

Supporting Information

Effective Separation of Single-walled Carbon Nanotubes and Their Very Different Electrochemical Behaviors

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Experimental

Materials

The nanotube samples (arc-discharge production) were acquired from Carbon Solutions ("AP-SWNT", carbonaceous purity 40–60%). Dimethyl 5-hydroxyisophthalate, 1-Bromooctadecane, Lithium aluminum hydride (LiAlH_4 , 60%), Phosphorus tribromide (PBr_3 , 99%), Tetrahydrofuran (THF), Dichloromethane (CH_2Cl_2), Methanol (CH_3OH), Ethyl acetate ($\text{CH}_3\text{COOCH}_2\text{CH}_3$) and N,N-Dimethylformamide (DMF) and 1,1'-Bi-2-naphthol were purchased from Aldrich. Nitric acid (HNO_3), concentrated hydrochloric acid (HCl , 37%), Potassium hydroxide (KOH), Potassium carbonate (K_2CO_3), Sodium chloride (NaCl) and anhydrous sodium sulfate (Na_2SO_4) from SIGMA-ALDRICH. The organic solvents were distilled prior to use. Membrane filters (PVDF, 0.22 μm pore size) were supplied by Fisher Scientific. Water was deionized and purified by being passed through a Labconco WaterPros water purification system.

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Measurements

Bench-top centrifuge (KH-160TDB), homogenizer (PowerGen 125), and bath sonicator (PINGFAN INSTRUMENT TD6) were used in the nanotubes purification and separation experiments. Optical absorption spectra were recorded on Shimadzu UV-3600 spectrophotometers. Raman spectra were obtained on a Renishaw Raman spectrometer equipped with a 50 mW diode laser source for 785 nm excitation. All the electrochemical measurements were carried out using a CHI 660D electrochemical workstation (CH Instruments, Shanghai, China).

Synthesis of separation agent 124plus

Synthesis of Dimethyl-5-octadecyloxyisophthalate

A stirred mixture of Dimethyl 5-hydroxyisophthalate (500 mg) in DMF (20 mL) with K_2CO_3 (400 mg, 1.2 eq) was refluxed for 30 min. Then the 1-Bromooctadecane (790 mg) was added. The resulting white solution was cooled to room temperature and then salting out with NaCl. The crude product was purified by silica-column chromatography (petrolume-ether/EtoAc= 10:1) to give white solid (940 mg, 85% yield). 1H NMR ($CDCl_3$, 600 MHz) δ : 8.26 (1H, t, $J= 1.4$ Hz), 7.74(2H, d, $J= 1.5$ Hz), 4.03 (2H, t, $J= 6.5$ Hz), 3.94 (6H, s), 1.80 (2H, 5 peaks, $J= 7.3$ Hz), 1.46 (2H, 5 peaks, $J= 7.6$ Hz), 1.26 (28H, m), 0.88 (3H, t, $J= 6.8$ Hz).

Synthesis of 1-octadecyloxy-3,5-bis(hydroxymethyl)benzene

To a stirred mixture of Dimethyl-5-octadecyloxyisophthalate (300 mg) in anhydrous THF (20 mL), $LiAlH_4$ (62 mg, 2.5 eq) was carefully added ($LiAlH_4$ was soluted in anhydrous THF) at ice-bath temperature. After stirring for 3h the reaction was quenched by EtOAc and 20% HCl. The solvent was evaporated and the residue was partitioned into water/EtOAc. The organic layer was dried over $MgSO_4$. The crude product was purified by silica-column chromatography (petrolume-ether/EtoAc= 3:1) to give white solid (120 mg, 45% yield). 1H NMR ($CDCl_3$, 400 MHz) δ : 6.93 (1H, s), 6.85 (2H, s), 4.67 (4H, d, $J= 5.9$ Hz), 3.97 (2H, t, $J= 6.4$ Hz), 1.78 (2H, 5 peaks, $J= 7.6$ Hz), 1.66 (2H, t, $J= 6.0$ Hz), 1.45 (2H, 5 peaks, $J= 7.6$ Hz), 1.26 (28H, m), 0.88 (3H, t, $J= 6.8$ Hz).

Synthesis of 1-octadecyloxy-3,5-bis-(bromomethyl)benzene

To a stirred solution of 1-octadecyloxy-3,5-bis(hydroxymethyl)benzene (250 mg) in 20 ml anhydrous CH_2Cl_2 at ice-bath temperature. PBr_3 (410 mg, 2.3 eq) was slowly

added. After 2h stirring under dry atmosphere, the reaction mixture was quenched by CH₃CH₂OH (10 mL). The organic solvent was evaporated and the residue was partitioned into water/CH₂Cl₂. The organic layer was dried over MgSO₄. The crude product was purified by silica-column chromatography (petrolume-ether/EtoAc= 8:1) to give white powder (260 mg, 80% yield). ¹H NMR (CDCl₃, 400 MHz) δ: 6.95 (1H, s), 6.85 (2H, s), 4.43 (4H, s), 3.96 (2H, t, *J*= 6.4 Hz), 1.77 (2H, 5 peaks, *J*= 7.4 Hz), 1.45 (2H, 5 peaks, *J*= 7.5 Hz), 1.26 (28H, m), 0.88 (3H, t, *J*= 6.8 Hz).

Synthesis of 11-(heptadecyloxy)-8,14-dihydro-9,13-(metheno)dinaphtho[2,1-b:1',2'-d][1,6]dioxacyclotridecine

To a stirred solution of 1-octadecyloxy-3,5-bis-(bromomethyl)benzene (100 mg) and KOH (23 mg, 2.2 eq) in 20mL DMF at 80°C. After 30min stirring, the (S)-(-)-1,1'-Bi-2-naphthol (60 mg, 1.1 eq) was added and heated to 100°C. After 21h stirring at 100°C, the resulting yellow solution was cooled to the room temperature and then salting out with NaCl. The crude product was purified by silica-column chromatography (petrolume-ether/EtoAc= 20:1) to give yellow solid (40 mg, 30% yield). ¹H NMR (CDCl₃, 400 MHz) δ: 7.87 (2H, d, *J*= 8.9 Hz), 7.80 (2H, d, *J*= 8.0 Hz), 7.41 (2H, d, *J*= 9.0 Hz), 7.34 (2H, m), 7.27 (2H, m), 7.24 (2H, m), 7.10 (1H, s), 6.43 (2H, s), 5.20 (2H, d, *J*= 12.4 Hz), 5.00 (2H, d, *J*= 12.4 Hz), 3.77 (2H, m), 1.66 (2H, 5 peaks, *J*= 7.4 Hz), 1.45 (2H, 5 peaks, *J*= 7.5 Hz), 1.26 (28H, m), 0.88 (3H, t, *J*= 6.8 Hz).

SWNTs Purification and Separation

The SWNTs sample from the arc discharge method (1 g) was first heated in a tube furnace at 400°C in the presence of air for 30min, followed by refluxing in aqueous nitric acid (2.6 M, 500mL) for 24 h. After being cooled to room temperature, the mixture was filtered, washed with deionized water repeatedly to the neutral pH and then dried in a vacuum oven to yield the purified sample (600 mg).

The purified SWNTs sample (100 mg) and separation agent 124 plus (50 mg) was then added to dry DMF (25 mL). The mixture was sonicated (40-80 Hz) for 24 h to form a relatively stable dispersion, followed by centrifuging at 2750 g for 25 min. The resulting residue was then used as the starting material of the separation. The resulting residue was put into a centrifuge tube together with separation agent plus (150 mg) and 25 mL of dry DMF was added drop wise into the mixture. After sonicated (40-80 Hz) for 24 h and centrifuging at 2000 g for 10 min, the supernatant was collected as s-

SWNTs, while the residue was used for another round of sonication-centrifuging material. The SWNTs in supernatant was then collected via filtration. After refluxed in THF for 12 h repeatedly and dried in vacuum oven, s-SWNTs (32 mg) was get as prepared material. The sonication-centrifuging method was then actualize under the same condition repeatedly until the supernatant is clear and colorless. After centrifuging, the same strategy would be allowed to the resulting residue, and m-SWNTs (36 mg) was finally get as prepared material.

SEM and TEM data of m- and s-SWNTs

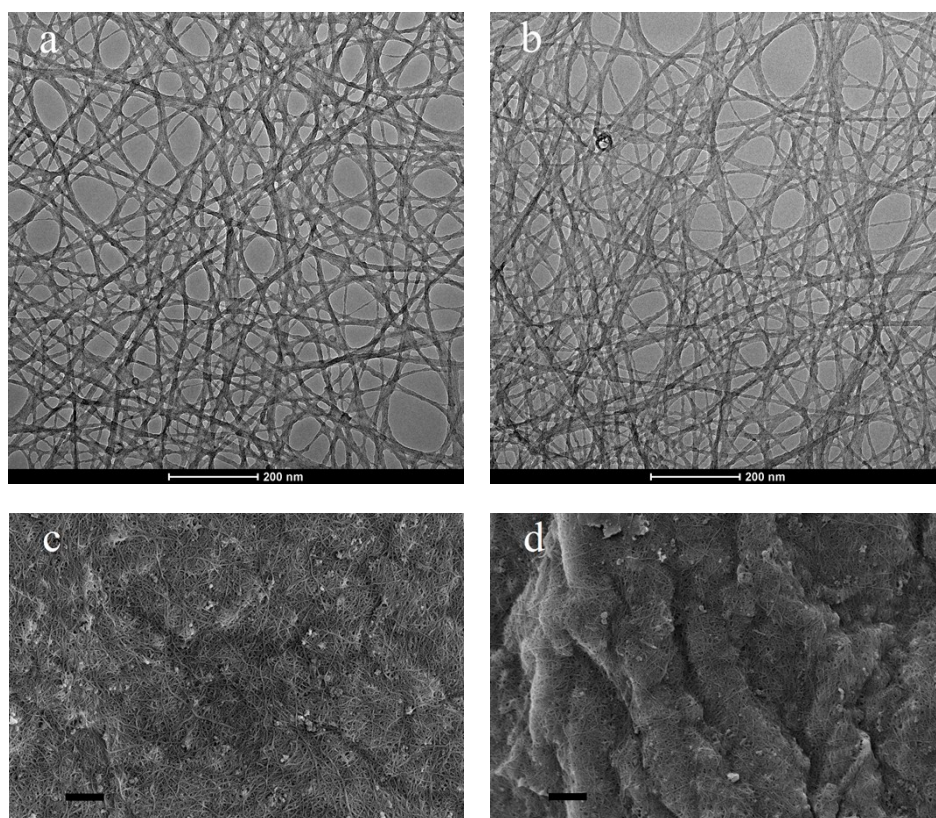


Figure S1. TEM images of s-SWNTs (a) and m-SWNTs (b); SEM images of s-SWNTs (c) and m-SWNTs (d).

Preparation of working electrodes

The GCE was first washed ultrasonically in ethanol for several minutes. Next, the GCE was polished carefully using 0.03 μm alumina slurries on a wet polishing cloth to obtain a mirror-like surface. Then, the electrode was washed ultrasonically with water, acid and ethanol for several minutes, sequentially. Finally, it was rinsed thoroughly with secondary distilled water and dried in air.

The separated SWNTs (5 mg) was put into a centrifuging tube together with dry DMF (5 mL), respectively. After solicited (40-80 Hz) for 12h, the mixture was expected to form a homogenous solvent. The solvent (40 μ L) was then respectively applied onto the clean GCE. In order not to introduce any other effects, we controlled the two electrode under the same experimental condition.

Doping experiment

Prior the doping experiment, the separated SWNTs modified electrode was obtain by the above method. Next, the electrochemical measurement was carried out on the doping electrode. Then, 30 μ L of TCNQ (0.01 M, DMF) and 30 μ L of DomP (0.01 M, DMF) was respectively applied onto the two electrode and dried under the room temperature. The modified electrode was then washed by DMF.

Electrochemical measurements

The electrochemical measurements were carried out using three electrode cell configuration with SWNTs modified GCE as the working electrode, platinum as the counter electrode, and Ag/AgCl as the reference electrode with 1.0 M Na_2SO_4 as the electrolyte. EIS was used for studying the interface properties of the surface-modified electrodes. s-SWNTs and m-SWNTs modified GCE in a solution of 1.0 mM $\text{Fe}(\text{CN})_6^{3- / 4-}$ and 0.1 M KCl were tested with EIS respectively showed in Figure 3 a. The cyclic voltammetry measurements of the SWNTs electrode was performed at scan rate of 100 mVs^{-1} in a potential window of 0 to 0.8 V. The galvanostatic charge/discharge curves under 0.5 A g^{-1} were conducted in aqueous Na_2SO_4 electrolyte and the results of s-SWNTs and m-SWNTs modified GCE were shown in Figure 3b. The excellent electrocatalytic activity of SWNTs towards the oxidation of dopamine (DA) was investigated by the differential pulse voltammetry (DPV) experiments at s-SWNTs and m-SWNTs modified GCE with 0.1 mM DA (Fig. 3d) in 0.1 M PBS (pH=7.0).

To compare with the doping electrode respectively, EIS was used of the doping electrodes, the doping electrodes was tested in a solution of 1.0 mM $\text{Fe}(\text{CN})_6^{3- / 4-}$ and 0.1 M KCl respectively showed in Figure 5 a. The cyclic voltammetry measurements of the doping electrode was performed at scan rate of 100 mVs^{-1} in a potential window of 0 to 0.8 V. The electrocatalytic activity was also carried out towards the oxidation of dopamine (DA) was investigated by the differential pulse

voltammetry (DPV) experiments on the doping electrode with 0.1 mM DA (Fig. 5b and Fig 5d) in 0.1 M PBS (pH=7.0) respectively.

The electrochemical capacitance

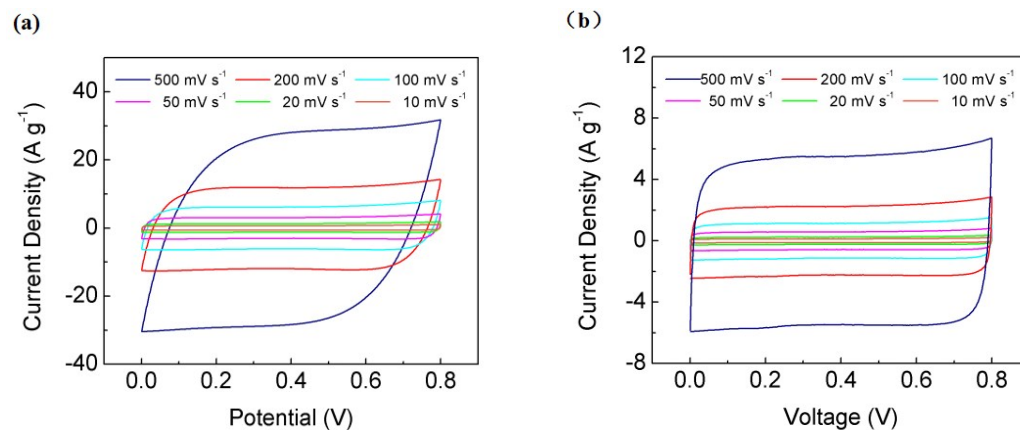


Figure S2. CVs in 1 M Na₂SO₄ solution at different sweep rates of s-SWNTs (a) and m-SWNTs (b).

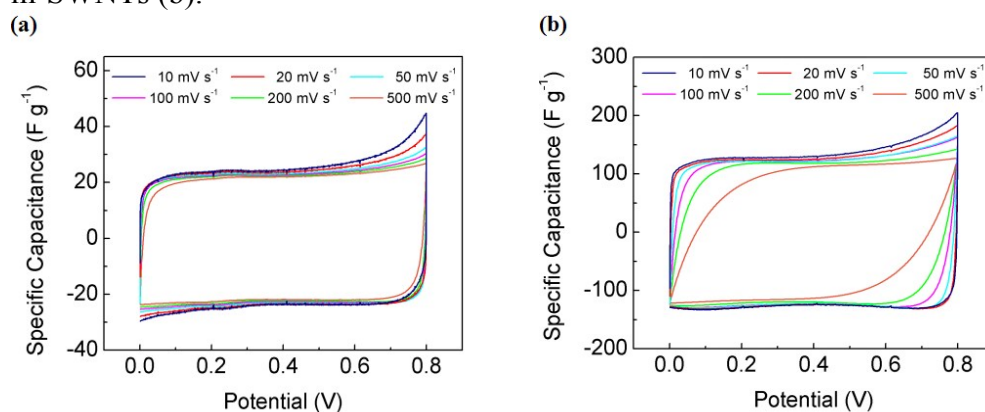


Figure S3 CVs in 1 M Na₂SO₄ solution at different sweep rates of m-SWNTs (a) and s-SWNTs (b).

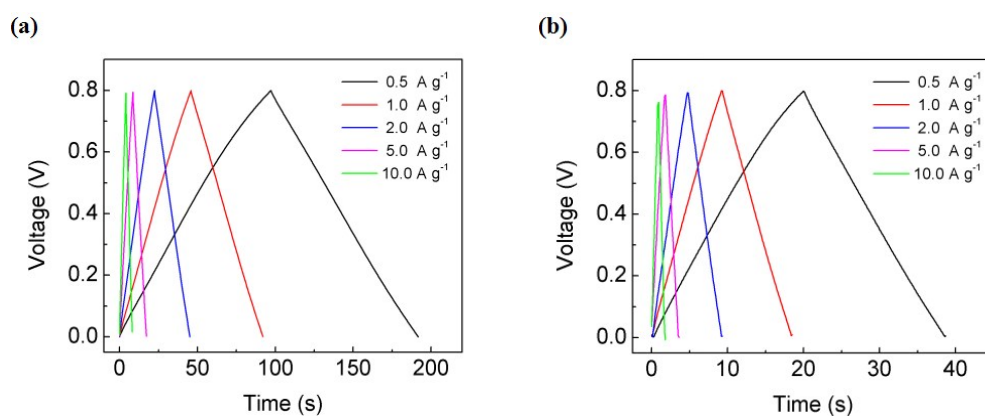


Figure S4 Galvanostatic charge/discharge curves at different current densities of s-SWNTs (a) and m-SWNTs (b).

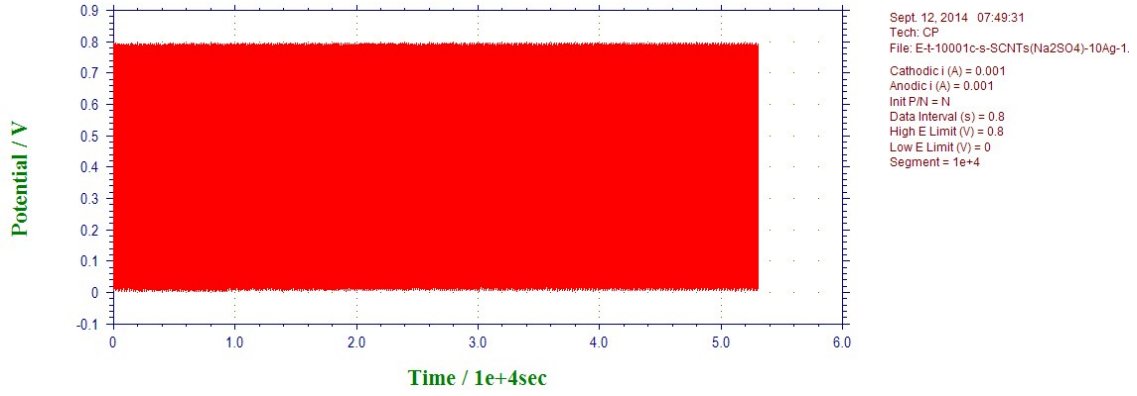


Figure S5 Ten thousand times charging and discharging curves of s-SWNTs.

The formula derivation process

The quantum capacitance of SWNTs was determined by their DOS near Fermi level, which could be expressed as [1]:

$$C_q = \frac{\partial q_1}{\partial \phi_s} = -\frac{\partial \mu}{\partial \phi_s} \frac{\partial q_1}{\partial \mu} = -e \frac{\partial q_1}{\partial \mu} \quad (1)$$

$$q_1 = e \int_{-\infty}^0 g(E)[1 - F(E, \mu)] dE - e \int_0^{\infty} g(E) F(E, \mu) dE \quad (2)$$

Then bring eq2 into eq1, we will get the following results. (The ϕ_s is the surface potential, and μ is the electric energy on surface. $e\phi_s = \mu$. q_1 is charge density.)

$$C_q = -e^2 \int_{-\infty}^0 g(E)[1 - F(E, \mu)] dE + e^2 \frac{\partial}{\partial \mu} \int_0^{\infty} g(E) F(E, \mu) dE \quad (3)$$

$$C_q = e^2 \int_{-\infty}^0 g(E) F_{th}(E, \mu) dE + e^2 \frac{\partial}{\partial \mu} \int_0^{\infty} g(E) F_{th}(E, \mu) dE \quad (4)$$

$$C_q = e^2 \int_{-\infty}^{\infty} g(E) F_{th}(E, \mu) dE \quad (5)$$

Where $F_{th} = \frac{\partial F}{\partial \mu} = \frac{1}{4k_B T} \text{sech}^2\left(\frac{E - \mu}{2k_B T}\right)$, the the C_q would be:

$$C_q = e^2 \int_{-\infty}^{\infty} g(E) \frac{1}{4k_B T} \operatorname{sech}^2\left(\frac{E - \mu}{2k_B T}\right) dE \quad (6)$$

Where $\operatorname{sech} = 2/(e^x + e^{-x})$, the symbol of Hyperbolic Secant function. K_b is the Boltzmann constant. The DOS of m-SWNTs could be expressed as a constant:

$$g(E, 0) = g_0 = \frac{8}{\sqrt{3}a\pi\gamma} \approx 2\text{nm}^{-1} \cdot \text{eV}^{-1} \quad (7)$$

The expression of DOS of s-SWNTs is more complex and could be simplify as:

$$g(E, j) \approx \frac{g_0}{2} \frac{|E|}{\sqrt{E^2 - E_{\text{vh}_j}^2}} \quad (8)$$

Where j is the secondary energy band index, E_{vh_j} is Van Hove singularity energy.

Consequently, the quantum capacitance of m-and s-SWNTs are given by

$$C_{q,m} = g_0 e^2 \quad (9)$$

$$C_{q,s} \approx \frac{4e^2 N_0}{k_B T} e^{-E_g/2k_B T} \cosh\left[\frac{\mu}{k_B T}\right] \quad (10)$$

Crystallographic data collection and refinement

The single-crystal diffraction data of complexes binaphthyl and separation agent 124 were recorded on a Bruker SMART APEX II CCD detector equipped with a graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) by using a φ/ω scan technique at 296(2) K. The structures of binaphthyl and separation agent 124 were solved by direct methods and refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXTL program and SHELXL-2014. The data for complexes were modified for absorption by using the program SADABS. Non-hydrogen atoms were refined with anisotropic thermal parameters. In these heavy-atom structures as it was not possible to see clear electron-density peaks in difference maps which would correspond with acceptable locations for the various H atoms bonded to water oxygen atoms, the refinements were completed with no allowance for these water H atoms in the models. And all hydrogen atoms of organic ligands were placed at idealized positions and refined with a riding on attached atoms with isotropic thermal parameters. In the absence of significant anomalous scattering, Friedel pairs were merged and the absolute structure was assigned arbitrarily. Crystallographic data of

binaphthyl and separation agent 124 are displayed in Table S1. CCDC reference numbers are 1039187 and 1039186 for binaphthyl and separation agent 124.

Table S1 Crystal data and structure refinements for binaphthyl and separation agent 124.

Complexes	Binaphthyl	Separation agent 124
Formula	C ₂₀ H ₁₄ O ₂	C ₂₈ H ₂₀ O ₂
Formula weight	286.31	388.44
Crystal system	Trigonal	Monoclinic
Space group	P3(1)	P2(1)
<i>a</i> [Å]	10.784(3)	9.4569(10)
<i>b</i> [Å]	10.784(3)	19.807(2)
<i>c</i> [Å]	10.863(3)	21.941(2)
α [°]	90	90
β [°]	90	96.830(2)
γ [°]	120	90
<i>V</i> [Å ³]	1094.0(6)	4080.7(7)
<i>Z</i>	3	8
D _{calcd.} [g·cm ⁻³]	1.304	1.265
μ [mm ⁻¹]	0.083	0.078
<i>F</i> [000]	450	1632
θ [°]	2.181-25.070	0.935-25.100
Reflections collected	5517 / 2362	20622 / 10957
GOF on <i>F</i> ²	1.036	1.017
<i>R</i> ₁ ^a [<i>I</i> >2 σ (<i>I</i>)]	R ₁ = 0.0372	R ₁ = 0.0473
<i>wR</i> ₂ ^b [<i>I</i> >2 σ (<i>I</i>)]	wR ₂ = 0.0673	wR ₂ = 0.1067

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

REFERENCES

1. Wong H.S.P.; Akinwande, D. Carbonnanotube and graphene device physics. Cambridge University Press, 2011