Supporting Information

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Carbon Nanotube–Polymer Composite for Light-Driven Microthermal Control

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Methods:

Synthesis of PL–BSA–SWNT complex. The PL–BSA–SWNT complex was synthesized as follows. A BSA–SWNT complex was prepared by the method described by Karajanagi et al.\textsuperscript{13} SWNTs (4 mg) (purity > 95%) (Hipco super-purified SWNTs; Carbon Nanotechnologies) were sonicated in N,N-dimethylformamide (DMF; 32 mL) (Wako) for 30 min by using an ultrasonication bath (USD-2R; AS ONE) to give a uniform dispersion. The SWNT/DMF dispersion (2 mL) was then loaded into a microcentrifuge tube, and the organic phase was gradually replaced by an aqueous phase by repeated washing with sodium borate buffer (0.1 M, pH 8.5). BSA (40 mg) (Wako) was dissolved in the dispersion of SWNTs in the aqueous buffer and the mixture was sonicated for 15 min on ice (< 8 °C). The resultant highly water-dispersible BSA–SWNT complex solutions (2 mL) were centrifuged at 11000 rpm for 3 min at 4 °C (MX-301; Tomy). The upper half of the supernatant after centrifugation was carefully collected, sodium borate buffer (1 mL) was added, and the mixture was subjected to a further round of centrifugation. This process was repeated until the supernatant was almost clear. Surplus BSA was removed by ultrafiltration [Millipore, cut-off molecular weight ($M_w$) = 100 kDa], and the filtrate was subjected to six cycles of centrifugation (6500 rpm, 15 min, 4 °C) and washing with sodium borate buffer (10 mL) . The resultant BSA–SWNT complex was redispersed in sodium borate buffer (50 mL) by ultrasonication for 3 min on ice (< 8 °C), and distearoyl N-(succinimidylglutaryl)-L-a-phosphatidylethanolamine (20 mg) (DSPE–NHS; COATSOME FE-8080SU5; Nihon Oil and Fats) was added into the solution. The mixture
was stirred vigorously for 2 h at 4 °C, subjected to ultrafiltration (cut-off $M_w = 100$ kDa) with centrifugation (6500 rpm, 15 min, 4 °C) to remove unreacted DSPE–NHS, and then washed six times with distilled water (10 mL). Finally, the aqueous PL–BSA–SWNT complex solution (50 mL) was pre-frozen with liquid nitrogen and lyophilized (EYELA Freeze Dryer FD-5N; Tokyo Rikakikai) for 48 h to give the solid-state PL–BSA–SWNT complex.

**Optical absorption assay.** The optical absorption spectrum of PL-BSA-SWNT complex was recorded by using a UV–Vis–NIR spectrometer (V-630; JASCO) at room temperature. The sample was dispersed in dichloromethane ($350 \mu g/mL$), and the solution (1 mL) was monitored in quartz-type cells (optical path = 1 cm) (S15-UV-10; GL Science).

**Structural analysis.** Structural characterizations of the PL–BSA–SWNT complex were performed by AFM (JSPM-4210; JEOL) using a tapping-mode cantilever (NSC35/no Al; MikroMasch). The dispersion properties of SWNT constructs in the PL–BSA–SWNT–PDMS and SWNT–PDMS composites were assessed by optical microscopy (IX71; Olympus) and SEM (JSM-6700F; JEOL) (acceleration voltage: 20 keV). Before the SEM observations were performed, the samples were coated with a 10-nm-thick layer of gold, evaporated by using an ion coater (IB-5; EIKO).

**Microfabrication.** To prepare the PL–BSA–SWNT/PDMS mixtures, PL–BSA–SWNT complex (2.5 mg) was sonicated in dichloromethane (25 mL) (Wako) for 60 min on ice ($< 8$ °C), and the resulting dispersion was mixed with PDMS (25 g) (Sylgard 184; Dow Corning) by sonication for 15 min on ice ($< 8$ °C). The dichloromethane was then completely removed by evaporation on a rotary vacuum evaporator (EYELA Auto Jack NAJ; Tokyo Rikakikai) at room temperature. The crosslinker was subsequently added to the PDMS at a ratio of 1:10, as specified by the manufacturer (Dow Corning). The mixture was then subjected to shear mixing for a short time (~5 min) to ensure uniform blending of the crosslinker and the host matrix. The mixture was then degassed in a vacuum for 30 min. Microchips based on comb-shaped microchannels
(35 µm in depth) with one inlet and three outlets were fabricated by soft lithography. A master was prepared by exposing and developing a photoresist pattern on a silicon wafer (SU-8 50; MicroChem). The PL–BSA–SWNT/PDMS/crosslinker mixture was poured onto the master. Ordinary PDMS/crosslinker mixture was also added to a silicon wafer without a photoresist pattern. High-temperature curing at 70 °C for 45 min was used to complete the crosslinking process in the polymer. After curing, PL–BSA–SWNT–PDMS composite and PDMS substrate were peeled away from the master and silicon wafer, respectively, and cut into rectangles in a manner that did not damage the microchannels. The master could be reused a number of times to produce multiple copies of the composite and substrate. The PL–BSA–SWNT–PDMS composite and PDMS substrate were closely bonded to each other by using a vacuum plasma coater (SC-708; Sanyu). For the NIR laser-irradiation experiments, the prepared microchips were cut along the line of a channel to form an L-shaped structure (Figures 3a and 3b). Finally, the inlet and outlets were connected to silicon tubing. The ordinary PDMS microchip was fabricated in the same way as the PL–BSA–SWNT–PDMS microchip, except for the process of mixing the SWNT complex and PDMS in dichloromethane. The SWNT–PDMS microchip was prepared in a manner similar to the PL–BSA–SWNT–PDMS microchip.

**Temperature assay.** A phosphate-buffered saline (PBS) (pH 7.3) (Oxoid) containing 5-TAMRA (110 nM) (Invitrogen) was introduced into the microchannel. The temperature distribution in the microchannel was determined from the fluorescence intensity distribution of 5-TAMRA in solution, and investigated by using a beam from a single laser (1064 nm) incorporated into the fluorescence microscopy set-up as described previously: the laser beam was focused inside the microchannel by using the objective (UPlanApo; Olympus, ×20). The fluorescence images before and during the NIR laser irradiation were recorded with a color charge-capture device video camera (DC220; DAGE) combined with a triple-band filter (DAPI/FITC/TRITC v2; Chroma Technology), and recorded on videotape for subsequent analysis. The fluorescence intensities of 5-TAMRA in the microchannel were analyzed by means of imaging-analysis software (MetaMorph; Universal Imaging).
Phase transition of polymer gel. PNIPAM (100 mg) (Aldrich; average $M_n = 20,000$–25,000, LCST $\sim 32 ^\circ C$) was dissolved in distilled water (10 mL) by sonication and the solution was filtered through a poly(vinylidene difluoride) (PVDF) membrane (Millipore; pore size = 220 nm). For fluorescence labeling studies, ANS (20 µM) (Invitrogen) in aqueous solution (100 µL) was mixed with the PNIPAM solution (900 µL). The solution (PNIPAM only or PNIPAM containing ANS) was introduced into the microchannel. The real-time phase transition of PNIPAM in the microchannel was assessed by using the same setup as used for temperature assay, but equipped with a custom filter set [excitation filter (BP 330-385; Olympus), dichroic mirror (FT 395; Zeiss), emission filter (LP 397; Zeiss)].

Supporting Video Legends:

Supporting Video 1

Ultrafast microthermal control by photoinduced PL–BSA–SWNT–PDMS.

Supporting Video 2

Destruction of the PDMS matrix by photoinduced SWNT–PDMS.

Supporting Video 3

Phase transition of PNIPAM in real time.