Electronic Supplementary Material

Tunable Separation of Single-Walled Carbon Nanotubes by Dual-Surfactant Density Gradient Ultracentrifugation

Pei Zhao¹, Erik Einarsson¹,², Georgia Lagoudas³, Junichiro Shiomi¹, Shohei Chiashi¹, and Shigeo Maruyama¹

¹ Department of Mechanical Engineering, The University of Tokyo, Tokyo 113-8656, Japan
² Global Center of Excellence for Mechanical Systems Innovation, The University of Tokyo, Tokyo 113-8656, Japan
³ Department of Bioengineering, Rice University, Houston 77005, USA

Supporting information to DOI 10.1007/s12274-011-0118-9

1. Experimental details

1.1 Separations by Case I, without an intermediate stage

Figure 1(b)—Trial 1

Dispersion:
0.125% w/v (7.5 mg) of SWNTs synthesized by the alcohol catalytic chemical vapor deposition (ACCVD) method [1] were dispersed in 6 mL of D₂O containing 0.5% w/v (0.03 g) of sodium deoxycholate (DOC). This suspension was then bath sonicated for 10 min, followed by horn ultrasonication for 1 h (UP400S, Hielscher Ultrasonics, 1 cycle, 400 W). The suspension was put into four 4.9 mL, 5.2 cm long polycarbonate centrifuge tubes (1.4 mL/tube, total amount of 5.6 mL, some of the suspension may vaporize during ultrasonication) and then ultracentrifuged at 78 kr/min (276,000 g, Hitachi CS 100GXL) at 22 °C for 15 min using an angled rotor (Hitachi Koki S100AT). Both acceleration and deceleration values were set to 9 (maximum). The upper portion of the supernatant was extracted as a DOC–SWNT dispersion.

Sample layer:
3.5 mL of the DOC–SWNT dispersion was mixed with 3.5 mL of 60% iodixanol (OptiPrep™, Sigma–Aldrich Co., Ltd) to form the sample layer. At this time the DOC concentration in the sample layer is diluted to 0.25% w/v.

Density gradient column:
Density gradient layers of 20, 30, and 40% concentration iodixanol were prepared with no surfactant in them, and then bath sonicated for 1 h. In a polycarbonate centrifuge tube (4.9 mL volume, 1.3 cm in diameter and 5.2 cm in length), 1 mL of the 40% layer was put at the bottom, followed by 1 mL of the 30% layer and then 1 mL of the 20% layer on top of that. The upper layers were both deposited drop by drop so as to minimize mixing. The tubes were then sealed, and laid horizontally for 1 h to make a continuous density gradient. In total four centrifuge tubes were used for the DGU process.

Ultracentrifugation process:
Using a syringe needle, 1.5 mL of the SWNT dispersion was injected into the middle of each density gradient
column (within the 30% iodixanol layer), and the columns were then put into metal capsules. The capsules were then placed in a swinging bucket rotor and ultracentrifuged at 52 kr/min (197,000 g, Hitachi Koki S52ST) at 15 °C for 22 h. In this case the acceleration and deceleration values were set to five (moderate).

**Figure 1(b)—Trial 2**

All DGU experimental parameters were the same as those used in Trial 1 except that the SWNT dispersion was prepared by dispersing 0.125% w/v (7.5 mg) of ACCVD-SWNTs in 6 mL of D₂O containing both 0.5% w/v (0.03 g) DOC and 1.25% w/v (0.075 g) SDS.

**Figure 1(b)—Trial 3**

All DGU experimental parameters were the same as those used in Trial 1 except that density gradient layers of 20, 30, and 40% concentration iodixanol were prepared with 1.5% (0.015 g) of SDS in each.

**Figure 1(b)—Trial 4**

All DGU experimental parameters were the same as those used in Trial 3 except that the SWNT dispersion was prepared by dispersing 0.125% w/v (7.5 mg) of ACCVD-SWNTs in 6 mL of D₂O containing both 0.5% w/v (0.03 g) DOC and 1.0% w/v (0.06 g) SDS.

**Figure 1(b)—Trial 5**

All DGU experimental parameters were the same as those used in Trial 3 except that the SWNT dispersion was prepared by dispersing 0.125% w/v (7.5 mg) of ACCVD-SWNTs in 6 mL of D₂O containing both 0.5% w/v (0.03 g) DOC and 1.25% w/v (0.075 g) SDS.

**Figure 1(b)—Trial 6**

All DGU experimental parameters were the same as those used in Trial 3 except that the SWNT dispersion was prepared by dispersing 0.125% w/v (7.5 mg) of ACCVD-SWNTs in 6 mL of D₂O containing both 0.5% w/v (0.03 g) DOC and 1.5% w/v (0.09 g) SDS.

**Figure 1(b)—Trial 7**

All DGU experimental parameters were the same as those used in Trial 3 except that the SWNT dispersion was prepared by dispersing 0.125% w/v (7.5 mg) of ACCVD-SWNTs in 6 mL of D₂O containing both 0.5% w/v (0.03 g) DOC and 1.75% w/v (0.105 g) SDS.

**Figure 1(b)—Trial 8**

All DGU experimental parameters were the same as those used in Trial 3 except that the SWNT dispersion was prepared by dispersing 0.125% w/v (7.5 mg) of ACCVD-SWNTs in 6 mL of D₂O containing only 1.25% w/v (0.075 g) SDS.

### 1.2 Separations for Case I, with an intermediate stage

**Figure 2(b)—Trial 9**

All DGU experimental parameters were the same as those used in Trial 3 except that the sample layer was formed by mixing 3.5 mL of DOC-SWNT dispersion with 3.5 mL of 60% iodixanol containing 0.0175 g of SDS. At this time the SDS concentration in the sample layer was 0.25% w/v.

**Figure 2(b)—Trial 10**

All DGU experimental parameters were the same as those used in Trial 9 except that the sample layer was formed by mixing 3.5 mL of DOC-SWNT dispersion with 3.5 mL 60% of iodixanol containing 0.035 g of SDS. At this time the SDS concentration in the sample layer was 0.5% w/v.

**Figure 2(b)—Trial 11**

All DGU experimental parameters were the same as those used in Trial 9 except that the sample layer was formed by mixing 3.5 mL of DOC-SWNT dispersion with 3.5 mL of 60% iodixanol containing 0.0525 g of SDS. At this time the SDS concentration in the sample layer was 0.75% w/v.
**Figure 2(b)—Trial 12**
All DGU experimental parameters were the same as those used in Trial 9 except that the sample layer was formed by mixing 3.5 mL of DOC–SWNT dispersion with 3.5 mL of 60% iodixanol containing 0.07 g of SDS. At this time the SDS concentration in the sample layer was 1.0% w/v.

**1.3 Separations for Case II, without an intermediate stage**

**Figure 3(b)—Trial 13**

**Dispersion and sample layer:**
0.125% w/v (10 mg) of SWNTs synthesized by the alcohol catalytic chemical vapor deposition (ACCVD) method were dispersed in 8 mL of D2O containing 0.5% w/v (0.05 g) DOC. This dispersion was then bath sonicated for 10 min, followed by horn ultrasonication for 1 h. The suspension was then ultracentrifuged at 78 kr/min at 22 °C for 15 min. The upper portion of the supernatant was extracted and directly used as the sample layer.

**Density gradient column:**
Density gradient layers of 20%, 30%, and 40% iodixanol concentration were prepared by mixing iodixanol with D2O containing 2% w/v SDS. In the centrifuge tube, 0.6 mL of the 60% layer without surfactants was first put at the bottom, followed by a 1 mL 40% layer, a 1 mL 30% layer, and then a 0.4 mL 20% layer on top of that. The tubes were then sealed and laid horizontally for 1 h to make a continuous density gradient.

**Ultracentrifugation process:**
1.5 mL of the SWNT dispersion was placed on top of the as-prepared density gradient. The capsules were then ultracentrifuged at 52 kr/min at 15 °C for 19 h.

**Figure 3(b)—Trial 14**
All DGU experimental parameters were the same as those used in Trial 13 except that the SWNT dispersion was prepared by dispersing 0.125% w/v (10 mg) of ACCVD-SWNTs in 8 mL of D2O containing both 0.5% w/v (0.04 g) DOC and 0.5% w/v (0.04 g) SDS.

**Figure 3(b)—Trial 15**
All DGU experimental parameters were the same as those used in Trial 13 except that the SWNT dispersion was prepared by dispersing 0.125% w/v (10 mg) of ACCVD-SWNTs in 8 mL of D2O containing both 0.5% w/v (0.04 g) DOC and 1.25% w/v (0.1 g) SDS.

**Figure 3(b)—Trial 16**
All DGU experimental parameters were the same as those used in Trial 13 except that the SWNT dispersion was prepared by dispersing 0.125% w/v (10 mg) of ACCVD-SWNTs in 8 mL of D2O containing only 1.25% w/v (0.1 g) SDS.

**1.4 Other supplementary separations**

**Figure S-2**
All DGU experimental parameters were the same as those used in Trial 13 except that the sample layer was formed by adding 1.25% w/v SDS to the extracted DOC–SWNT dispersion before it was placed on top of the as-prepared density gradient.

**Figure S-5(a)**
All DGU experimental parameters were the same as those used in Trial 13 except that no surfactants were contained in the density gradient layers.

**Figure S-5(b)**
All DGU experimental parameters were the same as those used in Trial 16 except that no surfactants were contained in the density gradient layers.
2. Supplementary Figures

**Figure S-1**  Density gradient ultracentrifugation results starting with HiPCO SWNTs [2] as a function of increasing concentration of SDS, using Case I and Case II (both without an intermediate stage). They show the reproducibility of our experimental methods for different raw SWNT samples.

**Figure S-2**  Density gradient ultracentrifugation results in Case II with an intermediate stage. After the preparation of 0.5% w/v DOC–SWNT dispersion, 1.25% w/v SDS was introduced at an intermediate stage. The density gradient contains 0.667%, 1.0%, and 1.33% w/v SDS in 20%, 30%, and 40% layers, respectively. It shows that with an intermediate stage, trials in Case II can have similar results as without this stage.
Figure S-3  Optical absorbance spectra from the time-dependent evolution of Trial 15
Figure S-4  Trials repeated using only H₂O (SWNTs were initially dispersed by H₂O and the density gradients were formed by H₂O) showing that differences in the hydration layers of SWNT micelles do not make a significant difference to the final DGU results.

Figure S-5  Density gradient ultracentrifugation results using Case II in a density gradient with no surfactant using (a) 0.5% DOC-dispersed SWNTs; and (b) 1.25% SDS-dispersed SWNTs. SDS–SWNT micelles show adsorption of surfactant molecules and higher density than DOC–SWNT micelles. The comparison between them reveals that SDS–SWNT micelles have higher densities than DOC–SWNT micelles.

References
