Electronic Supplementary Information

Selective Diels-Alder cycloaddition on semiconducting single-walled carbon nanotubes for potential separation application

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Materials and methods

HiPco SWCNTs were product of Carbon Nanotechnologies Inc. (Houston, TX) and used without further treatment. 1-Aminoanthraquinone was purchased from Wuqiao Shunda Chemical Corporation and 1- aminoanthracene was prepared by reduction reaction of 1-aminoanthraquinone with Zn powder according to the literature [1]. Diethylene glycol and 2-bromo-2-methylpropionyl bromide were distilled prior to use. Tetrahydrafuran (THF) was distilled from sodium/benzophenone. Styrene was washed three times with 5% NaOH aqueous solution, and then distilled after drying with $MgSO_4$. All the other reagents were of analytical grade and used as received.

Raman spectra were measured on a LABRAM-HR Laser Confocal Raman Spectrometer. All the SWCNTs samples were suspended in methanol by ultrasonication and vacuum filtered with a 0.22 μm PTFE membrane. The obtained thin films were used for Raman (Generally, 3 spots were measured) and X-ray photoelectron spectroscopies (XPS) measurement. XPS was recorded on a Thermo-VG Scientific ESCALAB 250 spectrometer. The films were also observed with a field emission scanning electron microscope (SEM, FEI Sirion200). The spectra in the UV-vis-NIR range were obtained using a Shimadzu DUV-3700 spectrometer. The samples were all suspended in THF by ultrasonication and were measured without centrifugation. Thermal gravimetric analyses (TGA) were conducted on a Shimadzu DTG-60H instrument with a heating rate of 10 °C/min in a nitrogen flow. The SWCNT-p was as-received without treatment and all samples were dried in a vacuum oven at 40 °C overnight before measurement. High resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL 2010 transmission electron microscope operated at an accelerating voltage of 200 kV. Atomic Force Microscopy (AFM) measurements were performed on a Digital Instrument Multimode V operating in tapping mode under ambient conditions at a scan rate of 0.8 Hz. The SWCNT samples were suspended in methanol by sonication at the concentration of 0.1 mg/mL and drop casted onto freshly cleaved mica substrates.

Preparation of SWCNT-NH_2 via [4+2] cycloaddition

A typical procedure for the preparation of SWCNT-NH_2 is described as follows. SWCNT-p (15 mg) was added into 30 mL of diethylene glycol in a 100 mL glass flask. After ultrasonicating the mixture for 30 minutes, 1-aminoanthracene (131 mg, 0.67 mmol) was added and the flask was immersed in oil bath. The reaction was carried out while stirring at the desired temperature for 24h. The product was collected by vacuum filtration using a 0.22 μm PTFE membrane. After washing with THF thoroughly, the product was dispersed in THF by ultrasonication and then filtrated by the membrane. The procedure was repeated three times to remove the adsorbed 1-aminoanthracene until the filtrate was colorless. SWCNT-NH_2 was obtained after drying in a vacuum oven overnight.

A control experiment

SWCNT-p (6 mg) was added into 12 mL of diethylene glycol in a 50 mL glass flask. After ultrasonicating the mixture for 30 minutes, 1-aminoanthracene (53 mg, 0.27 mmol) was added and the mixture was stirred at room temperature for 24h. The product was processed as above and denoted as SWCNT-control.

Preparation of SWCNT-PSt through ATRP

SWCNT-NH_2 (15 mg) was dispersed in anhydrous THF (25 mL) by 30 min of ultrasonication. After triethylamine (0.7 mL, 5 mmol) was added, 0.6 mL (5 mmol) of 2-bromo-2-methylpropionyl bromide in 5 mL of anhydrous THF was added dropwise into the mixture at 0 °C for 30 min. The resulting mixture was stirred for 3 h at 0 °C and then at room temperature for 24 h. The product was collected by vacuum filtration and washed thoroughly with THF. After drying overnight, the product SWCNT-Br was obtained.

The SWCNT-Br (10 mg), CuBr (9 mg), 2, 2′-bipyridine (28 mg) and styrene (6.24 g) were placed in a dry 10 mL glass flask. The mixture was sonicated for 5 min and degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum and immersed in an oil bath at 110 °C. After reaction for 6 hours, the reaction was stopped by opening the tubes. The product was diluted with THF and collected by filtration, the recovered product was washed thoroughly with THF to remove the ungrafted PSt. The SWCNT-PSt was obtained after overnight drying.

Separation of SWCNT-PSt

8 mg of SWCNT-PSt was dispersed in 15 mL of THF by sonication for 30 min. The unreacted SWCNT-p deposited slowly, and the sedimentation could be accelerated by centrifugation (3000 rpm). After the mixture was stable, the black-grey supernatant liquid was transferred into a flask. The procedure was repeated six times until the supernatant seemed colorless and transparent. The collected supernatant was volatilized or vacuum-distilled to remove the solvent and the separated soluble SWCNT-PSt (4 mg) was obtained after vacuum drying at room temperature overnight.

Characterization

Table S1 Disorder mode frequency (ω_d), I_D/I_G ratios and N atom percentage (data from XPS) of the SWCNT-p and various SWCNT-NH_2s prepared by Diels-Alder reaction at different temperatures for 24 h.

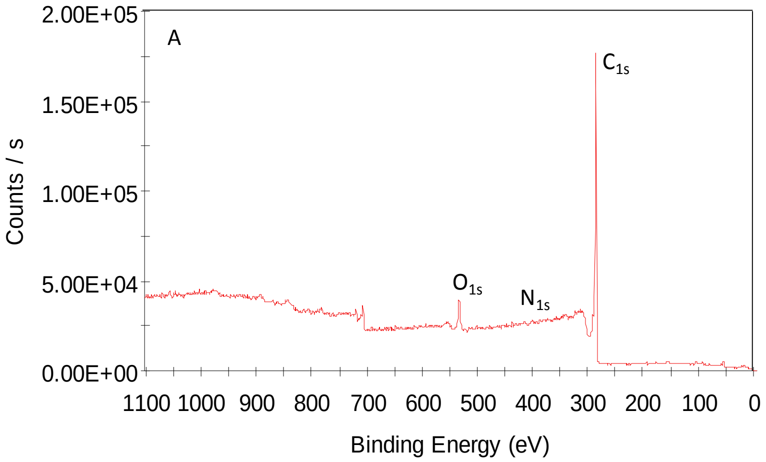
Sample[a]	ω_d	I_D/I_G	N atom%[b]
SWCNT-p	1338	0.062±0.007	0.55[c]
SWCNT-control[d]	—	—	0.60
SWCNT-NH_2-120	1341	0.125±0.003	1.70
SWCNT-NH_2-160	1341	0.167±0.008	2.43
SWCNT-NH_2-180	1344	0.185±0.004	2.89
SWCNT-NH_2-200	1344	0.276±0.019	3.94

a) The functonalized SWCNTs were prepared by Diels–Alder reaction of SWCNTs (15 mg) with 1-aminoanthracene (131 mg) in 30 mL of diethylene glycol for 24 h at various temperatures: 120 °C, 160 °C, 180 °C and 200 °C, and denoted as SWCNT-NH_2-120, SWCNT-NH_2-160, SWCNT-NH_2-180 and SWCNT-NH_2-200, respectively.

b) The values of N atom% were calculated based on XPS data, which were the surface composition of the samples.

c) The SWCNT-p was washed with methanol for four times, and then the XPS of the resultant SWCNTs-p was measured, the 0.55% of nitrogen atom was obtained probably due to unavoidable impurities.

d) A control experiment of SWCNT-p was carried out with the same conditions except temperature, and then the N% was measured by XPS. The 0.60% of nitrogen atom in the SWCNT-control indicates that the adsorbed 1-aminoanthracene could be almost washed away.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1.00E+05
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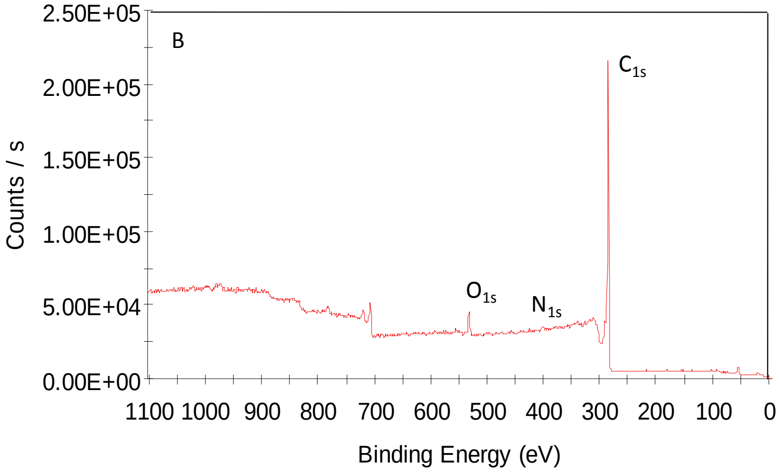
C_{1s}
O_{1s}
N_{1s}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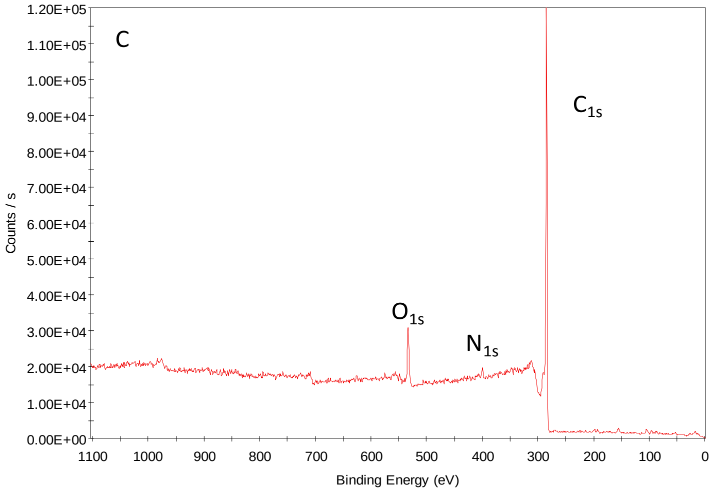
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5.00E+04
4.00E+04
3.00E+04
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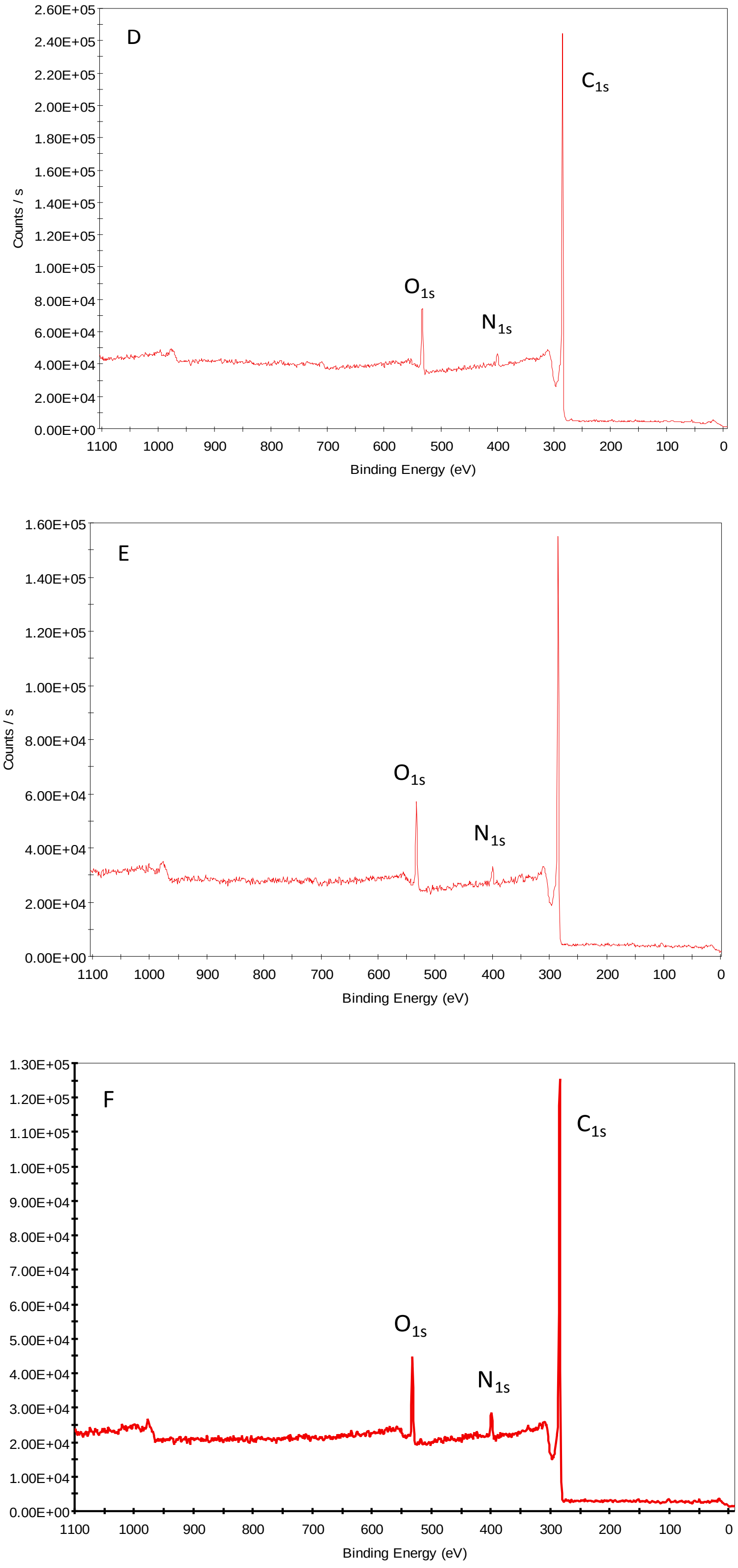


Fig. S1 The XPS spectra of SWCNT-p (A), SWCNT-mix (B), SWCNT-NH_2-120 (C), SWCNT-NH_2-160 (D), SWCNT-NH_2-180 (E), and SWCNT-NH_2-200 (F).

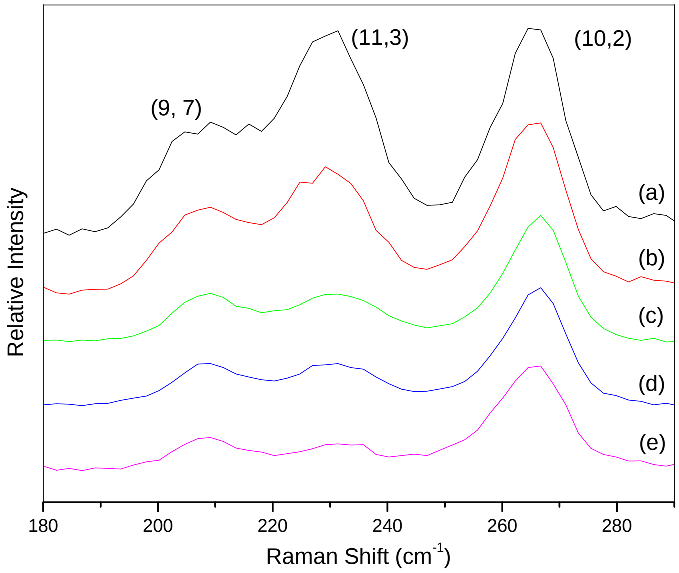


Fig. S2 RBM of Raman scattering spectra (λ_{ex} = 785 nm) for pristine and derivatized SWCNTs. (a) SWCNT-p, (b) SWCNT-NH_2-120, (c) SWCNT-NH_2-160, (d) SWCNT-NH_2-180, (e) SWCNT-NH_2-200. The peaks attribution was marked in the figure according to the reference [2]. Three types of s- SWCNTs are both depressed as the reaction temperature increases, and large s-SWCNTs of (9, 7) and (11, 3) have higher reactivity than small s-SWCNTs of (10, 2). It accords with the results of UV-vis-NIR and other Raman spectra.

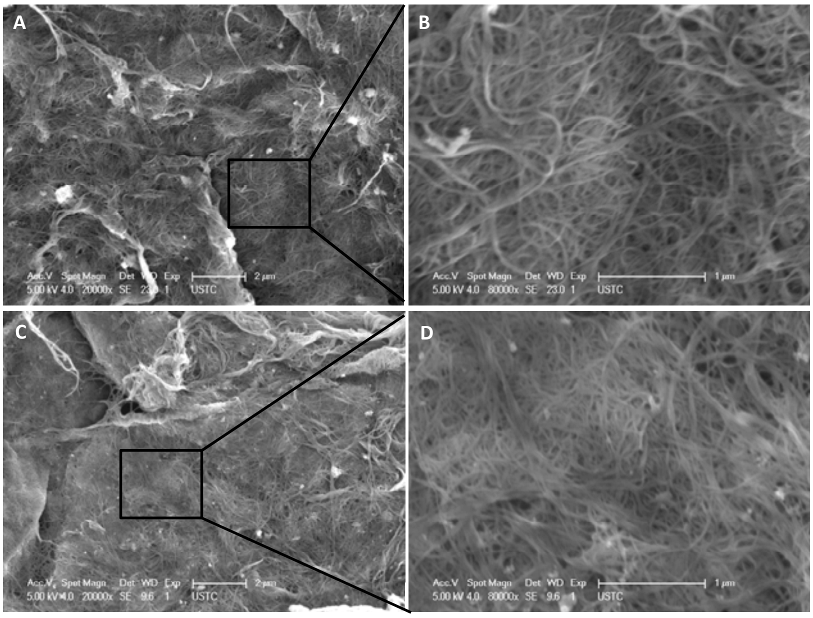


Fig. S3 Typical FE-SEM images of SWCNT membranes: (A) SWCNT-p, (C) SWCNT-NH_2-120, (B) and (D) high magnification of the indicated areas in (A) and (C), respectively.

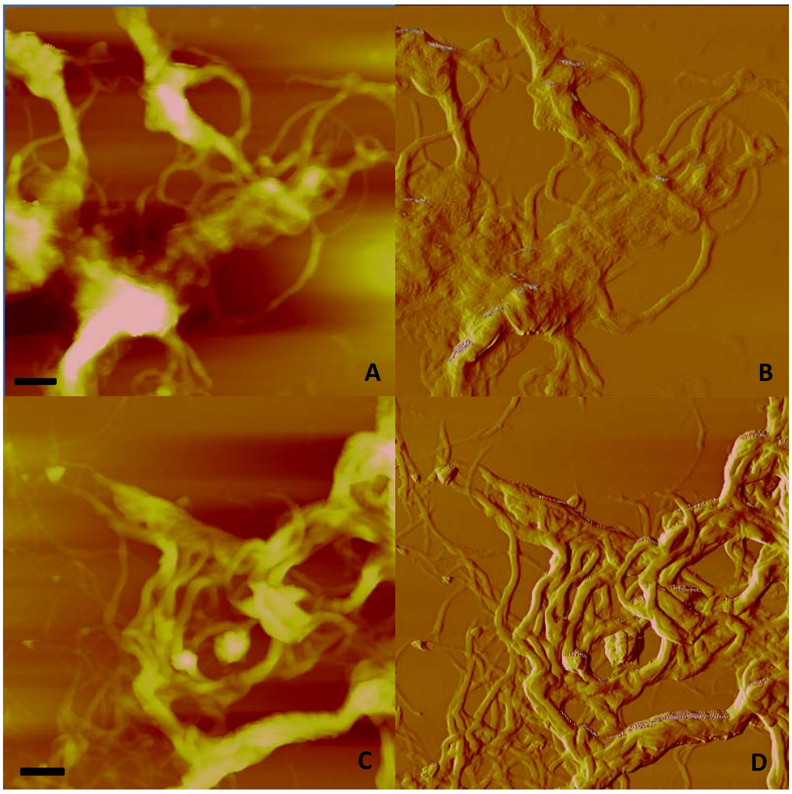


Fig. S4 AFM images of the SWCNT-p (A, B) and the SWCNT-NH_2-120 (C, D) obtained by dip-coating 0.1 mg/mL suspensions of the respective samples onto freshly cleaved mica substrates. A and C are height images, and B and D are amplitude images. All scale bars are 1μm.

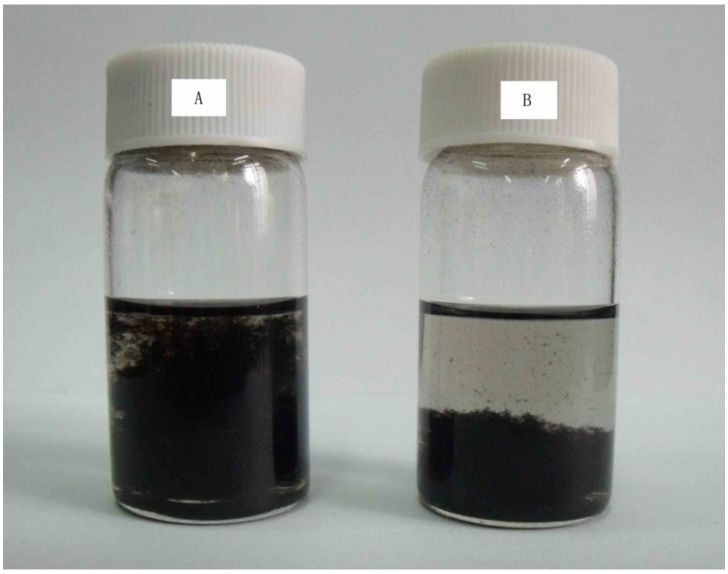


Fig. S5 Digital photographs of the SWCNT-NH_2-200 (A) and SWCNT-p (B) after standing for 6 hours. The samples (5mg) were both dispersed in 12mL of THF by ultrasound for 30 min.

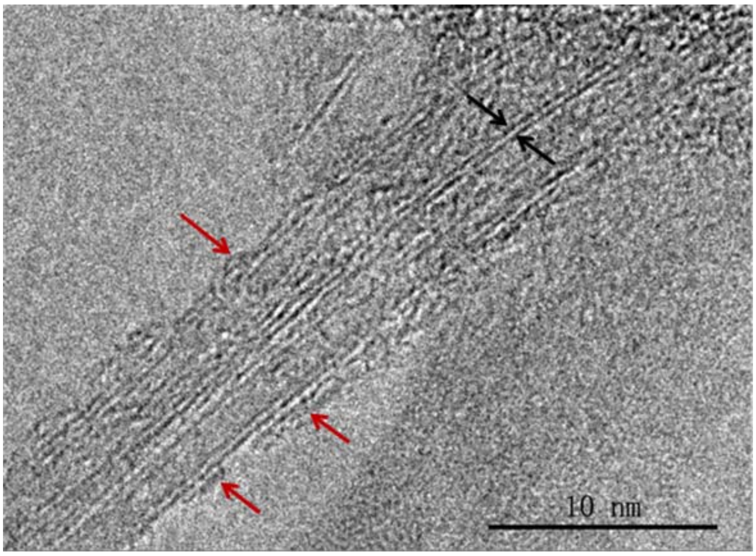
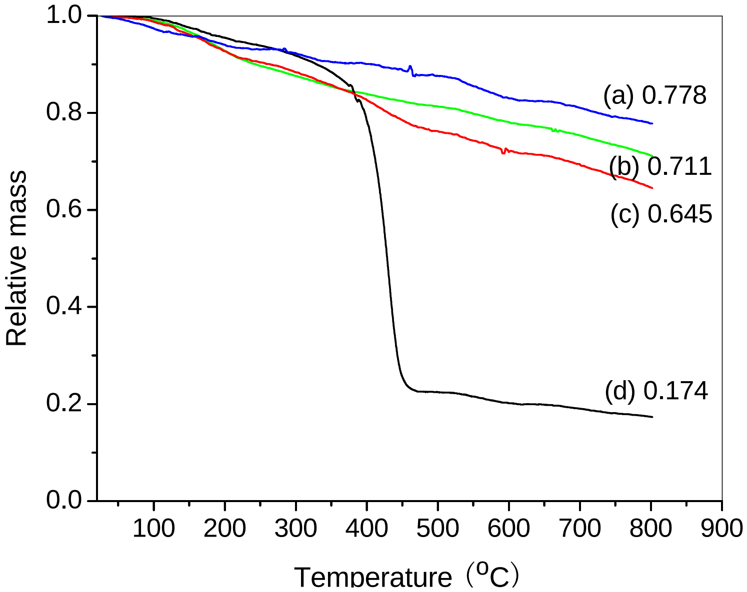


Fig. S6 HRTEM image of original SWCNT-PSt recorded at an accelerating voltage of 200 kV. The black arrows indicate the diameter of HiPco SWCNTs and the red arrows indicate the grafted polymer.



5 Fig. S7 TGA curves of SWCNT-p (a), SWCNT-NH_2-120 (b), SWCNT-Br (c), and original SWCNT-PSt (d) in a nitrogen atmosphere at a heating rate of 10 °C/min.

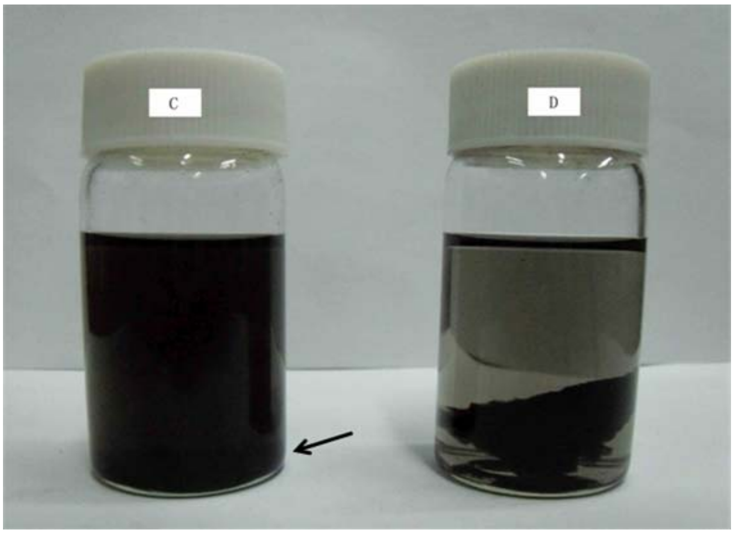


Fig. S8 Digital photograph of 11mg of the original SWCNT-PSt (C) and 4mg of SWCNT-p mixed with 7mg of PSt (D) in 18mL of THF after 24 hours of standing. The arrow indicates the deposit of unreacted SWCNT-p and some conceivable supersaturated SWCNT-PSt.

5 Reference

1. H. E. Fierz-David, L. Blangey and H. Streit, *Helvetica Chimica Acta*, 1946, **29**, 1718.
2. D. A. Heller, P. W. Barone, J. P. Swanson, R. M. Mayrhofer and M. S. Strano, *J. Phys. Chem. B*, 2004, **108**, 6905.