

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 H₂O 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 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

1 the SWCNT dispersion in 2.0 wt.% SC, 100 μ L of distilled water (DI water) and 30 μ L of 50 mM
 2 sodium hypochlorite (NaClO), and the solution was mixed with a vortexer at room temperature
 3 (below the LCST). Note that the aggregated SWCNTs were not removed during the continuous
 4 PNIPAM extraction process. Then, the prepared solution was heated to 45 $^{\circ}$ C. After incubation for
 5 15 minutes, the phase-changed solution was centrifuged at 8,000 g for 5 minutes, and the resulting
 6 liquid phase was collected. The globule phase from the second extraction step was used for the third
 7 extraction process, which was performed according to the same procedure described above.

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

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12 The purity of the (6,5) nanotubes in the liquid phase was quantitatively calculated by comparing
 13 the S_{22} absorption peak area of the (6,5) nanotubes with the sum of the absorbance in the range 400–
 14 700 nm. The optical absorption by the SWCNTs in the UV region, which can be fitted to a Lorentz
 15 function, overlaps with the absorption peaks in the visible-NIR region that correspond to the
 16 interband electronic transitions in the SWCNTs and therefore must be subtracted from the obtained
 17 absorption spectra to assess the purity of the (6,5) nanotubes. The Lorentz function for subtracting the
 18 overlaid background absorption in the visible to NIR region had a peak at 4.6 eV ($\lambda = 270$ nm), and
 19 the parameters in the function were set so that no absorbances below zero value were obtained in the
 20 whole region after subtracting the background absorption.

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

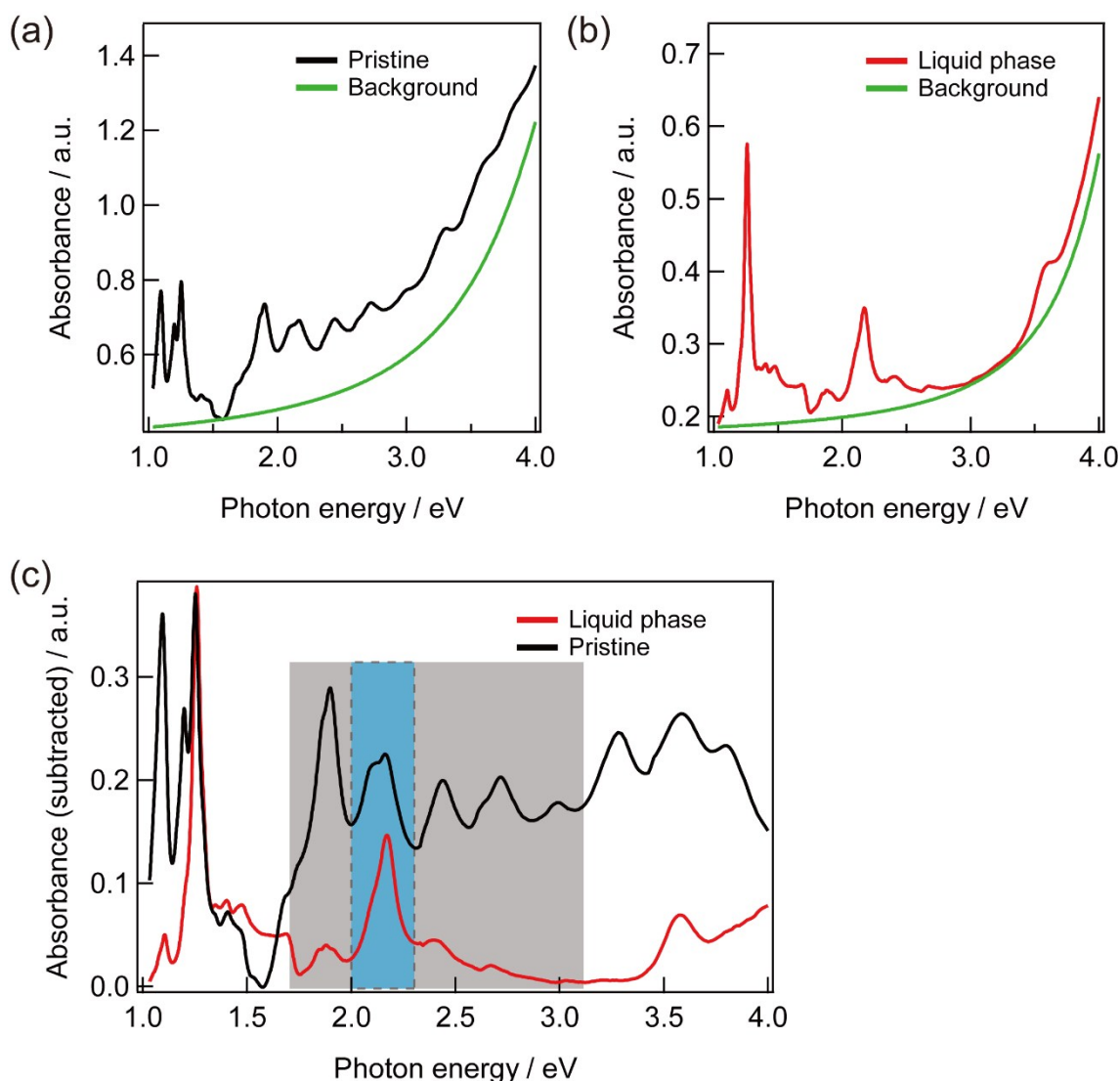
$$24 \quad I = \sum_i A(E) \Delta E \quad (1)$$

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

$$28 \quad (\text{purity}) = \frac{I(526 - 620 \text{ nm})}{I(400 - 700 \text{ nm})} \times 100(\%) \quad (2)$$

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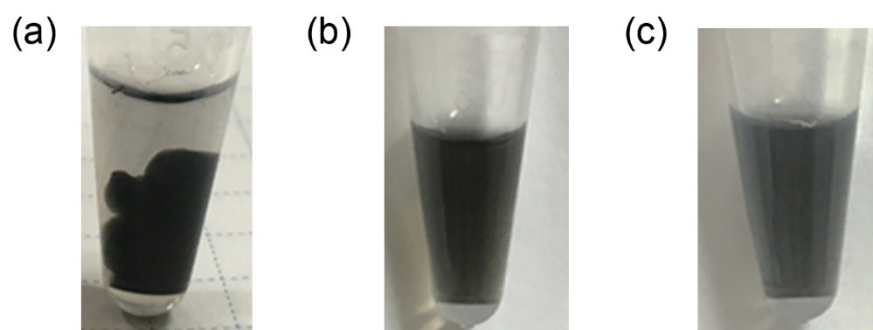
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Figure S1. Optical absorption spectra of (a) the pristine SWCNT solution and (b) the sample extracted in the liquid phase that was shown in Figure 3. The green solid lines in (a) and (b) represent the Lorentz functions used to subtract the background 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.

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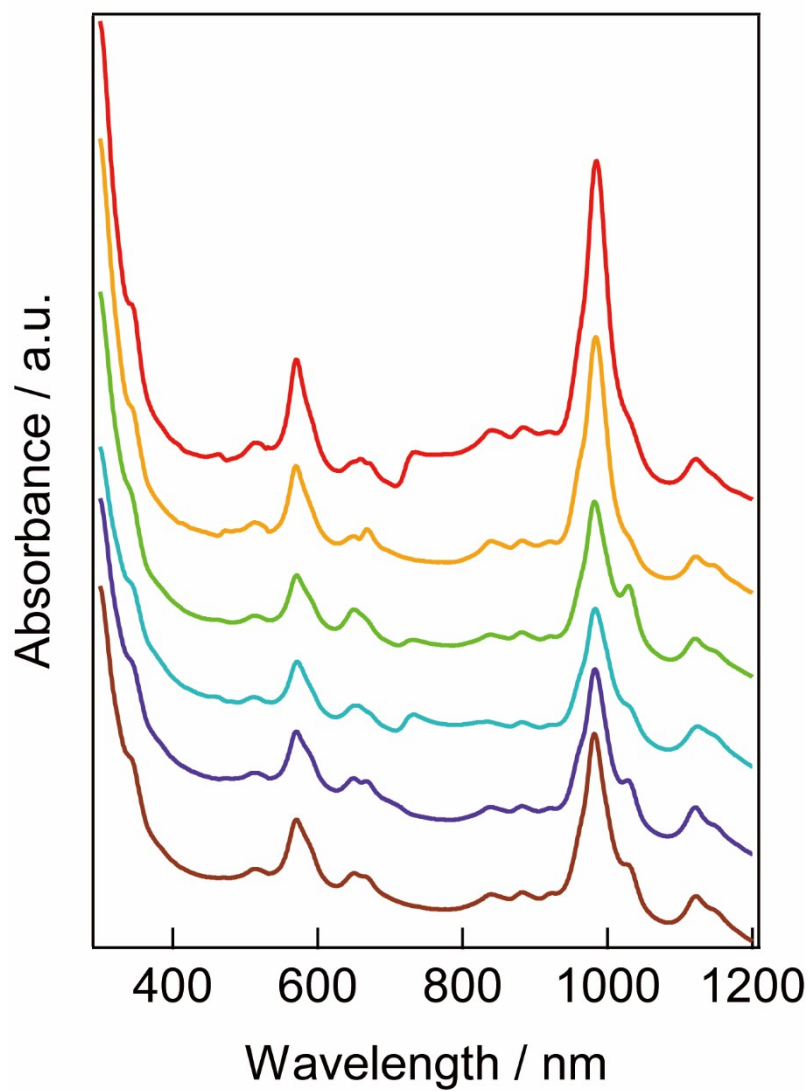


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2 **Figure S2.** Photographs of an aqueous PNIPAM solution with SWCNTs dispersed in H₂O
3 containing (a) SC, (b) Brij and (c) SDS, respectively. All solutions were heated to 45 °C and
4 incubated for 15 minutes.

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3 **Figure S3.** The six sets of optical absorption spectra of the extracted liquid phase of the CoMoCAT
4 SWCNTs. The PNIPAM concentration was 1 wt.% in the all samples. The spectra were normalized
5 to the absorbance at 350 nm for easy comparison.

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