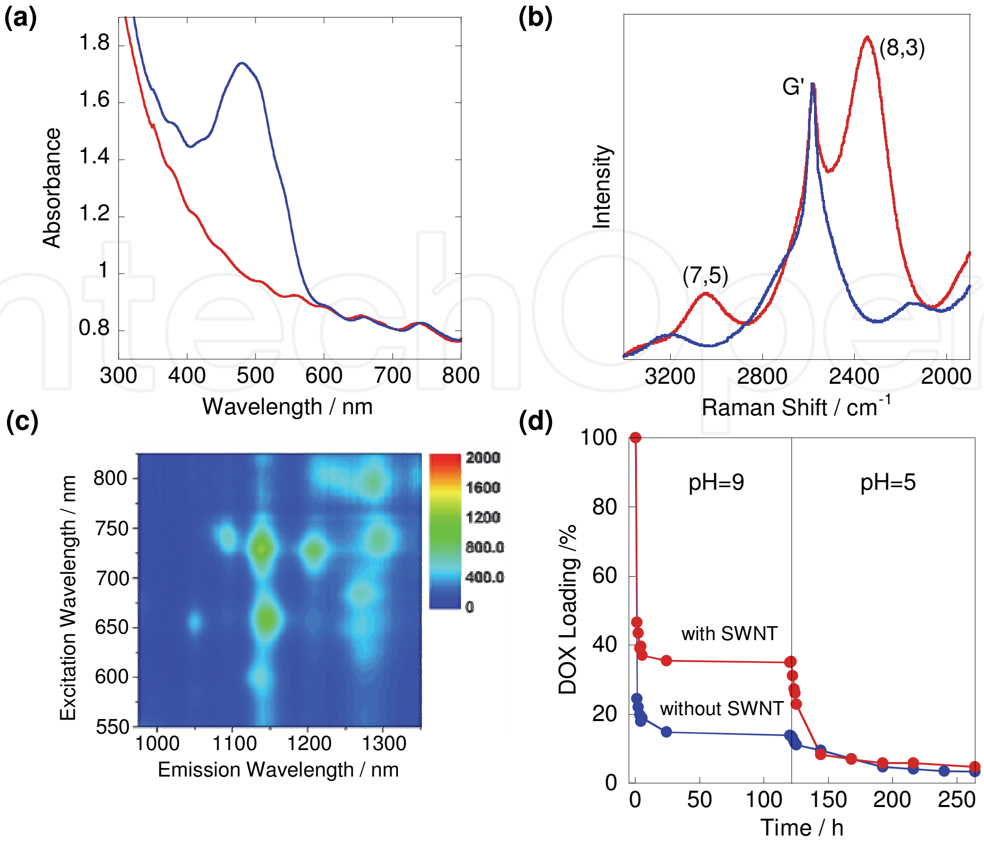

Fig. 11. DOX holding in the composite gel, (a) Absorption spectra of an SWNT/PNIPAM gel (red line) and an SWNT/PNIPAM gel dipped in a 1 mM DOX aqueous solution (blue line). (b) Raman spectra of the SWNT/PNIPAM gel before (red line) and after (blue line) dipping in a DOX solution. (c) 2D-PL mapping of the SWNT/PNIPAM gel after dipping in a DOX solution. (d) Plots of DOX loading of the SWNT/PNIPAM gel (red line) and the PNIPAM gel (blue line) as a function of dipping time. The gels after dipping in a DOX solution were washed with water for 1 min, followed by immersion in a NaOH aqueous solution (pH~9) for 122 h. The gels were then successively transferred into an HCl solution (pH~5).

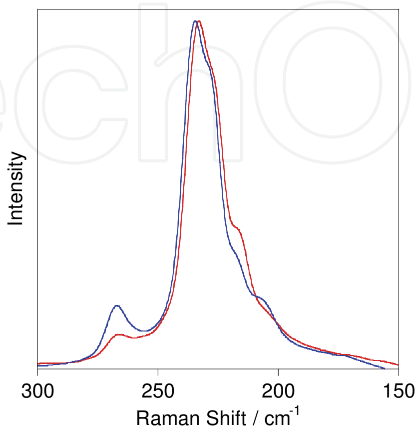

Fig. 12. Raman change after DOX holding, Raman spectra of SWNTs/PNIPAM gel. Raman spectra of SWNTs/PNIPAM gel before (red line) and after (blue line) incubation with 1 mM DOX solution for 2 days were illustrated.

The SWNT/PNIPAM gel was supposed to contain both bound DOX molecules on the SWNTs and unbound DOX. To remove the unbound DOX, the gel was immersed in an alkaline aqueous solution (pH~9). The absorption difference between the DOX-containing gel and the gel without DOX (red line in Fig. 11a) at 490 nm was monitored upon immersion and plotted after converting into the percentage of a DOX quantity based on the initial absorption difference (red line in Fig. 11d). DOX-containing PNIPAM gel without SWNTs was also prepared and monitored as a control sample (blue line in Fig. 11d). Large drops of the DOX quantities were observed after dipping, which corresponds to the removal of unbound DOX. After 24-h dipping, only 13.9% of the DOX remained in the PNIPAM gel, while 35.2% of the DOX remained for the SWNT/PNIPAM gel. The presence of bound DOX in PNIPAM suggested the fact that DOX was also bound on PNIPAM gel network. The large difference between two gels by 21.3% clearly indicated that the SWNTs act as a drug reservoir in the SWNT/PNIPAM gel to hold DOX through the interaction between the DOX and SWNT surfaces.

It has been reported that the interaction of the DOX and SWNT surface were weakened in the acidic aqueous solution (pH~5) due to the protonation of the amine group on the DOX.(Liu, et al., 2007) Indeed, successive immersion of the DOX-containing gels in an acidic (pH~5) aqueous solution leads to a DOX releasing from the SWNT/PNIPAM gel, and the quantity were reached almost identical to that in the PNIPAM gel under at the same condition (Fig. 11d). Therefore, the difference of DOX quantity between in the SWNT/PNIPAM and PNIPAM gels at pH~9 was confirmed as an amount of the DOX molecules on the SWNT surface and the quantity is calculated to be 2.7×10^{16} molecules. Such a high DOX loading would be due to the strong DOX affinity on large exposed SWNT surface.

3.4 Light-driven releasing of DOX from SWNT gels

Light is an attractive stimulus source from the viewpoints of its remote-controllability, quick responsibility, system simplicity, etc. We have reported that the NIR irradiation of the SWNT/PNIAPM gel induces a rapid volume phase transition of the gel due to an effective photo-thermal conversion of the SWNTs.(Fujigaya, et al., 2008) In this experiment, NIR irradiation of the DOX-containing SWNT/PNIPAM gel at pH~9 was carried out. The heat generation through the photothermal conversion of SWNTs caused by the NIR laser irradiation (1064 nm, spot size ~100 μm) rose the gel temperature to 35 ºC (red line in Fig. 13b) and induced a volume phase transition of the gel observed under optical microscope (data not shown) similar to the previously reported result.(Fujigaya, et al., 2008) UV-vis absorption spectrum at the part of irradiated area (~10 μm) was measured by means of multi channel detector and characteristic S_{22} band from 600 to 800 nm together with DOX peak at around 490 nm were clearly observed (red line in Fig. 13a). However, almost no spectral change was observed after the NIR irradiation (blue line in Fig. 13a). This implies that the heat generation from the SWNTs did not result in releasing of the DOX from the gel. It is assumed that the quick shrinking of the gel (~2s) prevents the DOX release from the gel. Ineffective photothermal heating of the SWNTs (red line in Fig. 13b) owing to the light scattering of the shrunken gel might also disturb DOX release from the SWNTs.

In order to avoid shrinking of the gel, PDMAAM that exhibits no phase transition up to 90 ºC was then incorporated as a component of a copolymer gel at the ratio of NIPAM:DMAAM=1:4. A copolymer gel containing the SWNTs showed no volume phase transition up to 90 ºC (data not shown). Similar DOX loading (~ 40%) was successfully obtained for the copolymer gel after incubation in a DOX solution followed by incubation in alkaline water. We carried out NIR irradiation of the SWNT/PNIPAM/PDMAAM gel. The DOX desorption from the SWNT surfaces was monitored (Fig. 13c) and plotted in Fig. 13d as a function of the irradiation time. An abrupt decrease in the absorbance of the DOX indicates the DOX releasing upon the NIR irradiation. The absence of gel shrinking

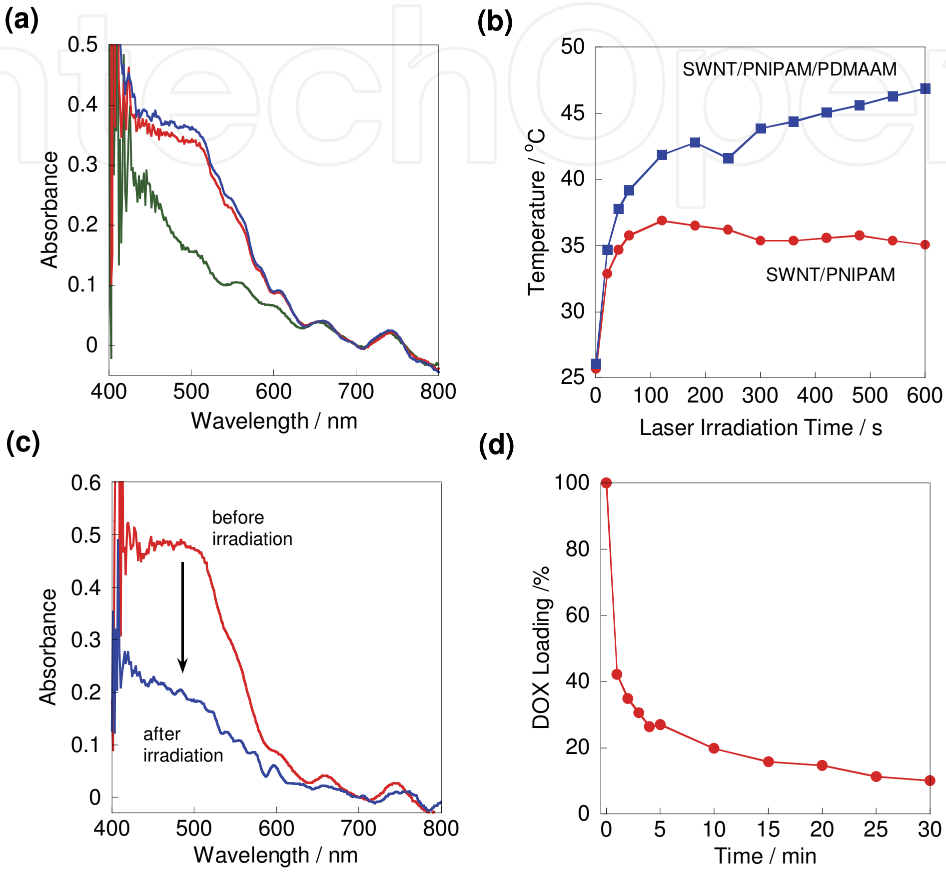

Fig. 13. DOX releasing upon NIR irradiation, (a) The absorption spectra of the SWNT/PNIPAM gel containing DOX molecules before (red line) and after (blue line) irradiation by an NIR laser light for 30 min (CW, 1064 nm, 160 mW). The gel was immersed in a NaOH solution during the laser irradiation. The absorption spectrum of the SWNT/PNIPAM gel not containing DOX is also shown by the green line. All spectra are normalized at 700 nm. Low S/N ratios of the spectra are due to the limitation of the observed area (~10 μm). (b) Temperatures of the gel surfaces of the SWNT/PNIPAM (red line) and SWNT/PNIPAM(1)/PDMAAM(4) (blue line) gels upon irradiation by an NIR laser light. The surface temperatures of the gels were monitored by an infrared thermography, and the temperatures of the gel surfaces are plotted as a function of the laser irradiation time. (c) Absorption spectra of a DOX-embedded SWNT/PNIPAM gel before (red line) and after (blue line) NIR (CW, 1064 nm, 120 mW) irradiation for 30 min in a NaOH solution. (d) Percentage of DOX loading in the SWNT/PNIPAM gel plotted as a function of the NIR irradiation time. Absorbance at 490 nm subtracted by the absorbance of an SWNT/PNIPAM (not containing DOX) was converted into a percentage based on the initial value. The spectra were measured using a multi-channel analyzer (exposure time: 20 ms, accumulation: 20 times).

(confirmed under optical microscope observation) and the smooth photothermal heating (blue line in Fig. 13b) leads to a successful DOX release from the gel as shown in Fig. 13c. It was revealed that 89.9% of the DOX molecules on the SWNT surfaces were released under a 30-min irradiation (Fig. 13d), which show a remarkable contrast with the DOX releasing in hot water (80 ºC), in which ~70% of the DOX released after a 24-h heating.(Liu, et al., 2007) It is now evident that the NIR irradiation accelerates the releasing of the adsorbed DOX molecule compared to the conventional heating using a mechanical heater. Such an efficient drug holding and controlled releasing of the drug would be useful for an advanced drug delivery system (DDS).

4. Conclusion

In conclusion, we demonstrated the first NIR laser light-driven phase transition (volume change) of the SWNTs/PNIPAM composite gel, in which the SWNTs acted as a “molecular heater” to raise the local temperature of the gel via the photothermal conversion of the SWNTs. One notable advantage that we would like to emphasize in this system is the remarkable durability for ON/OFF switching actuated by the NIR laser irradiation for more than 1200 cycles.

In addition, SWNTs have been successfully isolated in hydrogel frameworks formed from PNIPAM and PNIPAM-PDMAAM due to the formation of semi-IPN structures, in which the CH-π of the gel side chains plays an important role in stabilizing the semi-IPN structures. The obtained gels were used as a molecular reservoir for molecules of biological importance, such as DOX, a cancer drug. Furthermore, we demonstrated pH- as well as photo-responsive releasing of the adsorbed molecule from the gels. Since the NIR light laser used in the photo-responsive releasing can penetrate the human body, the potential application for the use of a gel containing isolated SWNTs as an NIR-driven controllable releasing drug reservoir is expected.

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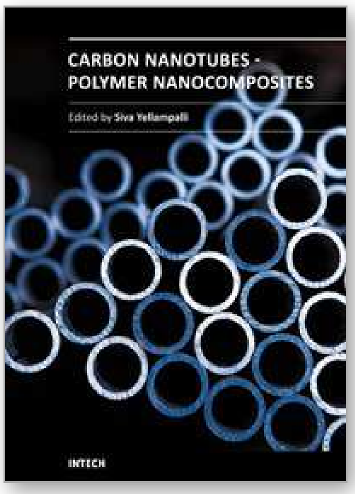

Carbon Nanotubes - Polymer Nanocomposites
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Polymer nanocomposites are a class of material with a great deal of promise for potential applications in various industries ranging from construction to aerospace. The main difference between polymeric nanocomposites and conventional composites is the filler that is being used for reinforcement. In the nanocomposites the reinforcement is on the order of nanometer that leads to a very different final macroscopic property. Due to this unique feature polymeric nanocomposites have been studied exclusively in the last decade using various nanofillers such as minerals, sheets or fibers. This books focuses on the preparation and property analysis of polymer nanocomposites with CNTs (fibers) as nano fillers. The book has been divided into three sections. The first section deals with fabrication and property analysis of new carbon nanotube structures. The second section deals with preparation and characterization of polymer composites with CNTs followed by the various applications of polymers with CNTs in the third section.

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Phone: +86-21-62489820
Fax: +86-21-62489821