Supporting Information for: Band Structure Dependent Electronic Localization in Macroscopic Films of Single-Chirality Single-Wall Carbon Nanotubes

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1. Chirality sorting process

Preparation of (6, 5), (6, 6), and (7, 4) suspensions:

For (6, 5) nad (7, 4) samples, CoMoCAT SG65i as-grown SWCNT powders (from MilliporeSigma) were dispersed into water with assist of 1% sodium deoxycholate (DOC, MilliporeSigma). For (6, 6) samples, CoMoCAT CG200 as-grown SWCNT powders (from MilliporeSigma) were dispersed. A tip-type ultrasonic homogenizer (XL-2000 Sonicator, QSonica) was used while the sample was immersed in a cold-water bath, followed by ultracentrifugation at 247,000 g for 1.5 h. Supernatants were collected after centrifugation for sorting. On the other hand, two polymers of different hydrophilicity were mixed together, with one (PEG, molecular weight (MW) = 6000 Da) more hydrophilic and one (dextran, MW $\approx$ 68 kDa) more hydrophobic. When SWCNT suspensions were mixed with this two-polymer system and other surfactants, including sodium dodecyl sulfate (SDS, MilliporeSigma) and sodium cholate (SC, MilliporeSigma), the careful selection and control of surfactant composition and concentration lead to the selective wrapping of SWCNTs depending on their electronic structures. These selectively wrapped SWCNTs have different hydrophilicity and are partitioned differently across two phases based on electronic structures. By extracting one phase containing more shares of targeted species and adding a fresh new polymer phase, the partition and sorting process continues to purify suspension till nearly single-chirality suspensions.

Preparation of (8, 5) suspension:

(8, 5) suspension was sorted and separated from SWCNT SG65i as-grown powder following similar procedures used in ATPE technique. The difference, however, is that instead of dispersing SWCNTs with surfactant combinations, the dispersant used is DNA molecules. The SWCNT/DNA mass ratio was 1:2 with SWCNT concentration being 0.5 or 1 mg/mL. DNA molecules have better selectivity and purity [1, 2, 3, 4] and the details of the separation process can be found in reference [3].

Preparation of (10, 3) suspension:

(10, 3) suspension was prepared using column chromatography and details are described in reference [5]. Briefly, 100 mg HiPco SWCNTs (R1831, 1.0 ± 0.3 nm in diameter, NanoIntegris) were dispersed in 100 mL of an aqueous solution containing 1.0% SDS (97%, Tokyo Chemical Industry) and 0.5% SC (98%, Tokyo Chemical Industry) for 3 h using a tip-type ultrasonic homogenizer (Sonifier 250D, Branson) while the sample was immersed in a cold-water bath, followed by ultracentrifugation at 210,000 g for 2 h using an angle rotor (S50A, Hitachi Koki). The upper 80% of the supernatant was collected for separation using a conventional chromatography system (AKTA explorer 10S, GE Healthcare) installed in a chamber maintained at $18 - 20$°C. About 80 ml of the SWCNT solution was loaded onto a column (Hiscale 50/20, GE Healthcare) filled with 430 ml gel beads (Sephacryl S-200 HR, GE Healthcare). After elution of unbound SWCNTs with an aqueous solution of SDS (1.0%) + SC (0.5%), the adsorbed SWCNTs were eluted and collected through stepwise elution chromatography with DOC (96%, Wako Chemical Industries), where the DOC concentration was increased from 0.12 to 0.18% in 0.01% steps for fixed concentrations of SDS (1.0%) + SC (0.5%). Single-chirality (10,3) SWCNTs were eluted at a concentration of SDS (1.0%) + SC (0.5%) + DOC (0.16%).

2. Additional SWCNT characterizations

A Bruker Multimode 8 AFM was used to measure the thickness of single-layer films. Figure S1 demonstrates the typical thickness of a (6,6) film to be $\sim$12 nm. The yellow dashed line in Fig. S1a indicates the line along which the height profile in Fig. S1b was measured. A typical scanning electron microscope (SEM) image shown in Fig. S2a was taken using a JEOL 6500F SEM. The corresponding X-ray spectroscopy data shown in Fig. S2b were taken using an X-ray photoelectron spectrometer (PHI Quantera XPS). The monochromatic X-ray source was Al Kα with an energy of 1486.7 eV, a beam spot size of 200 μm, and a power of 50 W.

There is no observable Na (sodium) peak, indicating the absence of sodium surfactants in this study. Also, there is no observable N (nitrogen) peak, indicating the absence of filter membrane residues because the membranes we used contained polyvinylpyrrolidone (PVP) ($(C_6H_9NO)_n$), which includes N. Both SEM and XPS confirm that any residues of surfactants and filter membrane are minimal. In addition, an optical method was employed to characterize the alignment quality of the produced films. Specifically, a 660 nm-wavelength laser diode was normally incident onto the film transferred onto a transparent substrate, and a photodetector measured the power of the transmitted light. As the laser polarization direction was rotated by a half-wave plate, aligned films displayed polarization-dependent attenuation while random films displayed isotropic attenuation, as shown in Fig. S3. This is because that optical absorption is strong when the light polarization is along the nanotube axis while it is weak in the perpendicular direction. The length distribution of individual SWCNTs were also characterized by Bruker Multimode 8 AFM. A representative AFM image of individual SWCNTs deposited on a SiO_2/Si substrate is shown in Fig. S4a. By counting the SWCNT lengths displayed in the AFM image, we obtained the length distribution, as shown in Fig. S4b, and the typical average length was ~ 200 nm.

The Raman spectrum for a prepared film shown in Fig. S5 was obtained with a home-built Raman spectroscopy system under 532 nm laser excitation. As described in Ref. 36 of the main text, the characteristic distance between defects in a SWCNT lattice, L_a, can be calculated by $L_a = \frac{560(\text{nm})}{E_l^4}(I_G/I_D)$, where E_l is the laser excitation energy in units of eV and I_G/I_D is the Raman intensity ratio of the G peak to the D peak. From the manufacturer's datasheets, SG65i has $I_G/I_D > 20$ at $E_l = 1.959$ eV, CG200 has $I_G/I_D > 15$ at $E_l = 1.959$ eV, and HiPco has $I_G/I_D > 25$ at $E_l = 2.33053$ eV. With these values, we can estimate L_a to be 761 nm, 570 nm, and 475 nm, respectively. The typical average length of SWCNTs in the films used in our study was ~ 200 nm (see Fig. S4), which is smaller than L_a. Furthermore, the average I_G/I_D for produced films at $E_l = 2.33053$ eV was ~ 3.5, as shown in Fig. S5, which is much smaller than

the ratio for the raw materials.

References

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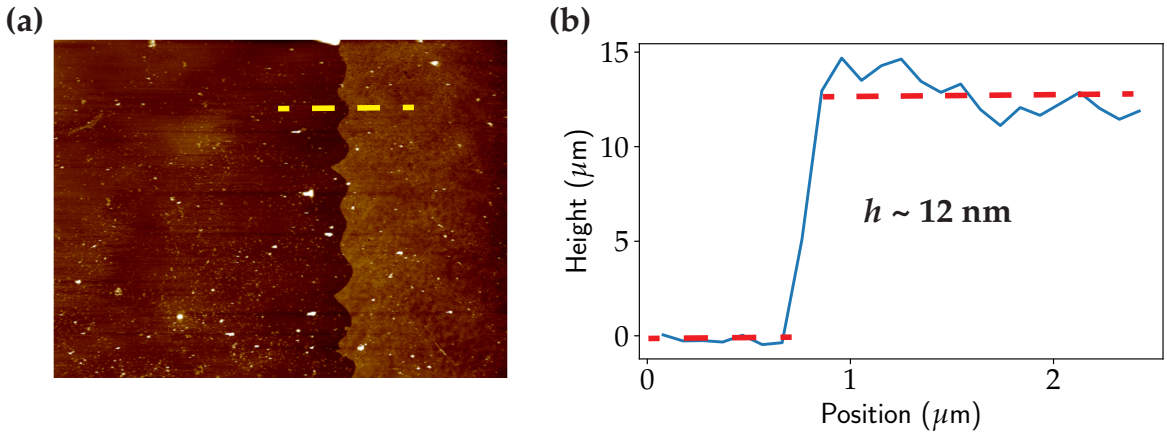

Figure S1: Thickness characterization of SWCNT films. (a) The AFM image of a representative (6,6) film on a SiO_2/Si substrate and (b) corresponding height profile across the yellow dashed line in (a).

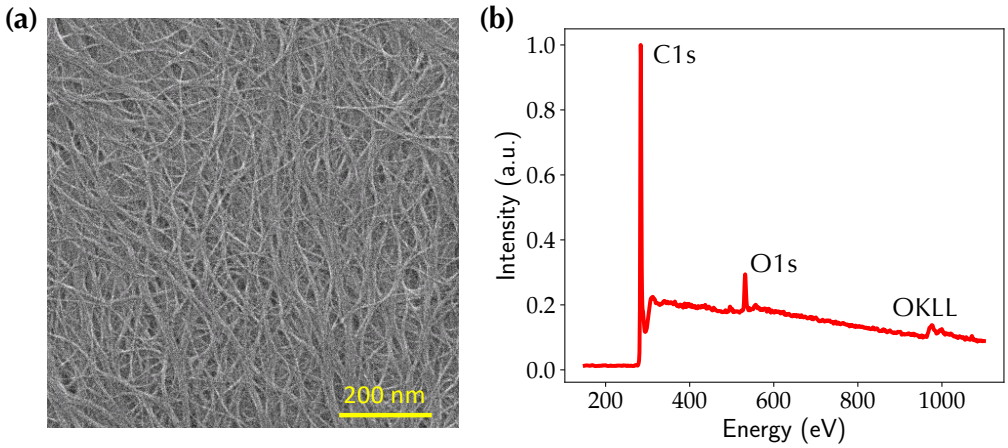

Figure S2: (a) A SEM image and (b) XPS spectrum of produced film.

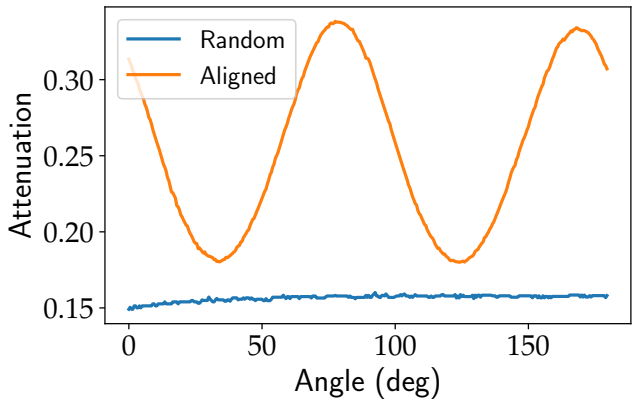

Figure S3: Polarization-dependent attenuation for aligned and random films.

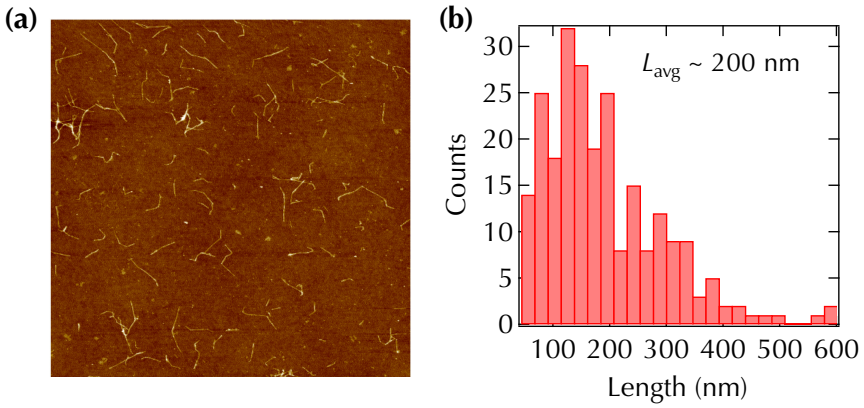

Figure S4: (a) The AFM image of individual SWCNTs deposited on a SiO_2/Si substrate and (b) corresponding length distribution.

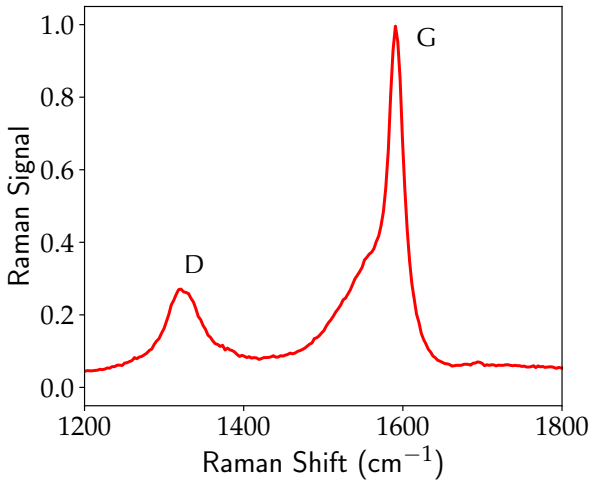

Figure S5: A representative Raman spectra.