Supporting Information for

Selective extraction of semiconducting single-walled carbon nanotubes with a thermoresponsive polymer

Experimental details for the poly(N-isopropylacrylamide) (PNIPAM) extraction of single-walled carbon nanotubes (SWCNTs).

Two different types of SWCNTs were used: CoMoCAT (Signis® CG100, Sigma-Aldrich, USA; diameter: 0.7 – 1.3 nm) and HiPCO (Raw, Nanointegris; diameter: 0.8 – 1.2 nm). A 9 mg portion of CoMoCAT or an 80 mg portion of HiPCO was dispersed in 10 mL of H$_2$O containing 2.0 wt.% sodium cholate (SC; Wako, Japan) using a probe tip ultrasonicator (TOMY, UR-20R, Japan) over 1.5 h in a cold bath. The dispersion was then centrifuged (TOMY, Suprema 21, Japan) at 16,200 g for 3 h with a swing rotor. A 50 µL aliquot of the SWCNT dispersion and 10 µL of a 50 mM sodium hypochlorite (NaClO; Nacalai Tesque Inc., Japan) aqueous solution were mixed in an Eppendorf tube a with vortex mixer, which was followed by mixing with 200 µL of a 1 wt.% PNIPAM (carboxylic acid terminated, avg. Mn: 10,000, Sigma-Aldrich, USA) aqueous solution. The prepared solution was heated to 45 °C and incubated for 15 minutes. To completely remove the globules of PNIPAM, the solution was centrifuged at 8,000 g for 5 minutes. Finally, the liquid phase was collected. In the comparison of surfactants in the SWCNT dispersion, Brij® S 100 (Mw. ~ 4,670, Sigma-Aldrich, USA) and sodium dodecyl sulfate were used instead of SC.

Optical absorption spectra of the obtained samples were collected on a UV-vis-NIR spectrophotometer (UV-3600, SHIMADZU corp., Japan) with a 10 mm path length semi-microcuvette. For the optical absorption spectra, four sets of collected samples extracted under the same conditions were examined at one time. The SWCNTs captured inside the PNIPAM globules were re-dispersed after collection of the liquid phase by mixing the sample with ion-exchanged water with a vortexer.

Continuous PNIPAM extraction of the semiconducting SWCNTs.

The first extraction of the semiconducting SWCNTs above the LCST and the collection of the liquid phase was performed as mentioned above. To the obtained globule phase were added 50 µL of
the SWCNT dispersion in 2.0 wt.% SC, 100 µL of distilled water (DI water) and 30 µL of 50 mM sodium hypochlorite (NaClO), and the solution was mixed with a vortexer at room temperature (below the LCST). Note that the aggregated SWCNTs were not removed during the continuous PNIPAM extraction process. Then, the prepared solution was heated to 45 °C. After incubation for 15 minutes, the phase-changed solution was centrifuged at 8,000 g for 5 minutes, and the resulting liquid phase was collected. The globule phase from the second extraction step was used for the third extraction process, which was performed according to the same procedure described above.

Quantitative analysis of the purity of the extracted (6,5) SWCNTs (Figure S1).

The purity of the (6,5) nanotubes in the liquid phase was quantitatively calculated by comparing the $S_{22}$ absorption peak area of the (6,5) nanotubes with the sum of the absorbance in the range 400–700 nm. The optical absorption by the SWCNTs in the UV region, which can be fitted to a Lorenz function, overlaps with the absorption peaks in the visible-NIR region that correspond to the interband electronic transitions in the SWCNTs and therefore must be subtracted from the obtained absorption spectra to assess the purity of the (6,5) nanotubes. The Lorenz function for subtracting the overlaid background absorption in the visible to NIR region had a peak at 4.6 eV ($\lambda = 270$ nm), and the parameters in the function were set so that no absorbances below zero value were obtained in the whole region after subtracting the background absorption.

The absorption peak area of $S_{22}$ for the (6,5) nanotubes and the total absorbance in the range 400–700 nm were calculated by multiplying the absorbance by the energy range of photons as follows:

$$ I = \sum_i A(E) \Delta E $$  \hspace{1cm} (1)

where $I$ is the total area of optical absorption; $A(E)$ is the absorbance at the energy of photons (eV); and $\Delta E$ is the energy of the photons (eV). The purity of the (6,5) nanotubes was calculated by using the following equation:

$$(\text{purity}) = \frac{I(526 - 620\text{nm})}{I(400 - 700\text{nm})} \times 100(\%)$$  \hspace{1cm} (2)
Figure S1. Optical absorption spectra of (a) the pristine SWCNT solution and (b) the sample extracted in the liquid phase that was shown in Figure 3. The green solid lines in (a) and (b) represent the Lorenz functions used to subtract the background absorption whose peaks are located in the UV region. (c) Optical absorption spectra after subtracting the background absorption as shown in (a) and (b) for the pristine SWCNTs (black solid line) and the sample extracted in the liquid phase (red solid line). The blue and gray shaded regions represent the absorption peak area of S$_{22}$ for the (6,5) nanotubes and the total S$_{22}$ and M$_{11}$ absorption area in the range 400–700 nm, respectively. Each absorption area is used in the calculation of the purity by multiplying the absorbance by the energy range of the photons.
Figure S2. Photographs of an aqueous PNIPAM solution with SWCNTs dispersed in H₂O containing (a) SC, (b) Brij and (c) SDS, respectively. All solutions were heated to 45 °C and incubated for 15 minutes.
Figure S3. The six sets of optical absorption spectra of the extracted liquid phase of the CoMoCAT SWCNTs. The PNIPAM concentration was 1 wt.% in all samples. The spectra were normalized to the absorbance at 350 nm for easy comparison.