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Nanotube–Polymer Composites

Carbon Nanotube–Polymer Composite for Light-Driven Microthermal Control**

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Carbon nanotubes (CNTs) have attracted considerable attention because of their various applications.[1–8] In particular, the development of functional CNT–polymer composites has been a hot research topic in the last years.[7,8] However, contrary to many theoretical expectations, the physical potential of CNT–polymer composites has not been fully utilized because of the low dispersibility of CNTs in polymer matrices.[7,8] Therefore, surface engineering of the CNTs is considered to be indispensable for exploiting their physical potential.[7] Here, we present a novel organic-solvent-dispersible single-walled CNT (SWNT) complex that has good dispersibility in poly(dimethylsiloxane) (PDMS)—a model polymer matrix which represents an attractive material for lab-on-a-chip technologies, such as micro- or nanofabrication.[9,10] Controlling the temperature of a reaction mixture on a chip is of particular importance for many such applications.[10] A light-driven PDMS microchip that encapsulates the SWNT complexes was shown to be capable of ultrarapid temperature control in a microspace.

Covalent and noncovalent functionalizations of SWNTs are useful techniques for improving the dispersibility of the nanotubes in organic solvents.[8] Covalent functionalization, however, disrupts the one-dimensional electronic structure and the desirable optical properties of the SWNTs.[11,12] The noncovalent approach, on the other hand, is considered to be a promising technique because it results in better retention of the electronic structure of the CNTs.[11,12] We therefore synthesized a phospholipid, PL, bovine serum albumin, BSA, functionalized single-walled nanotube, SWNT, (PL–BSA–SWNT) complex by using a noncovalent technique (see Figure 1a and the Supporting Information for details). The BSA molecules bind noncovalently to the surface of the SWNTs through hydrophobic interactions, π–π interactions, and interactions via the amine functionalities of the protein.[13,14] The hydrophobic alkyl chains of the PL increase the dispersibility of the BSA-functionalized SWNT (BSA–SWNT) complexes in both nonaqueous solvents[15] and the PDMS polymer matrix.[16] Pristine SWNTs and the BSA–SWNT complex are not dispersible in dichloromethane (Figure 1b, 1 and 2), whereas the PL–BSA–SWNT complex is readily dispersible in various organic solvents, but not in water (Figure 1b, 3–7). Bundle-free or isolated SWNTs have been reported to exhibit characteristic signals in the visible (Vis) and near-infrared (NIR) regions of their optical absorbance spectra as a result of van Hove transitions.[17] The Vis/NIR optical absorption spectrum of a dispersion of the PL–BSA–SWNT complex in dichloromethane showed first metallic (M_{11}) and second semiconducting (S_{22}) bands in the ranges 440–600 nm and 550–800 nm, respectively (Figure 1c). In addition, we structurally characterized the PL–BSA–SWNT complex by means of atomic force microscopy

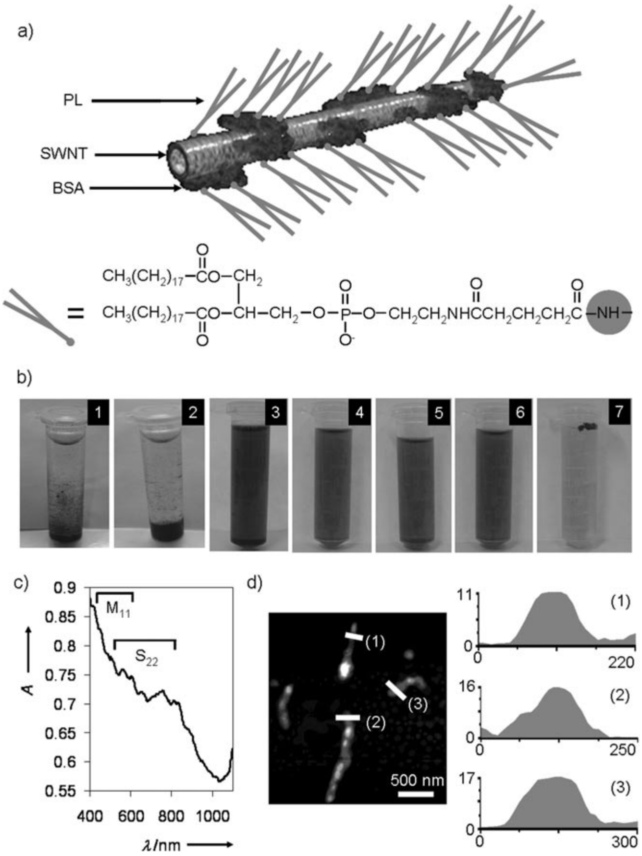

Figure 1. Organic-solvent-dispersible SWNT complex. a) Image of the PL–BSA–SWNT complex. b) Photographs of dispersions of various SWNT constructs (1: SWNT, 2: BSA–SWNT, 3–7: PL–BSA–SWNT) in organic solvents (1–3: dichloromethane, 4: chloroform, 5: toluene, 6: ethyl acetate) and in water (7). c) Vis/NIR spectrum of a PL–BSA–SWNT/dichloromethane solution (350 μg mL^{-1}). d) AFM image of PL–BSA–SWNT complexes deposited on a mica substrate (left), and height profiles [nm] along lines 1–3 (right).

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(AFM). AFM analysis of the PL–BSA–SWNT complex revealed that SWNT complexes are individually deposited on a mica substrate (Figure 1 d, left). The PL–BSA conjugates are observed on the SWNTs as white dots, and the average height of the PL–BSA–SWNT complexes is about 10–20 nm (Figure 1 d, right). Taking into consideration that the average diameter of the high-pressure CO (HiPCO) SWNTs is 0.8–1.2 nm,[18] and that the size of BSA is about 6.4 nm,[19] the height measurement suggests that the SWNTs are sandwiched between PL–BSA conjugates, as shown in Figure 1 a.

Next, we investigated PDMS-encapsulated PL–BSA–SWNT complexes (PL–BSA–SWNT–PDMS). The PL–BSA–SWNT–PDMS films had a high transparency and high flexibility (Figure 2 a). The dispersion properties of two SWNT constructs (namely, PL–BSA–SWNT and pristine SWNT) in a PDMS polymer matrix were investigated by means of optical microscopy and scanning electron microscopy (SEM; Figure 2 b,c). No aggregation of the SWNTs was observed in the case of PL–BSA–SWNT–PDMS, whereas the nonfunctionalized SWNTs showed a considerable degree of aggregation in PDMS. These results clearly show that in contrast to nonfunctionalized SWNTs, the PL–BSA–SWNT complexes are well dispersed in a PDMS matrix.

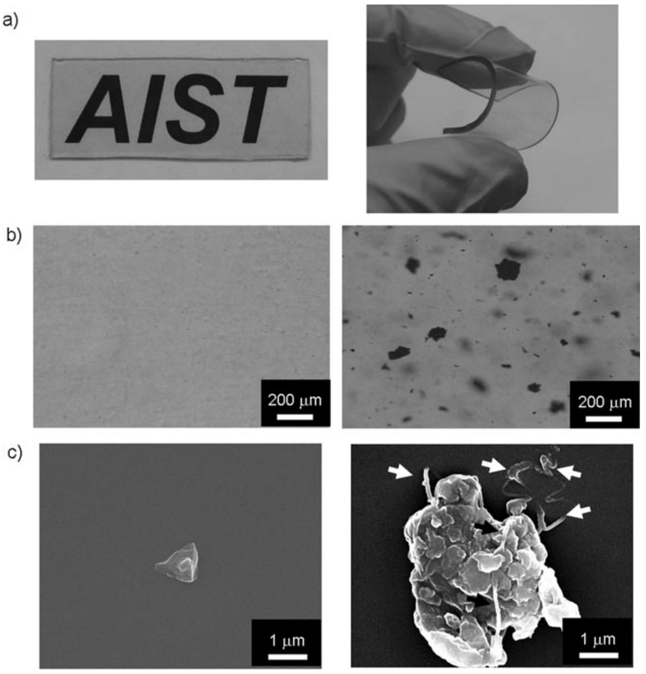

Figure 2. Characterization of the PL–BSA–SWNT–PDMS composite. a) Photographs of a PL–BSA–SWNT–PDMS composite film. b) Optical micrographs of PL–BSA–SWNT–PDMS (left) and SWNT-PDMS (right); magnification: ×5. c) SEM images of surfaces of PL–BSA–SWNT–PDMS (left) and SWNT-PDMS (right); acceleration voltage: 20 keV (the arrows in black and in white represent SWNTs).

The control of the temperature of a reaction mixture in micro- and nanochips is necessary for various applications, as mentioned above.[10] Recently, we[20,21] and other researchers[5,6] demonstrated that photoinduced nanocarbons, such as carbon nanohorns and CNTs, can operate as exothermic nanomaterials. We prepared an SWNT hybrid microchip to investigate the photoinduced exothermic properties of the PL–BSA–SWNT–PDMS composite (see Figure 3 a, b and the Supporting Information for details). The temperature distribution in a microchannel was measured by determining the degree of fluorescence intensity of 5-carboxytetramethylrhodamine succinimidyl ester (5-TAMRA),[22] which is a temperature-responsive reagent in a reversible fashion, upon NIR irradiation (Figure 3 c). An aqueous solution of

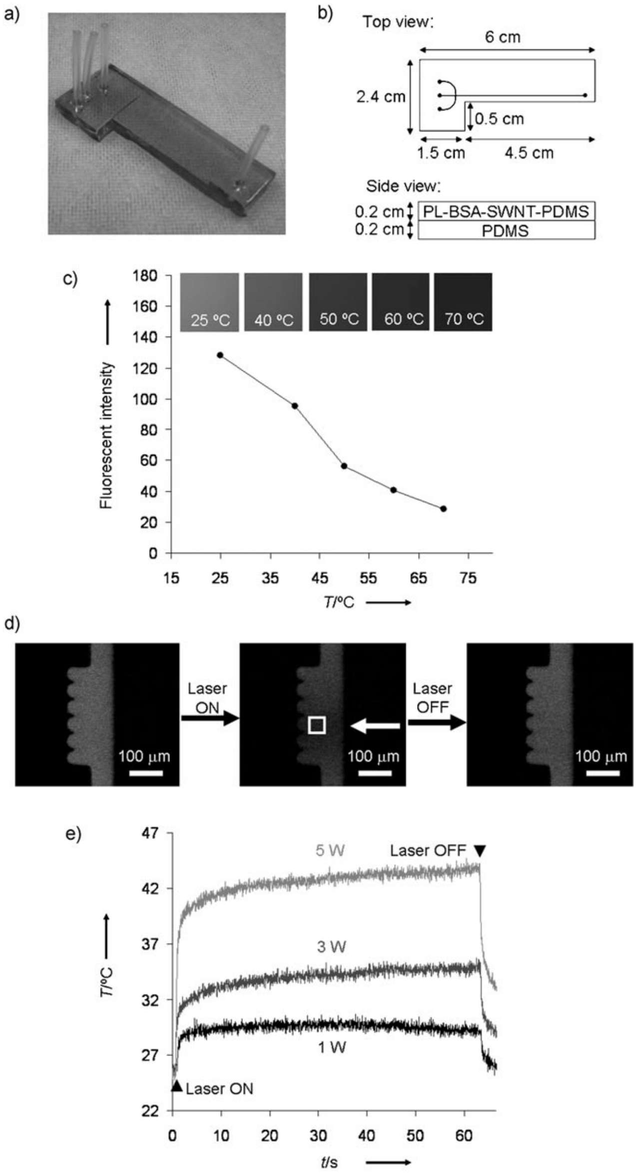

Figure 3. Photothermal conversion behavior in a microchannel. a) Photograph of a PL–BSA–-SWNT-PDMS microchip. b) Design drawing of the PL–BSA–SWNT–PDMS microchip. c) Temperature-dependent fluorescent intensity of 5-TAMRA. d) A direct observation of the ultrafast temperature control in the microchannel. The white square shows the location at which the temperature was analyzed. The white arrow shows the direction and position of the laser beam. Magnification: ×10; laser power: 5 W; wavelength: 1064 nm. e) Temperature curves of the photoinduced PL–BSA–SWNT–PDMS microchip under continuous NIR laser irradiation (1064 nm) at various power levels.

5-TAMRA was introduced into a comb-shaped microchannel and irradiated with a 5-W NIR laser (see Figure 3d and Video 1 of the Supporting Information). Surprisingly, quenching of the fluorescence of 5-TAMRA in the microchannel as a whole was observed almost immediately (below 0.03 s) upon NIR laser irradiation. In addition, the fluorescence of 5-TAMRA was also restored immediately (below 0.03 s) upon stopping the NIR irradiation. This ultrafast quenching and restoration of the fluorescence of 5-TAMRA can be explained in terms of two factors: First, CNTs typically have an extremely high thermal conductivity.[23,24] Second, the fluid sample inside the microchannel has a volume of as little as 720 pL and, consequently, a small heat capacity.[25–27] Under NIR laser irradiation, the PL–BSA–SWNT–PDMS microchannels underwent significant changes in temperature when the laser power was pulsed on and off (see Figure 3e). The maximum temperature at laser powers of 1, 3, and 5 W increased from 25 °C to 30, 35, and 44 °C, respectively. After stopping irradiation, different decreases in temperature were observed for the different laser powers by relevant quantities of photo-exothermic SWNTs. In all three cases, the temperature fell back to 25 °C within 30 s of stopping the NIR irradiation. In the case of an ordinary PDMS microchip without SWNTs, there was no temperature increase (that is, no quenching of the 5-TAMRA fluorescence) at any laser power, whereas NIR irradiation of an SWNT-PDMS microchip destroyed the PDMS matrix as a result of excess exothermal energy from light-harvesting SWNT aggregates (see Video 2 of the Supporting Information). These results clearly show that a photoinduced PDMS microchip that encapsulates well-dispersed PL–BSA–SWNT complexes is capable of achieving an effective and extremely rapid control of the temperature of solutions contained in microchannels within that microchip.

Finally, we investigated the phase transitions of a poly(*N*-isopropylacrylamide) (PNIPAM) gel in a microchannel in response to photoinduction of a PL–BSA–SWNT–PDMS composite (see Figure 4 and Video 3 of the Supporting Information). PNIPAM, one of the most intensively studied environmentally responsive polymers, undergoes a phase transition in aqueous solution at a lower critical solution temperature (LCST) of about 32 °C.[28] We immediately observed the black, high-contrast image derived from the phase transition of the PNIPAM gel upon NIR irradiation (see Figure 4, top). The phase transition of PNIPAM was also monitored by using 1-anilinonaphthalene-8-sulfonic acid (ANS) as a fluorescent probe to stain hydrophobic aggregates of the PNIPAM gel (see Figure 4, bottom).[29,30] Fluorescent microscopy studies performed on ANS-containing PNIPAM clearly showed the presence of a blue-colored microchannel as soon as NIR irradiation began. It is well known that the spectrum of ANS shows an increase in the fluorescence intensity and a blue shift of the emission maximum when the acid is in contact with—or penetrating into—a hydrophobic region of PNIPAM at temperatures above the LCST.[30] After stopping the irradiation, these light-field and fluorescent images were restored to their original states, with a rapid response similar to that found in the temperature assay, as described above. In addition, there was no change at all in the light-field or fluorescent observations when the control PDMS microchip (that is, that without SWNTs) was irradiated (this was true for all laser powers, namely, 1–5 W). These results confirm that SWNT complexes function efficiently in the polymer matrix as laser-triggered powerful “nanoheaters”.

In summary, we developed a simple method for dispersing SWNTs—not only in various organic solvents but also in a PDMS polymer matrix—through the formation of a noncovalent complex with a commercially available protein and phospholipid. A light-triggered PDMS microchip that encapsulates the functionalized SWNT complex is capable of achieving a very rapid control of the temperature of an aqueous solution contained in a microchannel. Furthermore, we observed a phase transition in a polymer gel as a result of the photo-exothermic process that takes place in the photoinduced hybrid microchannel. Our system should be useful in various lab-on-a-chip applications, such as precise organic syntheses and single-molecule manipulations.

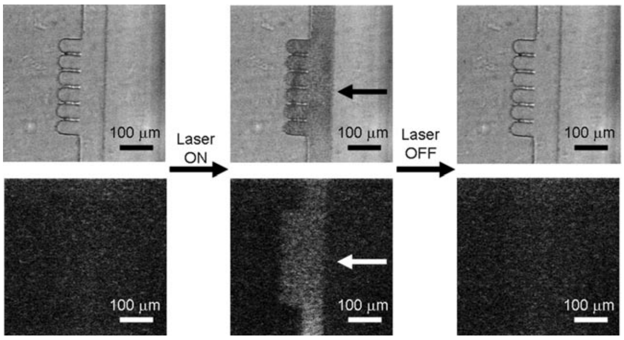

Figure 4. Direct observation of the phase transition of PNIPAM. Light-field images (top) and ANS fluorescence images of the phase transition of PNIPAM (bottom). The arrows in the images show the direction and position of the laser beam. Magnification: ×10; laser power: 1 W; wavelength: 1.064 nm.

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