

# Supporting Information

## Functionalized CNT-Azobenzene-PVA-Based Self-Healing Aqueous Gel as a Conductive Photoresponsive Actuator

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## Materials:

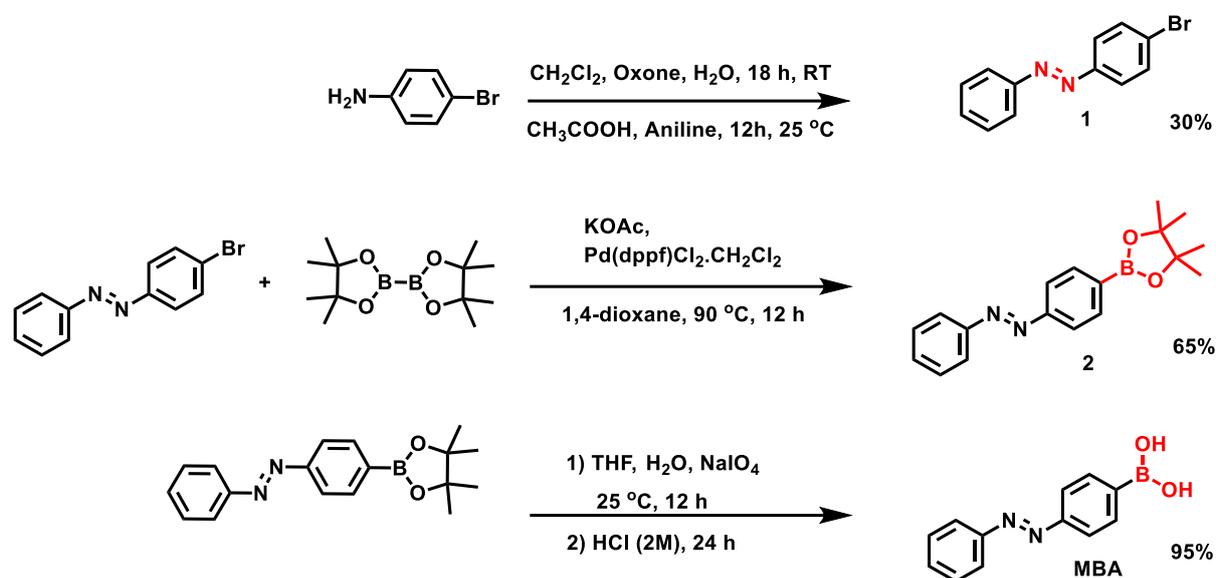
4-Bromoaniline, 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane),  $\text{KMnO}_4$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NaIO}_4$  (Spectrochem),  $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$  (TCI), OXONE, aniline (Spectrochem), SWCNT (SRL) were used as received. The solvent dry 1,4-dioxane (Finar), THF (Finar),  $\text{CH}_2\text{Cl}_2$  was purified prior to use according to the reported procedure and stored in molecular sieves. Thin layer chromatography was carried out using silica gel 60/UV<sub>254</sub> purchased from Merck specialties Pvt. Ltd. and visualized either by UV fluorescence or by iodine chamber. Column chromatography was performed using silica gel (100-200 mesh), bed was made by using (60-120 mesh) purchased from Spectrochem Pvt. Ltd. and mixtures of pet ether-ethyl acetate used for elution were distilled before use. All the reactions were carried out in oven dried round bottomed flasks under an atmosphere of argon unless otherwise mentioned.

The  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were recorded at Bruker-400/500 MHz NMR spectrometer instrument. The chemical shift values for  $^1\text{H}$  (TMS as internal standards) and  $^{13}\text{C}$  NMR are recorded in  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$ . The value of coupling constant ( $J$ ) is stated in Hertz (Hz). FT-IR spectra were obtained on Perkin Elmer Spectrum Two spectrophotometer in 4000-600  $\text{cm}^{-1}$  range with a resolution of 4  $\text{cm}^{-1}$ . Raman analysis was done by Horiba JY LabRAM HR 800. UV-Vis absorption spectra were recorded with a Shimadzu 1800 spectrophotometer. Rheology experiments were done by Anton Paar Rheometer 301. Conductivity measurement was carried out using Agilent 4156 C semiconductor probe analyser. Light response study did by Fluortronix 365-370 nm 60W UV LED lamp with peak irradiance 3.5W/ $\text{cm}^2$  @2mm and Fulham throoled 450 nm, 75 W Visible light lamp. TEM imaging was done by JEOL JEM F200 HRTEM. Resolution: 0.19 nm, Accelerating Voltage: 20kV-200kV., FEI NOVA NANOSEM 450. Resolution: 1nm, Accelerating Voltage: 1kV - 30kV, the samples were sputtered with gold by using SCD 040 Balzers Union sputtered. Microtomography analysis done by Model: Xradia 510 Versa, Make: Carl Zeiss Microscopy GmbH, Pleasanton, USA (X-ray energy – 80 kV, Software: Dragonfly Pro, version 3.5). The water contact angle was measured by Drop Shape Analyzer-DSA25-KRUSS-GmbH.



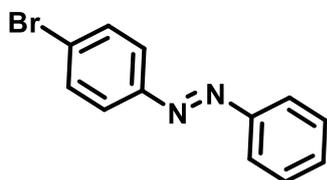
## Experimental Procedures

### Synthesis



**Scheme S1.** Synthesis of MBA.

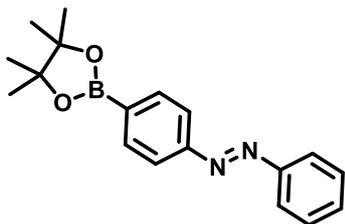
#### 1-(4-bromophenyl)-2-phenyldiazene (1):<sup>(S1)</sup>



To a solution of 4-bromoaniline (2g, 11.6 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL), a solution of OXONE (11.7 g, 23.2 mmol) in water (70 mL) was added and the reaction mixture was stirred for 18 hours in room temperature. After the completion of the reaction, the product was extracted with  $\text{CH}_2\text{Cl}_2$ , and the organic layer was evaporated to give the nitroso compound. The product is directly used for the next step without any further purification.

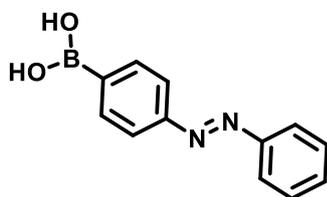
Aniline (250.34 mg, 2.69 mmol) and nitroso compound (500 mg, 2.69 mmol) was dissolved in acetic acid and the reaction mixture was stirred for 12 h. After the completion of the reaction, the product was extracted with petroleum ether, and the organic layer was washed with a saturated aqueous solution of  $\text{NaHCO}_3$ . The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated and the crude product was purified with flash chromatography (Petroleum ether: Ethyl acetate 20/1). The product was obtained as an orange crystalline solid (200 mg, 30%).

**1-phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)diazene (2):**<sup>(S2)</sup>

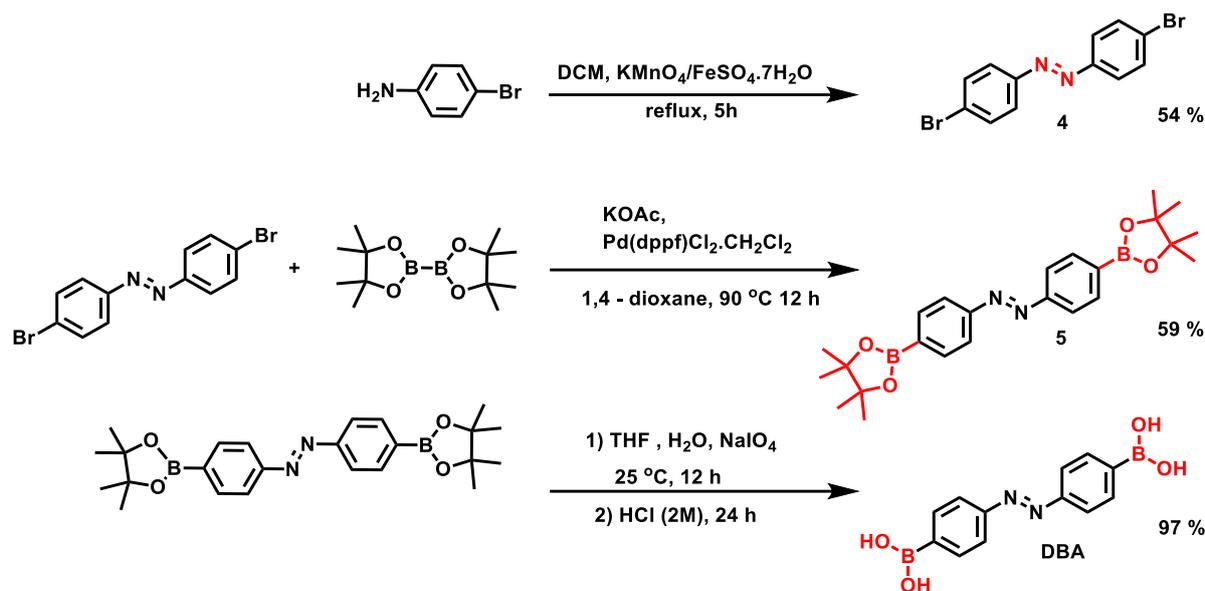


To a degassed solution of anhydrous 1,4-dioxane, 4-bromoazobenzene (500 mg, 1.91 mmol), bis(pinacolatodiborane) (729.3 mg, 2.89 mmol), Pd(dppf)Cl<sub>2</sub>.CH<sub>2</sub>Cl<sub>2</sub> (70.25 mg, 0.09 mmol) were added. Potassium acetate (376 mg, 3.83 mmol) was then added and the reaction mixture and the reaction mixture was degassed one more time, before allowing the whole mass to stir overnight at 90 °C, under a nitrogen atmosphere. Then the crude mixture was filtered over celite, concentrated under vacuum, and purified by column chromatography on silica gel, using petroleum ether and ethyl acetate (5%) as the eluent to give the corresponding compound as an orange solid (384 mg, 65% yield).

**(4-(phenyldiazenyl)phenyl)boronic acid (MBA):**<sup>(S3)</sup>

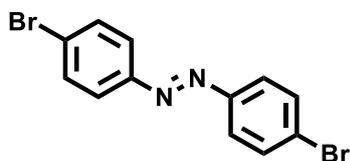


To the solution of **2** (300 mg, 0.97 mmol) in THF (24 mL) and water (6 mL) and NaIO<sub>4</sub> (625 mg, 2.92 mmol) is added. The mixture is stirred overnight at room temperature. HCl (2M, 1 mL) was added and the mixture was stirred for another 24 hours. The reaction mixture was passed through celite, poured into water, and extracted with ethyl acetate. The solvent was removed under reduced pressure on a rotary evaporator. (209 mg, 95% yield).



**Scheme S2.** Synthesis of **DBA**.

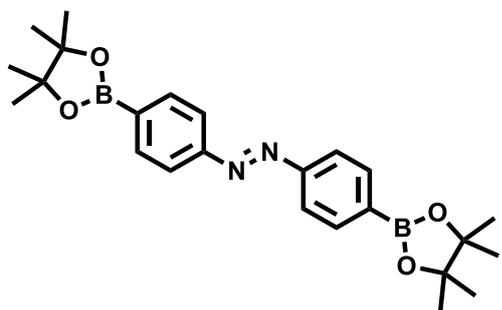
### 1,2-bis(4-bromophenyl)diazene (**4**):<sup>(S4)</sup>



4-Bromoaniline (3.5 g, 2 mmol) was taken into a 250 mL round bottom flask, dissolved in dichloromethane and into this a homogeneous mixture of the oxidant (20.0 g) was added (the homogeneous mixture of the oxidant was prepared by grinding an equal amount of  $\text{KMnO}_4$  (10 g) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (10 g) in a mortar gently). The heterogeneous mixture was refluxed for 5 h. After the complete consumption of the starting material, the reaction mixture was cooled to room temperature and filtered through Celite, and the residue was washed with dichloromethane, and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and purified by column chromatography (60-120 mesh), using petroleum ether as eluent to give the corresponding compound as an orange-red solid **4** (3.76 g, 54% yield).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.78 (d,  $J = 8.8$  Hz, 4H), 7.64 (d,  $J = 8.8$  Hz, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ),  $\delta$  151.16, 132.41, 125.77, 124.42. HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{12}\text{H}_8\text{Br}_2\text{N}_2$  [M]<sup>+</sup> 341.018, found 340.917.

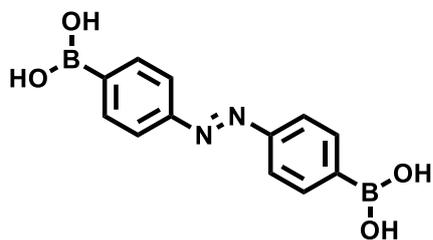
**1, 2-bis (4-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)phenyl) (5):**<sup>(S5)</sup>



To a degassed solution of anhydrous 1,4-dioxane, 4,4'-dibromoazobenzene **1** (400 mg, 1.2 mmol), bis(pinacolatodiborane) (1.08 g, 4.25 mmol), Pd(dppf)Cl<sub>2</sub>.CH<sub>2</sub>Cl<sub>2</sub> (50 mg, 0.06 mmol) were added. Potassium acetate (577 mg, 5.88 mmol) was then added and the reaction mixture and the reaction mixture was degassed one more time, before allowing the whole mass to stir overnight at 90 °C, under a nitrogen atmosphere. Then the crude mixture was filtered over celite, concentrated under vacuum, and purified by column chromatography on silica gel, using petroleum ether and ethyl acetate (5%) as the eluent to give the corresponding compound as an orange solid **2** (300 mg, 59% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.95 (d, *J* = 8.5 Hz, 4H), 7.89 (d, *J* = 8.5 Hz, 4H), 1.38 (s, 24H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 154.38, 135.63, 122.05, 84.07, 24.89. HRMS (ESI<sup>+</sup>): calcd for C<sub>24</sub>H<sub>32</sub>B<sub>2</sub>N<sub>2</sub>O<sub>4</sub> [M]<sup>+</sup>435.15, found 435.26.

**(Diazene-1, 2-diylbis(4,1-phenylene))diboronic acid (DBA):**<sup>(S3)</sup>

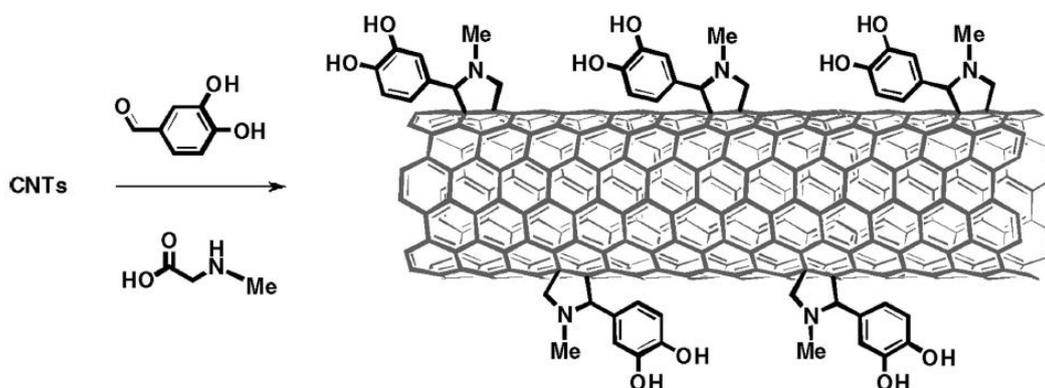


To the solution of 1,2-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)diazene **2** (140 mg, 0.3 mmol) in THF (24 mL) and water (6 mL) and NaIO<sub>4</sub> (424 mg, 1.98 mmol) is added. The mixture is stirred overnight at room temperature. HCl (2M, 0.5 mL) was added and the mixture was stirred for another 24 hours. The reaction mixture was passed through celite,

poured into water, and extracted with ethyl acetate. The solvent was removed under reduced pressure on a rotary evaporator. (89 mg, 97% yield).

$^1\text{H NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  8.29 (s, 4H), 7.98 (d,  $J = 8.3$  Hz, 4H), 7.83 (d,  $J = 8.3$  Hz, 4H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  153.15, 135.28, 121.56, 118.86 HRMS (ESI $^+$ ): calcd for  $\text{C}_{12}\text{H}_{12}\text{B}_2\text{N}_2\text{O}_4$  [M] $^+$  271.0983, found 271.1056.

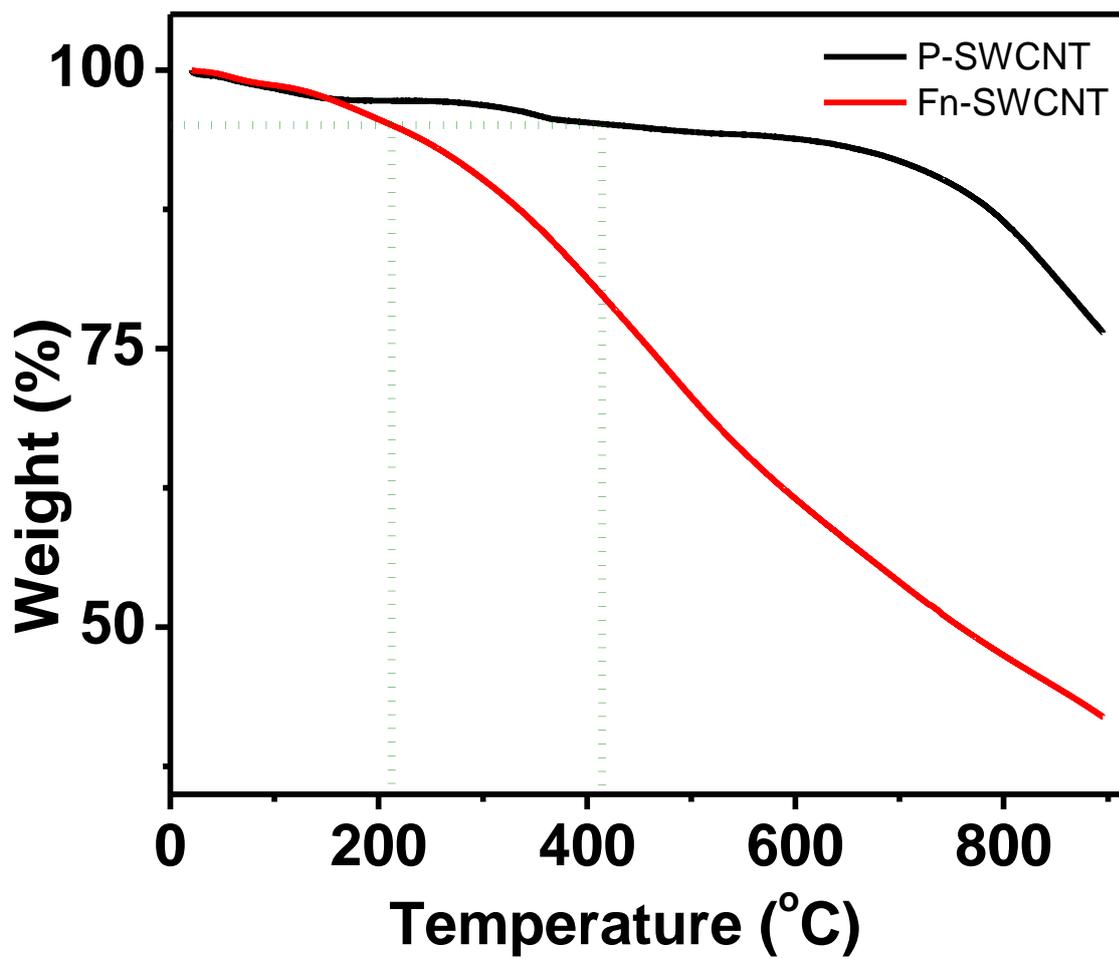
### Fn-SWCNT



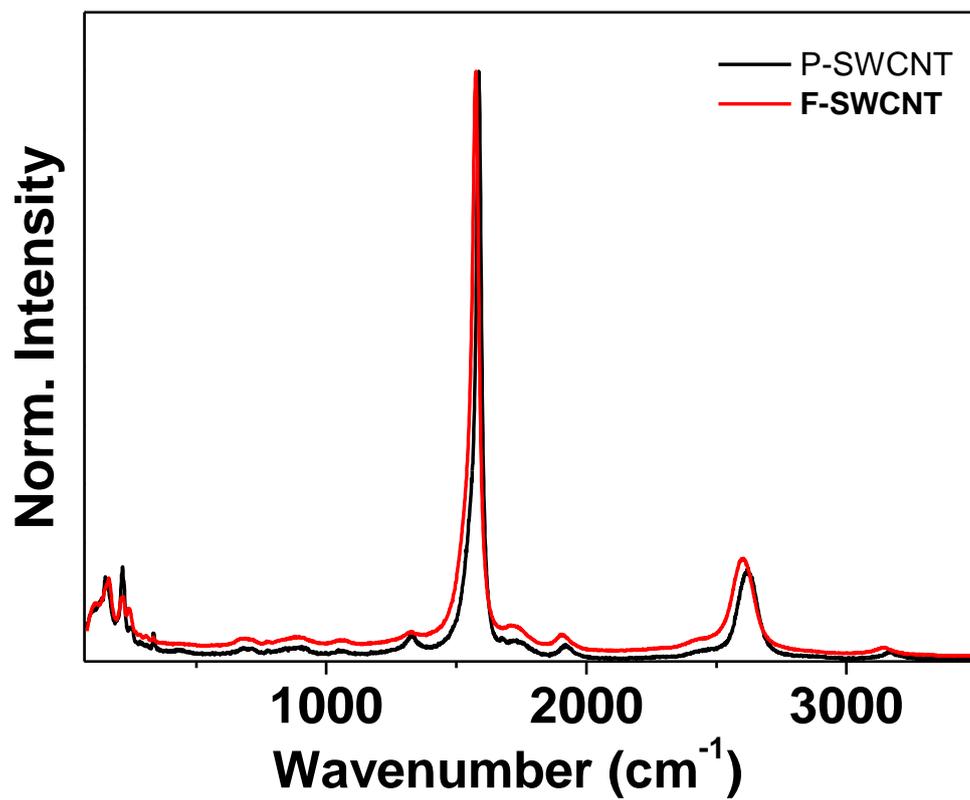
**Scheme S3.** Synthesis of **Fn-SWCNT**.

Fn-SWCNT prepared according to the reported procedure<sup>(S6)</sup> 20 mg of SWCNTs, 200 mg of 3,4-dihydroxybenzaldehyde, and 200 mg of N-methylglycine were suspended in 50 mL of DMF and heated at 120 °C for 5 days. The mixture was then filtered through Millipore filters (0.45  $\mu\text{m}$  FG) and washed thoroughly with DMF. The filtrate was sonicated in DMF for 1 h and then removed; the resulting suspension was filtered again through Millipore filters (0.45  $\mu\text{m}$  FG). This procedure was repeated three additional times with sonication in (1) DMF, (2) 1:1 (v/v) ethanol/ $\text{CHCl}_3$ , and (3) diethyl ether. The remaining black solid was dried under vacuum (10-2 bar) for 3 days.

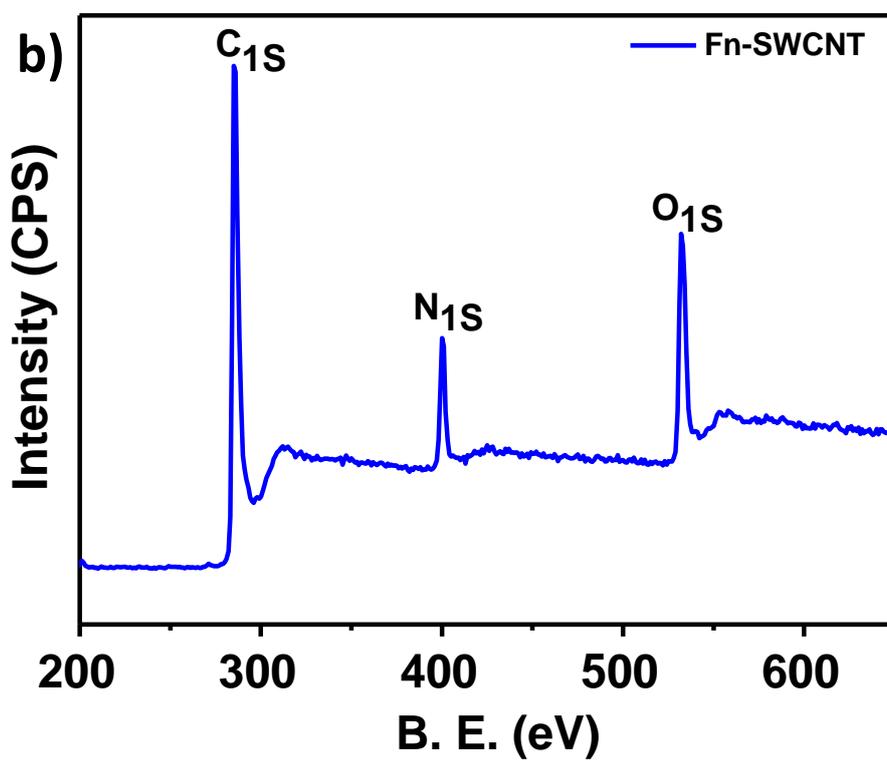
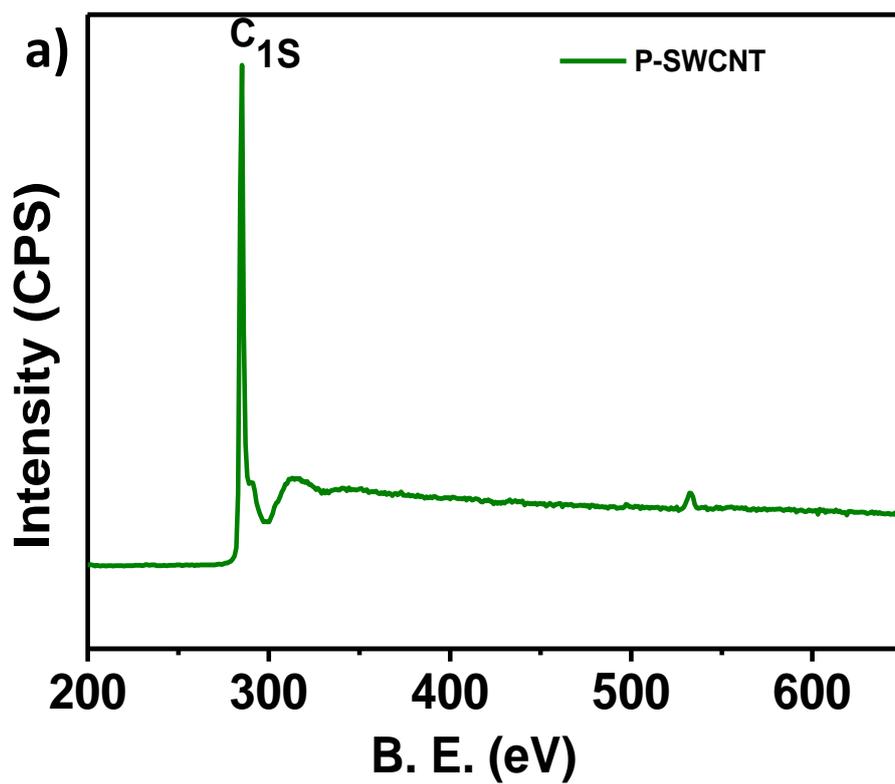
## Figures



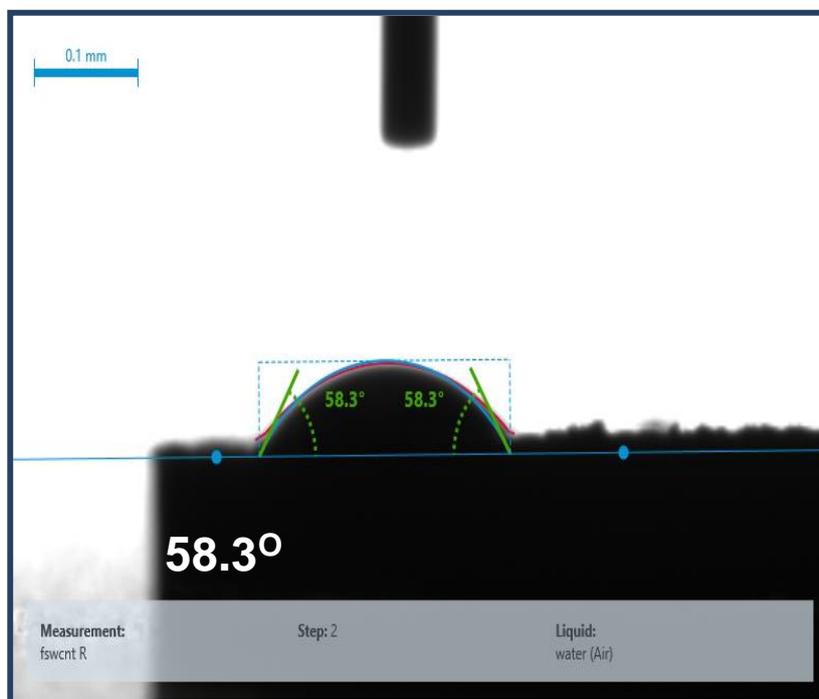
**Figure S1:** Comparison of the TGA of P-SWCNT and Fn-SWCNT.



**Figure S2:** Comparison of the Raman spectra of P-SWCNT and F-SWCNT.

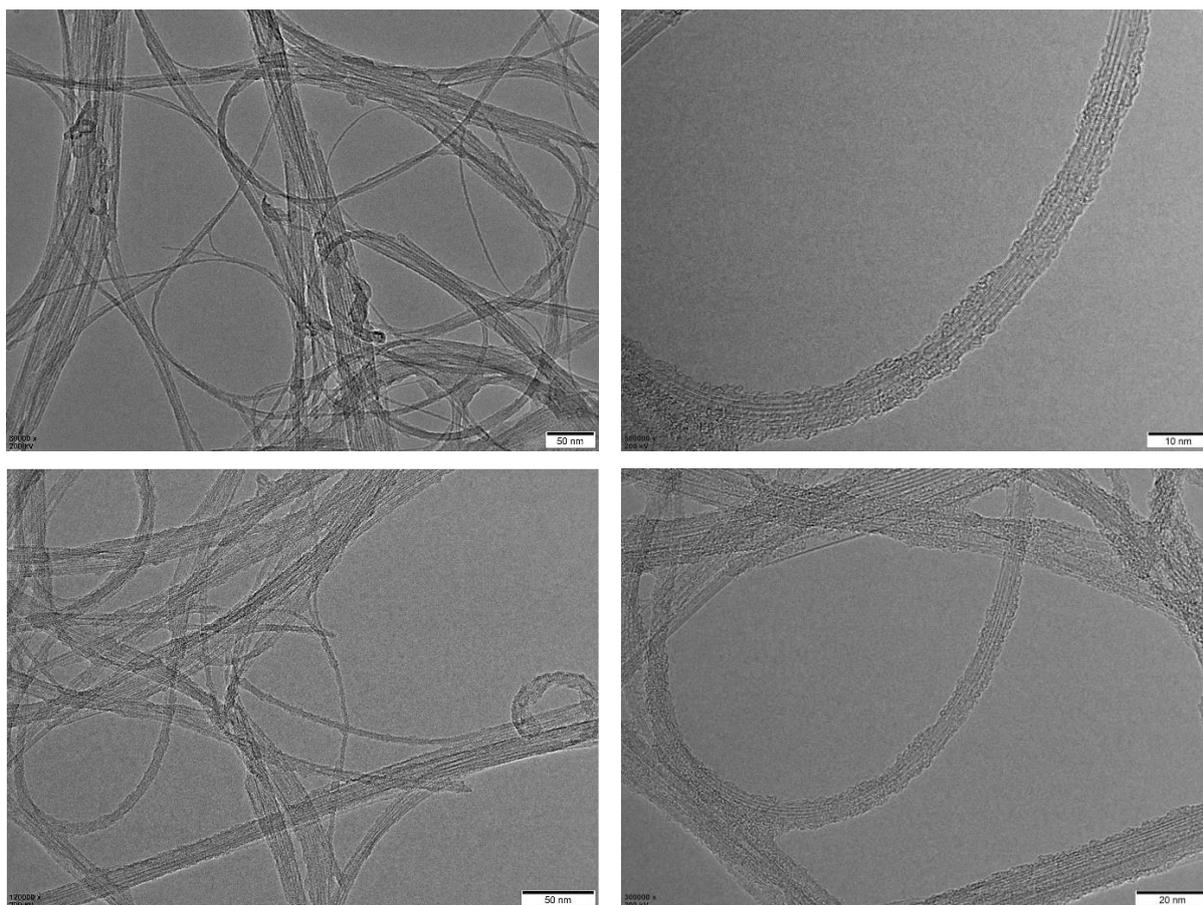


**Figure S3:** Comparison of the XPS spectra of a) P-SWCNT and b) Fn-SWCNT.

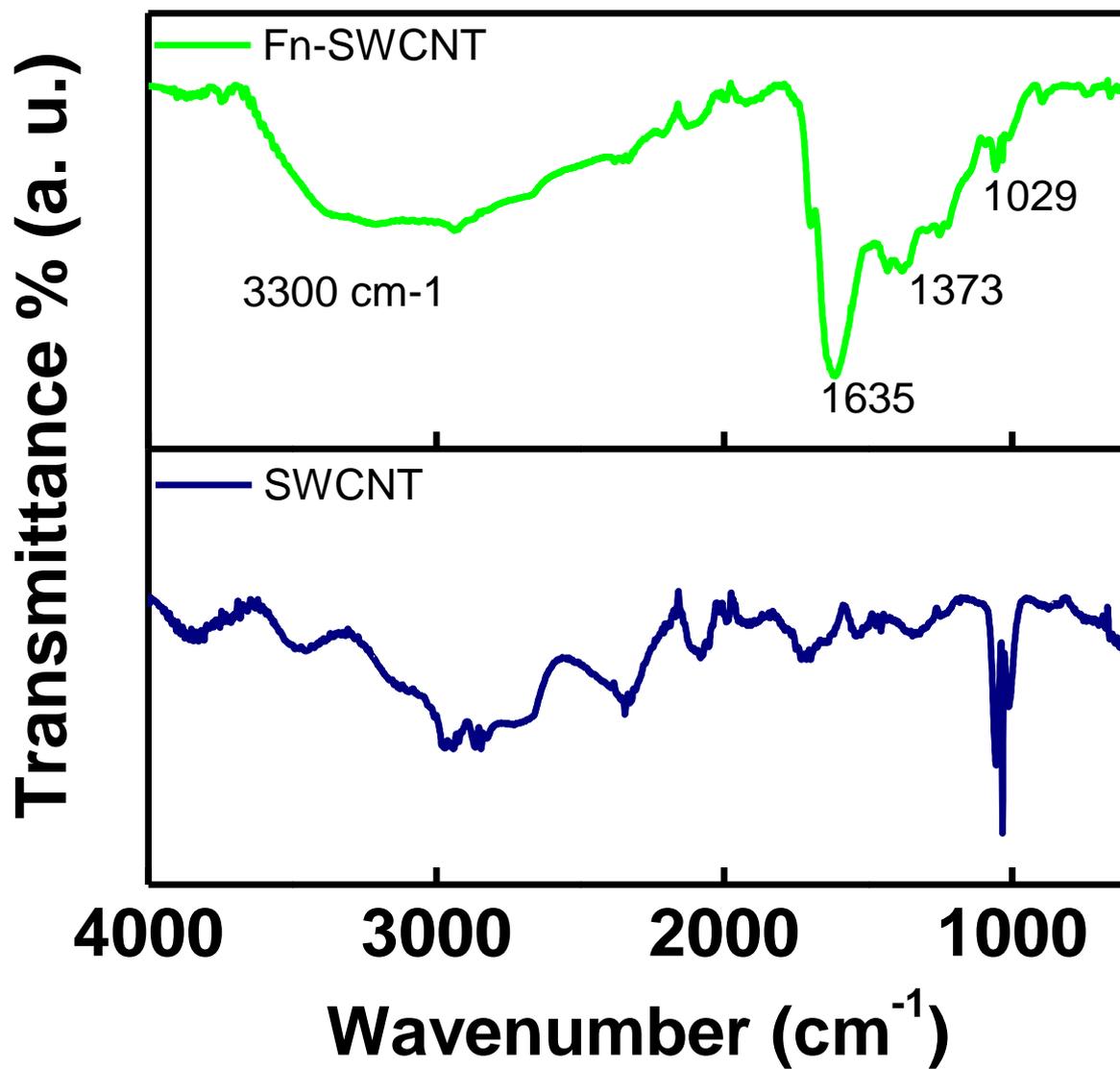


**Figure S4:** Water contact angle measurement of **Fn-SWCNT**.

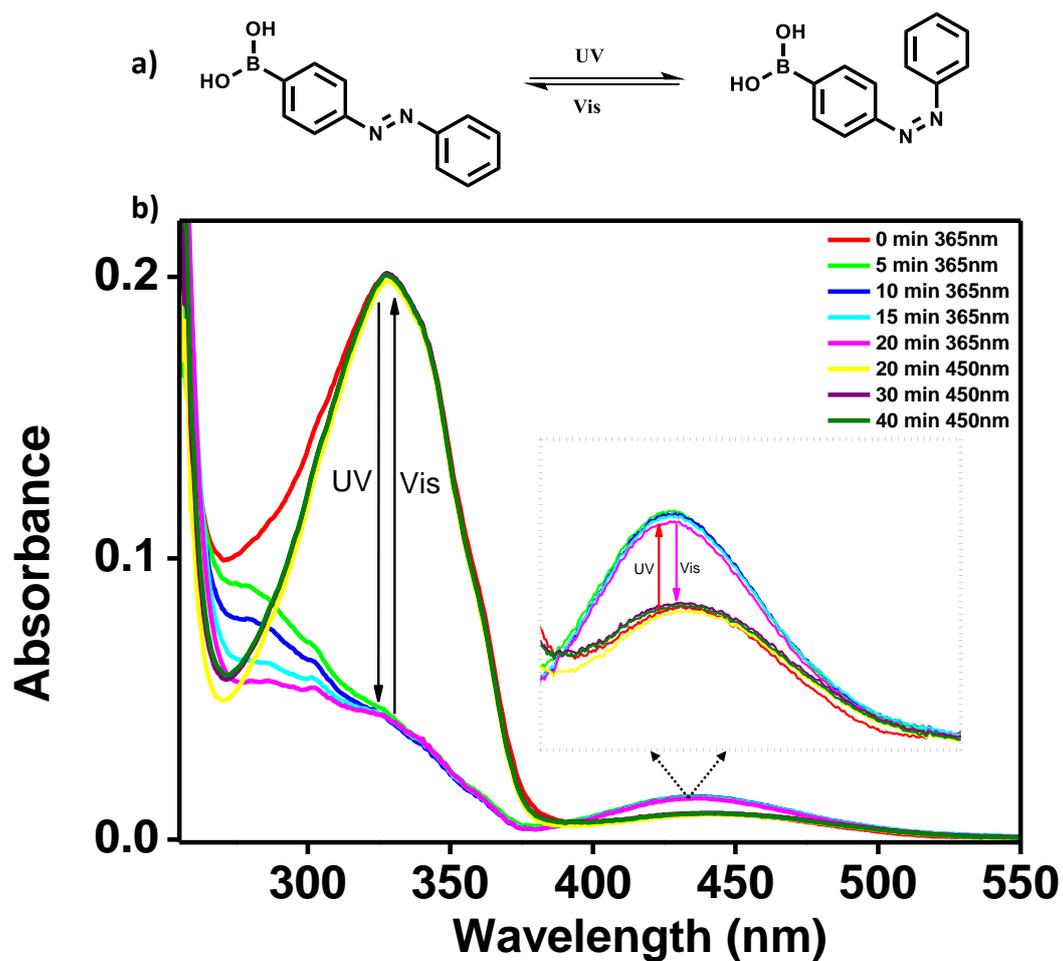
*Contact angle of **Fn-SWCNT** is 58.3° due to the presence of catechol groups in the **Fn-SWCNT** indicating a more hydrophilic nature.*



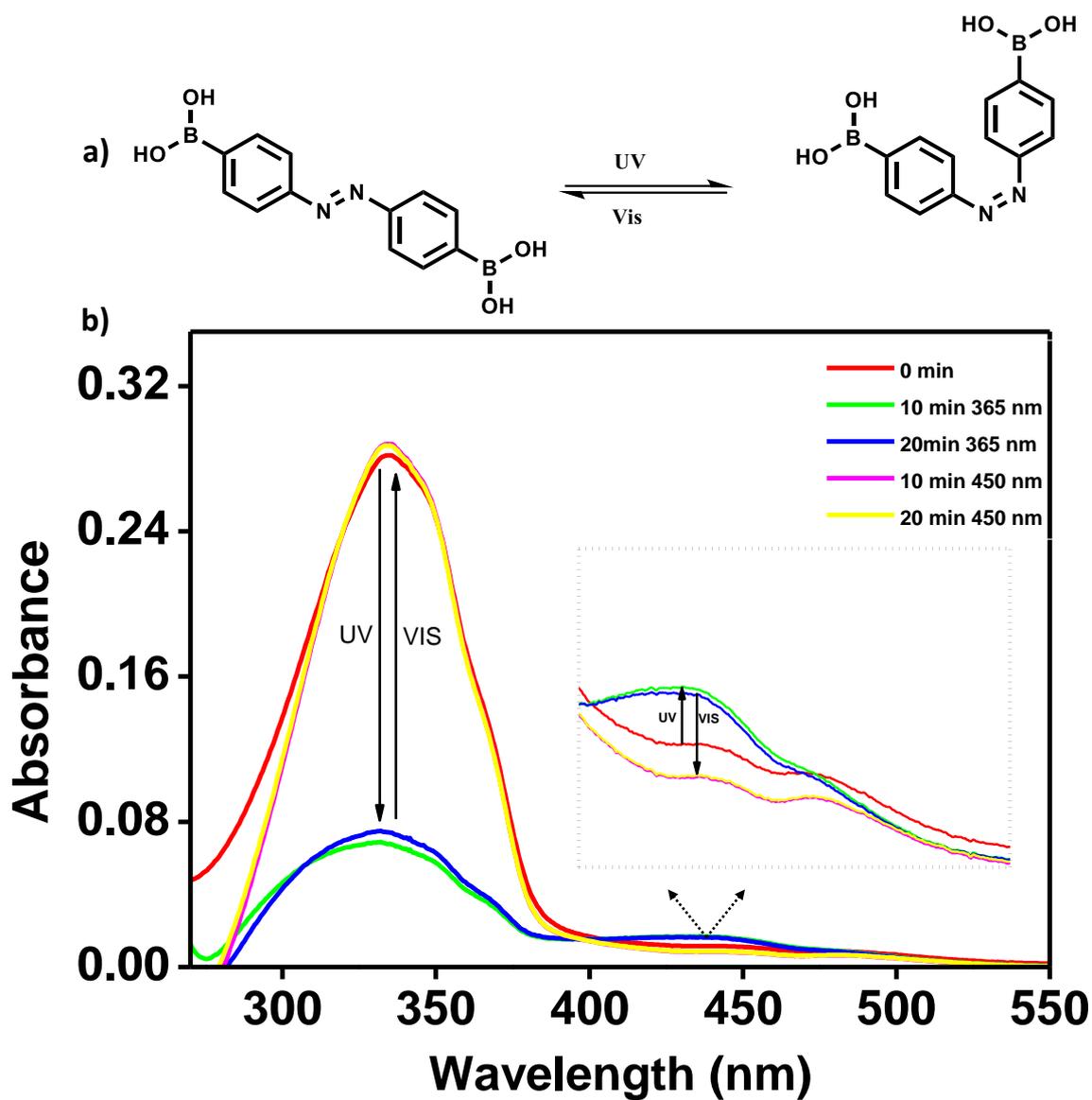
**Figure S5:** HR-TEM images of **Fn-SWCNT**.



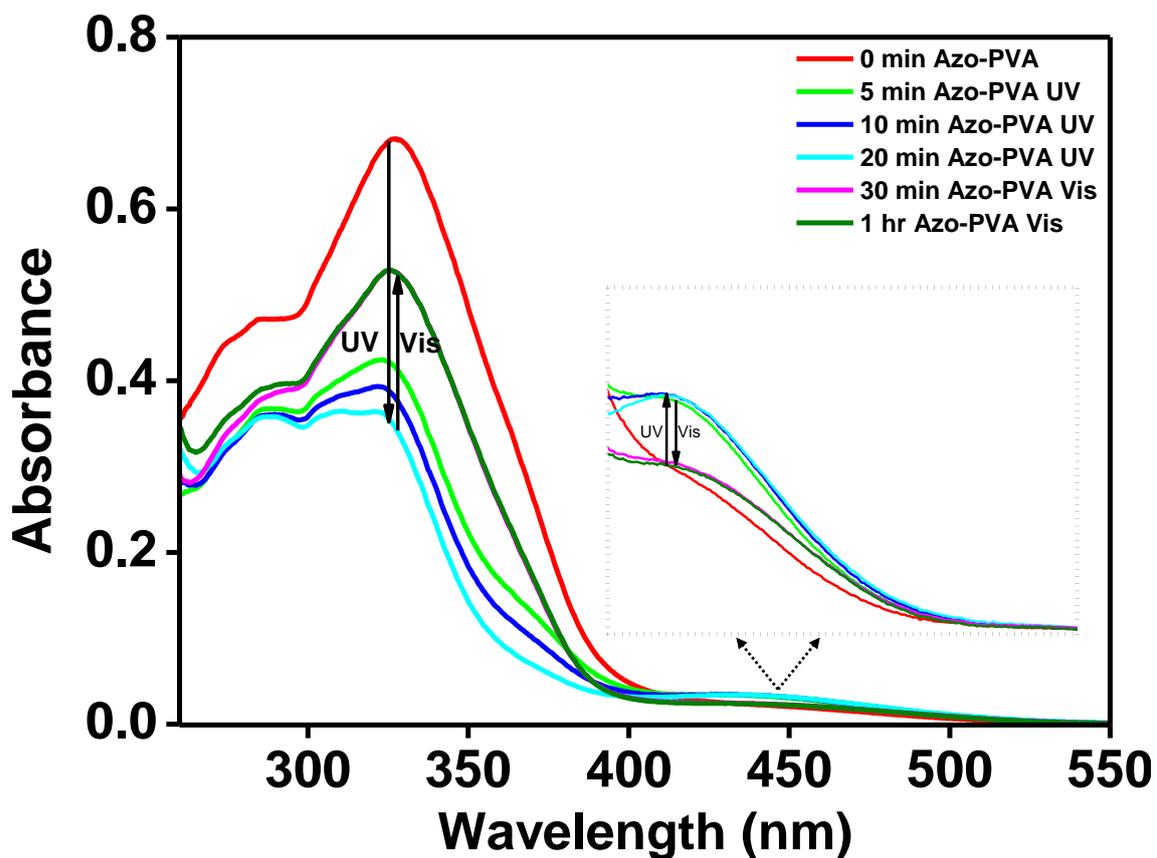
**Figure S6:** Comparison of the FT-IR spectra of P-SWCNT and Fn-SWCNT.



**Figure S7:** a) Schematic of *cis-trans* isomerization of **MBA** during UV and Vis light irradiation. b) Absorption spectral changes of **MBA** in DMSO upon UV and Vis light irradiation. Inset shows the increase in *cis* isomeric peak (435 nm) upon UV irradiation.



**Figure S8:** a) Schematic of cis-trans isomerization of **DBA** during UV and Vis light irradiation. b) Absorption spectral changes of **DBA** in DMSO upon UV and Vis light irradiation. Inset shows the increase in cis isomeric peak (438 nm) upon UV irradiation.



**Figure S9:** Absorption spectral changes of MBA-PVA in DMSO solution upon UV and Vis light irradiation. Inset shows the increase in *cis* isomeric peak (435 nm) upon UV irradiation.

*Prepared a stock solution of PVA (1 wt%, 13000-24000 MW) and MBA (5 mM in DMSO). Then this solution was diluted (0.1 mL stock solution to 10 mL DMSO) to record the absorption spectral changes.*

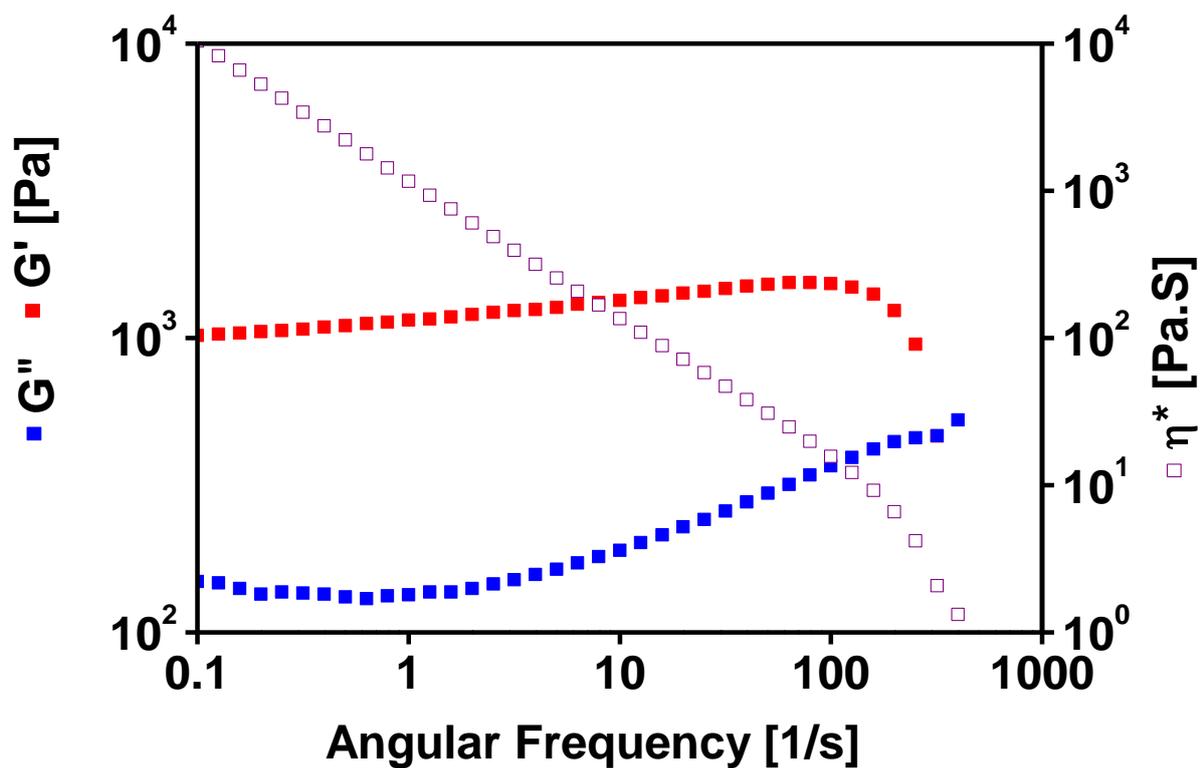


Figure S10: Frequency sweep experiment of Azo-PVA gel.

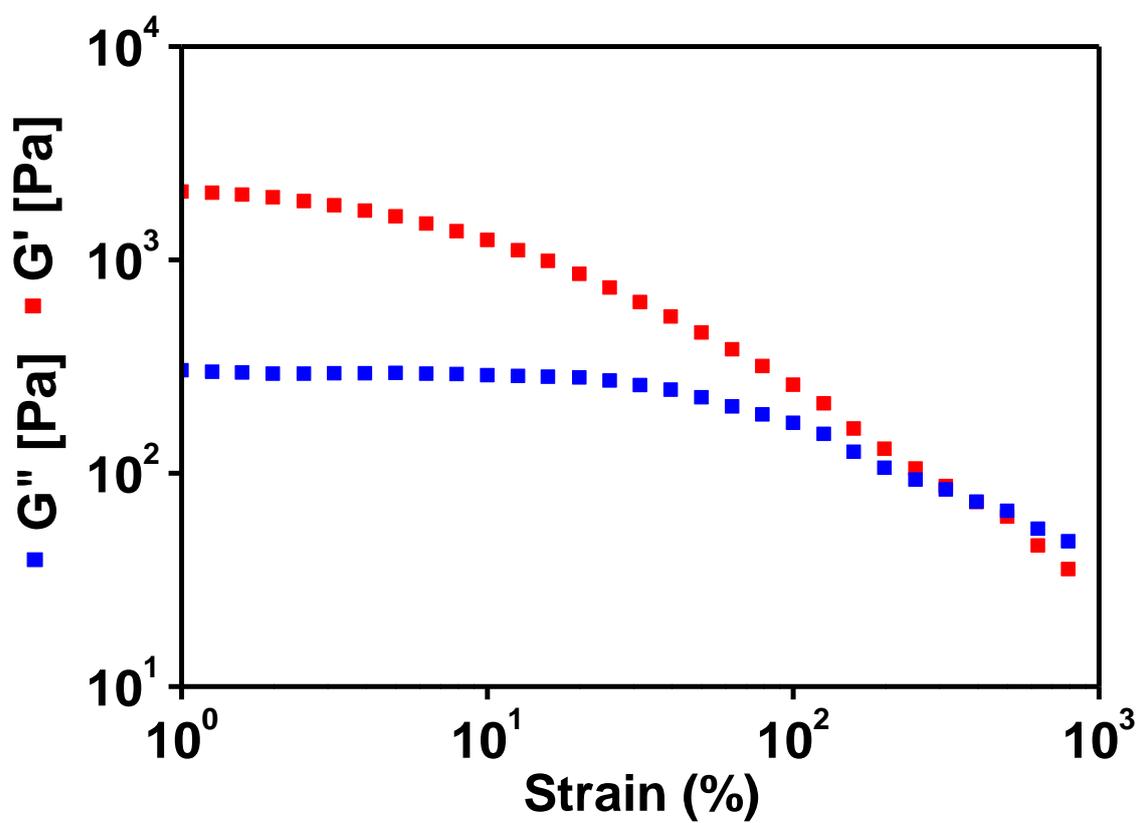


Figure S11: Strain sweep experiment of Azo-PVA gel.

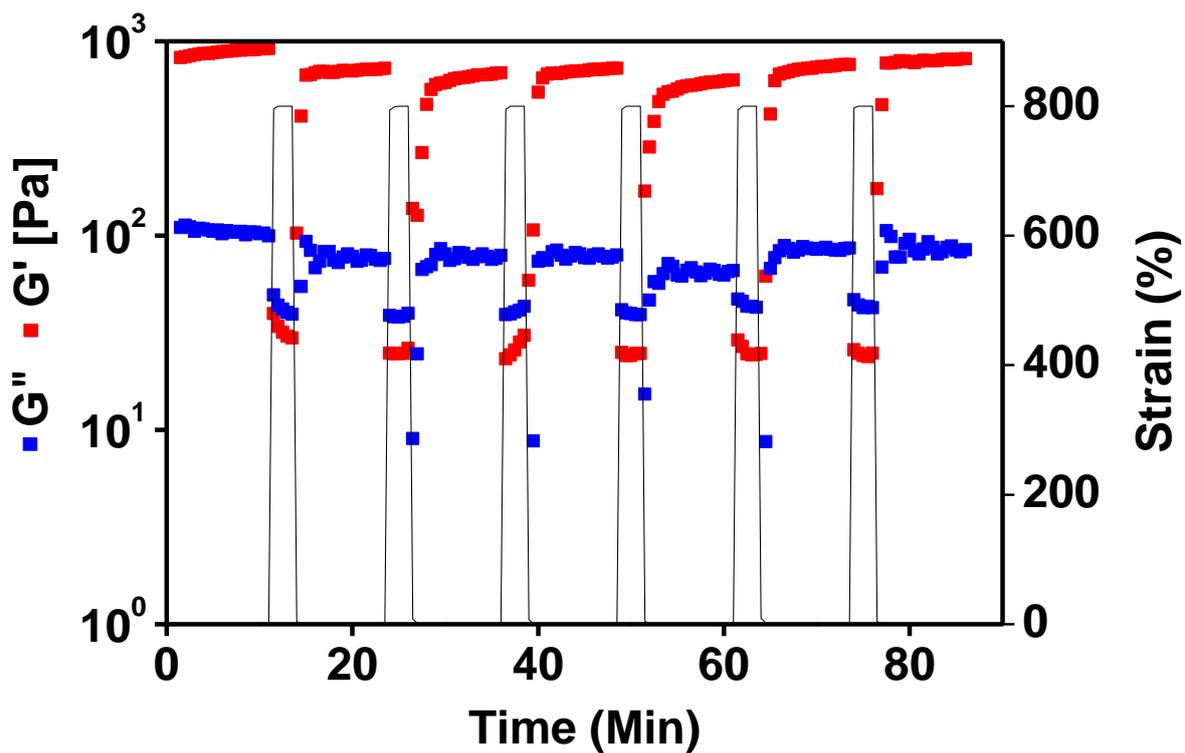


Figure S12: Self-recovery studies of Azo-PVA gel.

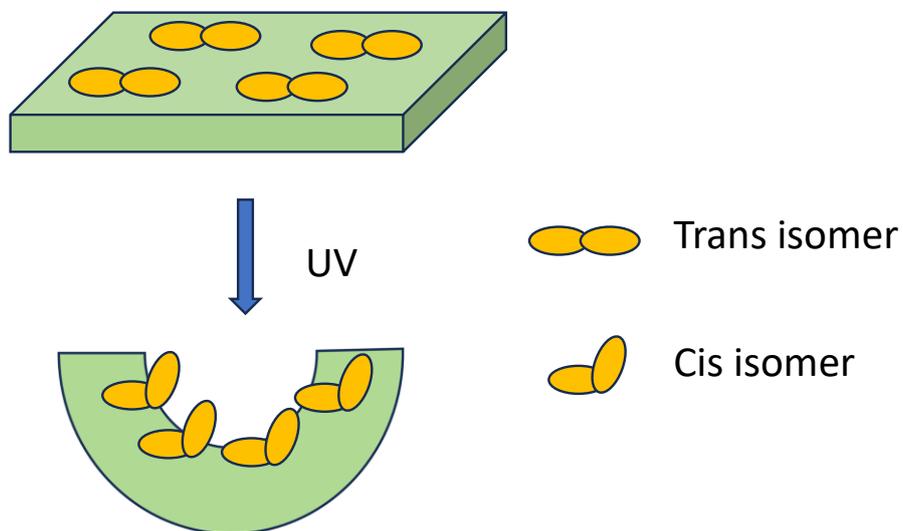
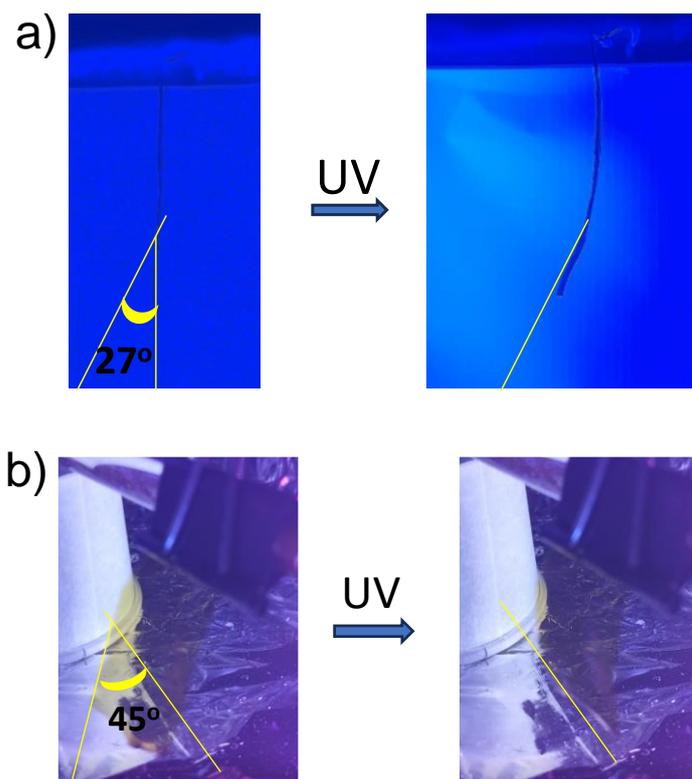
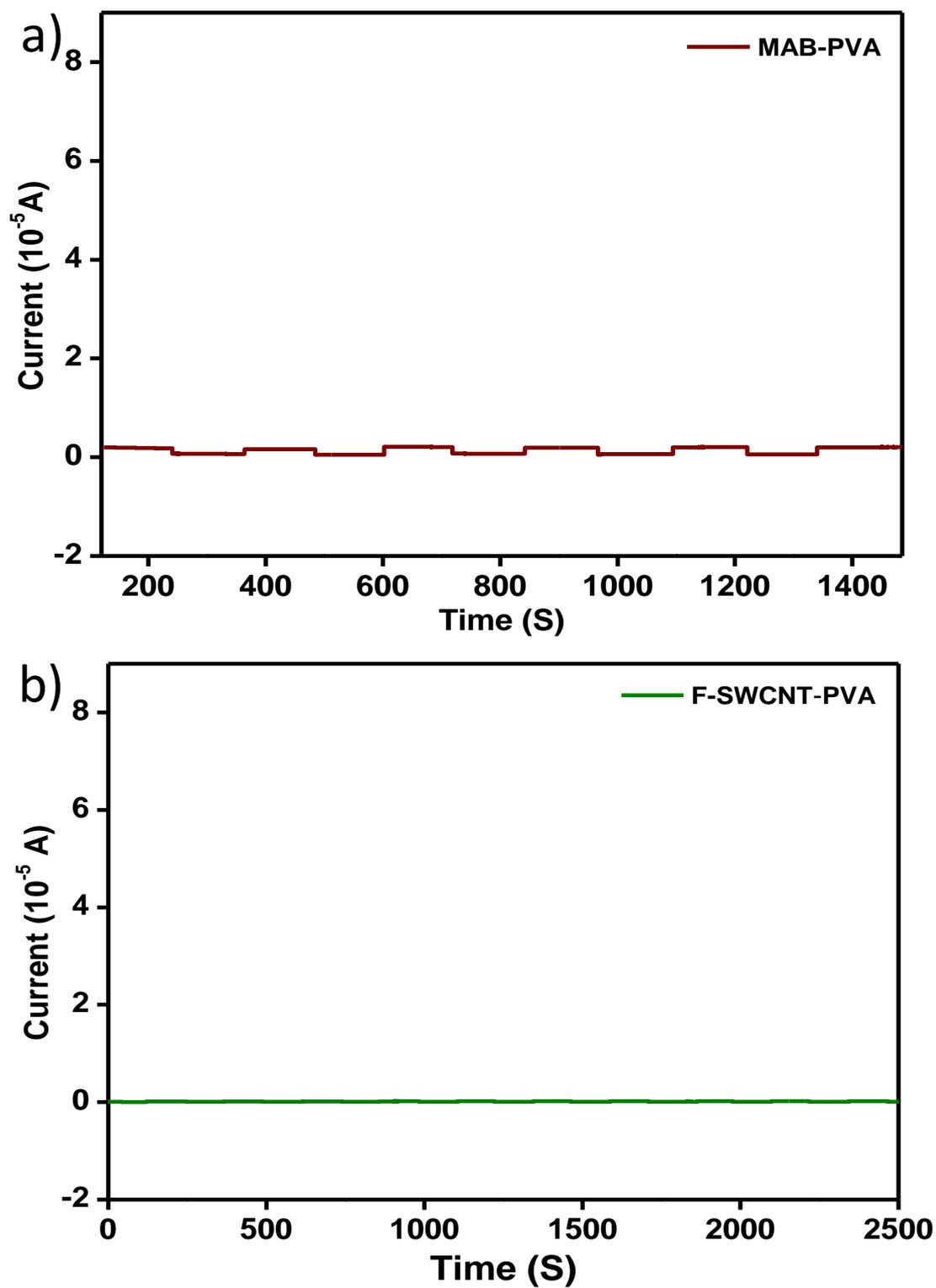


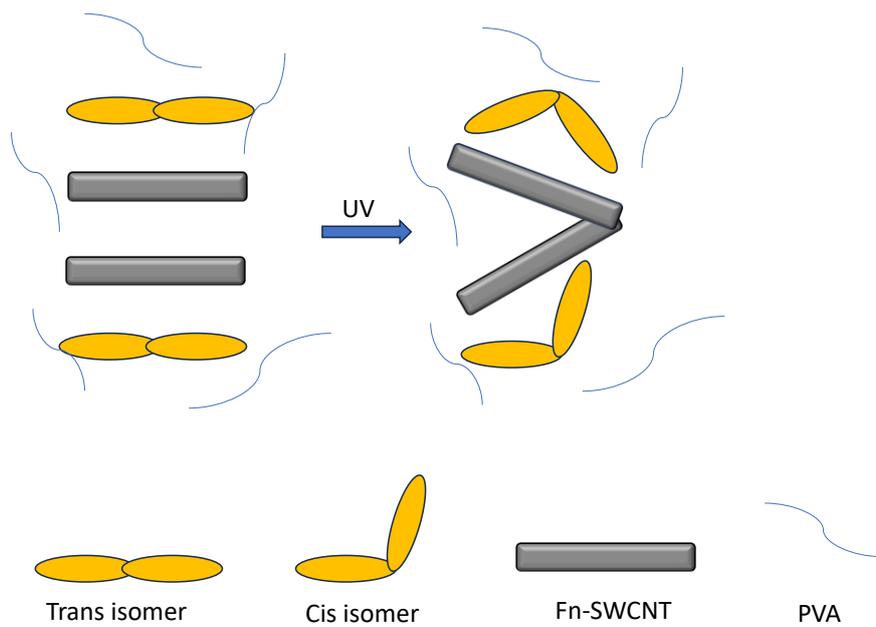
Figure S13: Schematic illustration of bending movement Azo-PVA film.



**Figure S14:** The bending angle of a) **Fn-SWCNT-Azo-PVA** film after 5 min and b) a) **Azo-PVA** film after 1 min irradiation.



**Figure S15:** Photocurrent switching studies with UV and Vis light irradiation on a) **Azo-PVA** and b) **Fn-SWCNT-PVA** films.



**Figure S16:** Schematic representation of cis-trans isomerization inside **Fn-SWCNT-Azo-PVA** film.

## Tables

**Table S1:** Comparison of the conductivity in literature reports.

<b>Polymer</b>	<b>Nanotube</b>	<b>Content (wt%)</b>	<b>Conductivity (S m<sup>-1</sup>)</b>	<b>Ref.</b>
<b>Polystyrene</b>	SWCNT	1	10 <sup>-3</sup>	<i>Polymer</i> , 2006, <b>47</b> , 7740-7746.
<b>Polystyrene</b>	SWCNT	1	0.2	<i>Composites, Part A</i> , 2010, <b>41</b> , 842–849
<b>Epoxy</b>	SWCNT	0.6	0.2	<i>J. Colloid Interface Sci.</i> , 2017, <b>506</b> , 620-632.
<b>PVA</b>	MWCNT	25	9.17	<i>Appl. Phys. Lett.</i> , 2008, <b>93</b> , 033104.
<b>Polystyrene</b>	MWCNT	15	0.05	<i>Carbon</i> , 2014, <b>69</b> , 372-378.
<b>Polystyrene</b>	MWCNT	19	4x10 <sup>-5</sup>	<i>J. Colloid Interface Sci.</i> , 2010, <b>344</b> , 395-401.
<b>PVA</b>	<b>SWCNT</b>	<b>5</b>	<b>0.3</b>	<b>This work</b>

## References

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