A novel strategy for high-performance transparent conductive films based on double-walled carbon nanotubes

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1 Experiment

Materials

The starting monomers, 3,6-dibromo-9-(heptadecan-9-yl)-9H-carbazole (I), 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (II), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (III), 4,4'- bis(4,4,5,5) 5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1'-biphenyl **(IV)**, and catalyst tetrakis(triphenylphosphine)palladium (Pd (PPh₃)₄) were purchased from Energy Chemical and used as raw products without further purification. Toluene was dried with molecular sieve type 3A. Tetrahydrofuran (THF) and saturated potassium carbonate (K₂CO₃) solution were used as two-phase solvent without any treatment before used. Three kinds of carbon nanotubes (CNTs) used in this work were purchased commercially. They are Hipco-CNTs (SWCNTs produced via the highpressure decomposition of carbon monoxide, NanoIntegris, Batch#P22-003), Arc-CNTs (SWCNTs grown by arc discharge, Carbon Solution, Lot#AP-A204) and double walled carbon nanotubes (DWCNT, Cheaptubes, SKU#0101).

Analyses

¹H NMR spectra were measured on a Bruker300M spectrometer. Gel permeation chromatography (GPC) was undertaken with a waters1515 of Waters Company from America. Thermo gravimetric analyses (TGA) were conducted on a TG 209 F1of NETZSCH company from German. Sonication process was conducted on a tip-top ultrasonic disperser (Sonics VCX-500). Centrifugation was conducted on an AllegraTM X-22R centrifuge from Beckman Coulter. UV-Vis-NIR spectra were

recorded on a Cary Series UV-Vis-NIR spectrophotometer. Raman spectra were recorded on a LABRAM HR laser resonance Raman detector from France Horiba. Sheet resistance was measured by a four-point probe meter (MCP-T360, Mitsubishi Chemical Analytech).

2 Synthetic procedures

Synthesis of polymers

A certain amount of monomers and catalytic amount of Pd (PPh₃)₄ (23.11 mg, 0.02 mmol, 0.02 equiv) were added to a 100mL two necked round-bottom flask equipped with a magnetic stir bar. 15mL THF was injected to dissolve the powder mixture and stirred mildly. Subsequently, saturated K₂CO₃ aqueous solution (10mL) was injected into the reaction flask. Then, both the organic phase and aqueous phase were frozen with liquid nitrogen. The whole reaction system was vacuumed for 30 minutes in the function of oil pump. After the degas process, the two-phase reactant was stirred vigorously and refluxed for several days in the protection of nitrogen. After cooling down to room temperature, the reaction mixture was poured into a large amount of cold methanol to generate plenty of cotton-shaped precipitates, which were collected by filtration and washed with methanol supernatant, deionized water and acetone respectively and dried under vacuum at 30°C overnight. In order to narrow the distribution of molecular weight, the polymer was purified by Soxhlet extraction with hexane, ethanol and methylene dichloride successively. Finally, methylene dichloride extracted the most and we use this extraction as the experimental product.

PCC. Monomer I (563.45 mg, 1.0 mmol) and monomer II (657.58 mg, 1.0

mmol). Yield 450 mg, 55.76%. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.56 \sim 7.56$ (m, 12H), 4.78 (broad, 1H), 4.66 (broad, 1H), 2.47 ~ 2.40 (broad, 4H), 2.03 (broad, 4H), 1.29~1.18 (m, 48H), 0.84 (t, 6H), 0.76 (t, 6H). GPC indicates that PCC has a number-average molar mass (Mn) of 5879, weight average molar mass (Mw) of 10193 and poly-dispersity (PDI) of 1.734.

PCB. Monomer I (563.45 mg, 1.0 mmol) and monomer III (330.03 mg, 1.0 mmol). Yield 168 mg, 35.15%. ¹H NMR (300 MHz, CDCl₃): δ = 8.49 ~ 7.87 (m, 10H), 4.61 (broad, 1H), 2.35 (broad, 2H), 1.97 (broad, 2H), 1.15 (m, 24H), 0.82 (m, 6H). GPC indicates that Mn = 5243, Mw = 6527. PDI = 1.245.

PCDB. Monomer I (563.45 mg, 1.0 mmol) and monomer **W** (406.13 mg, 1.0 mmol). Yield 415 mg, 74.91%. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.76 \sim 7.51$ (m, 14H), 4.61 (broad, 1H), 2.33 (broad, 2H), 1.95 (broad, 2H), 1.37~1.14 (m, 24H), 0.82 (m, 6H). GPC indicates that Mn = 5481, Mw = 11266, PDI = 2.056.





Fig. S1 ¹HNMR spectra of (a) PCC, (b) PCB and (c) PCDB



Fig. S2 (a) Absorption spectra and (b) TG curves of PCC, PCB and PCDB

3 Preparation of CNT dispersions

3 mg of PCC, PCB and PCDB were added to 6 mL dried toluene respectively. Next, 1.5 mg of three kinds of CNTs mentioned above was added to the three polymer solutions respectively to gain nine suspensions. The suspensions were sonicated using a tip-top ultrasonic disperser (Sonics VCX-500) for 30 minutes at 225 W at 20 °C followed by centrifugation at 20000 g for 30 minutes. The up solutions were collected as dispersions and confirmed by UV-Vis-NIR absorption and Raman spectra.



Fig. S3 (a) Absorption spectra of PCC-FWCNTs and (b) maximum absorbance value of PCC-dispersed CNTs with different diameters

Fig. S4 (a) Optical photo of five slides randomly selected and (b) their optical

differences

4 Calculation of DWCNT, PCC concentration and DWCNT yield in dispersion

The concentration of DWCNTs was calculated as follow:

a. A membrane to collect DWCNTs was weighted 12.18mg

- 5mL DWCNT dispersion was filtrated and the DWCNT film was wash by THF till the detergent lose fluorescence
- c. The DWCNT film was dried at 80°C and the total weight was 12.59mg, the weight of DWCNTs was 0.41mg
- d. 0.41÷5=0.082, the concentration of DWCNTs in the dispersion was 0.082mg/mL
 The concentration of PCC was calculated as follow:
- a. Prepare 1mg/mL PCC in toluene as original solution
- b. Dilute the original solution with toluene to 0.01, 0.008, 0.005 and 0.0025mg/mL and record the UV-Vis spectra (Fig. S5a), respectively.
- c. Draw a linear fitness (Fig. S5b) of each absorbance value in the maximum absorption wavelength (357nm) and the slope was 45.42321
- Measure the UV-Vis spectrum of DWCNT dispersion diluted 100 times and find the absorbance value of 0.25113 in 357nm
- e. 0.25113÷45.42321×100=0.55mg/mL

The result was slightly higher than the starting concentration of 0.5mg/mL, which could be explained by the evaporation of toluene during the sonication process.

The yield of DWCNTs was calculated as follow:

a. 0.082÷0.25÷0.9=36.4%

Where 0.082mg/mL was the resulting concentration, 0.25mg/mL was the starting concentration of DWCNTs and 90% was DWCNT purity.

Fig. S5 (a) UV-Vis spectra of PCC solution with different concentration and (b) linear fitness of absorbance (357nm) to concentration

5 Preparation of DWCNT TCFs

The original DWCNT dispersion was diluted ten times with toluene. The transparent conductive film was prepared on a clean slide via dip-coating. After dipping 30min under 50°C, the slide was processed under nitrogen flow and subsequently dried under 120°C for 30min. The surface resistance of the TCF was measured by four-point probe meter and the transmittance was conducted on the Cary Series UV-Vis-NIR spectrophotometer.

Fig. S6 SEM images of DWCNT TCFs with the magnification of 10.0k

Fig. S7 SEM images to show the bundles of DWCNT TCFs