

## **Fabrication of durable, flexible, single-walled carbon nanotube transparent conductive films**

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### **Materials**

SWCNTs (1.0–1.2 nm in diameter, 5–20 μm in length) made by the arc-discharge method were purchased from Nano Solution Co., Ltd. (South Korea). 4,4'-dichlorodiphenylsulfone (DCDPS), and 4,4'-Hexafluoroisopropylidene diphenol (6FBPA), potassium carbonate were purchased from Alfa-Aesar, TCI and Dae-jung (South Korea), respectively. These compounds were dried at 100 °C for at least 10 h in a vacuum oven before the synthesis. N-Methyl-2-pyrrolidone purchased from Dae-jung was purified by stirring with NaOH and distilled from P2O5 under reduced pressure. Toluene was refluxed over Na metal to remove water and was freshly distilled before use. Fuming sulfuric acid (30% SO3) was procured from Iridous (South Korea). 3,3'-disodiumsulfonyl-4,4'-dichlorodiphenylsulfone (SDCDPS) was synthesized as per the reported procedure.[S1]

## **Characterizations**

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrum of the polymer was recorded using a Nicolet 6700 spectrophotometer. <sup>1</sup>H NMR spectrum was obtained from a 500 MHz Agilent Superconducting FT-NMR spectrometer using dimethyl sulfoxide-d<sub>6</sub> as the solvent. UV-Vis-NIR spectra of the SWCNT solutions were measured using Cary 5E (Varian) spectrophotometer with 1 nm steps. The de-bundled SWCNTs in the dispersion solution were characterized using an H-7600 TEM from Hitachi and AFM. Droplets of the solution were applied directly to carbon-coated copper grids for TEM measurement. Non-contact (tapping) AFM performed with an n-tracer SPM (Nanofocus). The cantilever was made of silicon resonant frequency of the range of 200-400 kHz and a nominal radius of over 10 nm. Images were obtained at room temperature in air. The structural characteristics of the SWCNTs on the substrate were investigated using an NTEGRA Spectra confocal Raman spectrometer (NT-MDT) with an excitation wavelength of 532 nm. The transmittances and sheet resistances of the TCFs were measured using an OPTIZEN 3220UV UV-vis spectrophotometer (MECASYS Co.) at 550 nm and a CMTSR1000N four-point probe measurement (A.I.T.), respectively. The flexibility and durability of the SWCNT-based TCFs were estimated by measuring the change in resistance using a computer system with a digital multimeter (Agilent 34401A) during the cyclic bending test. The cyclic test was performed on rectangular TCF samples. The tests were carried out using a home-made fatigue machine at 2 Hz, while maintaining a constant linear vertical movement with a 7 mm stroke. A cyclic bending stress was applied to the films dynamically using a moving jig.

## **Synthesis of sulfonated poly (ether sulfone) (SPES)**

The detailed synthesis and structure of the polymer prepared are shown in Figure S1. Polymerization reaction was carried out in a 250 mL, a three-necked round-bottomed flask equipped with a nitrogen inlet and outlet, a stir bar, and a Dean-Stark trap fitted with the condenser. The polymerization procedure was as follows: SDCDPS (4.00g, 8.1mmol), 6FBPA (2.73g, 8.1mmol), potassium carbonate (2.47g, 17.8 mmol), NMP (40 mL) and toluene (20 mL) were introduced into the reaction flask. The mixture was then heated to reflux (150 °C, oil bath temperature) for 4 h to remove water azeotropically with toluene. After removal of the toluene from the Dean-Stark trap, the reaction temperature was

increased to 185 °C and maintained for another 44 h till the reaction solution became viscous. The resulting solution was cooled to room temperature, filtered out the residual potassium carbonate, and precipitated into excess of the isopropanol. The polymer was isolated by filtration, washed thoroughly with 7:3 ratio of isopropanol and water solution, and dried under vacuum at 100 °C for 24 h (Figure S1).

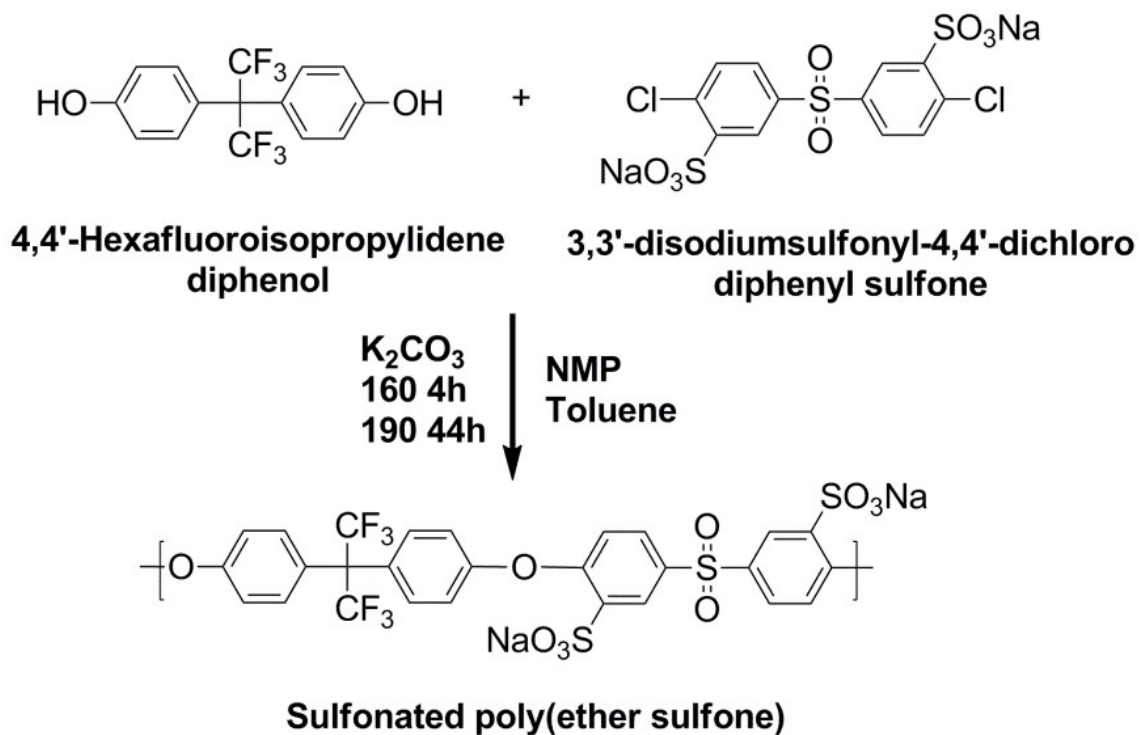
The <sup>1</sup>H NMR and ATR-FTIR spectra of the resulting polymer are shown in Figure S2 and Figure S3, respectively. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, δ): 8.3 (a), 7.9-7.8 (b), 7.5-7.3 (e), 7.2-7.0 (c,d). ATR-FTIR (cm<sup>-1</sup>): 1670, 1582, 1507, 1470, 1327, 1245, 1173, 1075, 1030, 970, 927, 885, 887, 826, 710, 690.

### **Preparation of SWCNTs dispersion**

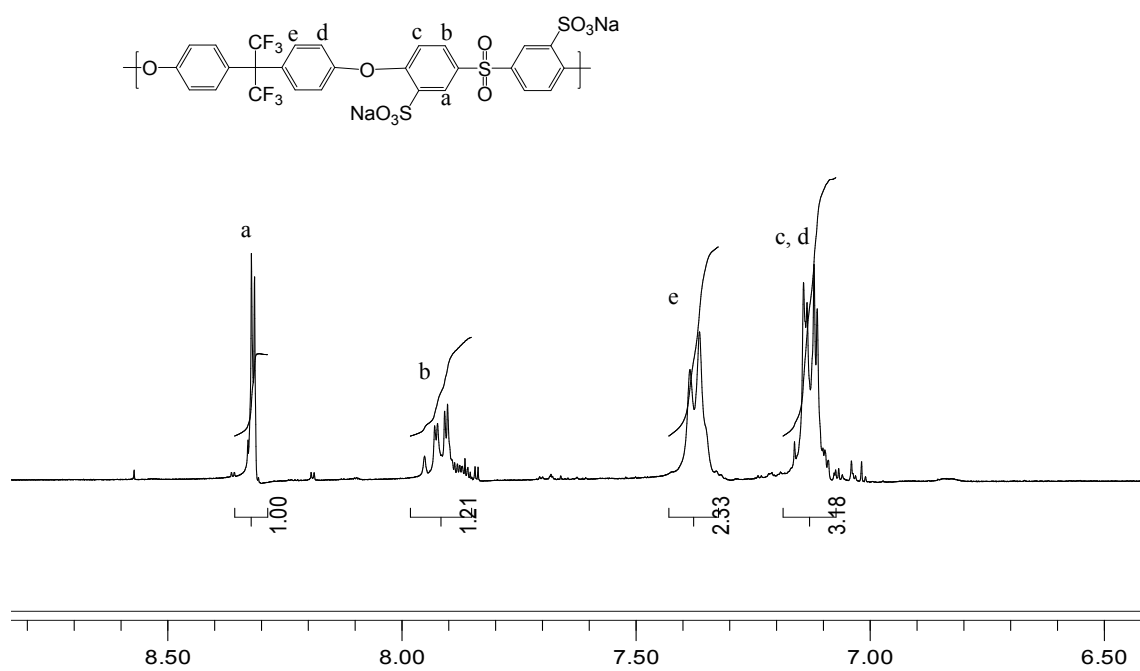
The SPES stock solution was first prepared by 1.0 weight % SPES (sodium salt) was dissolved in deionized water. Then, five times the weight of cation exchange resin was added to the solution and stirred for 30 min to convert the salt form to acid form as the solution changed to pH ~1.5 from pH > 6.5. The resin was filtered out and the SPES stock polymer solution was used for CNT dispersion. 20 mg SWCNTs was added to the 20 mL of SPES (0.1, 0.5 and 1.0 %) solution and dispersed using a bath-type sonicator (WUC-D22H, DAIHAN Scientific Co. 40kHz, 200 Watt) for 3 h. The dispersed SWCNT solution was centrifuged for 10 min at 9425g (g-force) to remove both bundled SWCNTs and the metal catalyst. The well-dispersed SWCNT solution was obtained from the supernatant.

### **Fabrication of transparent conductive films (TCFs)**

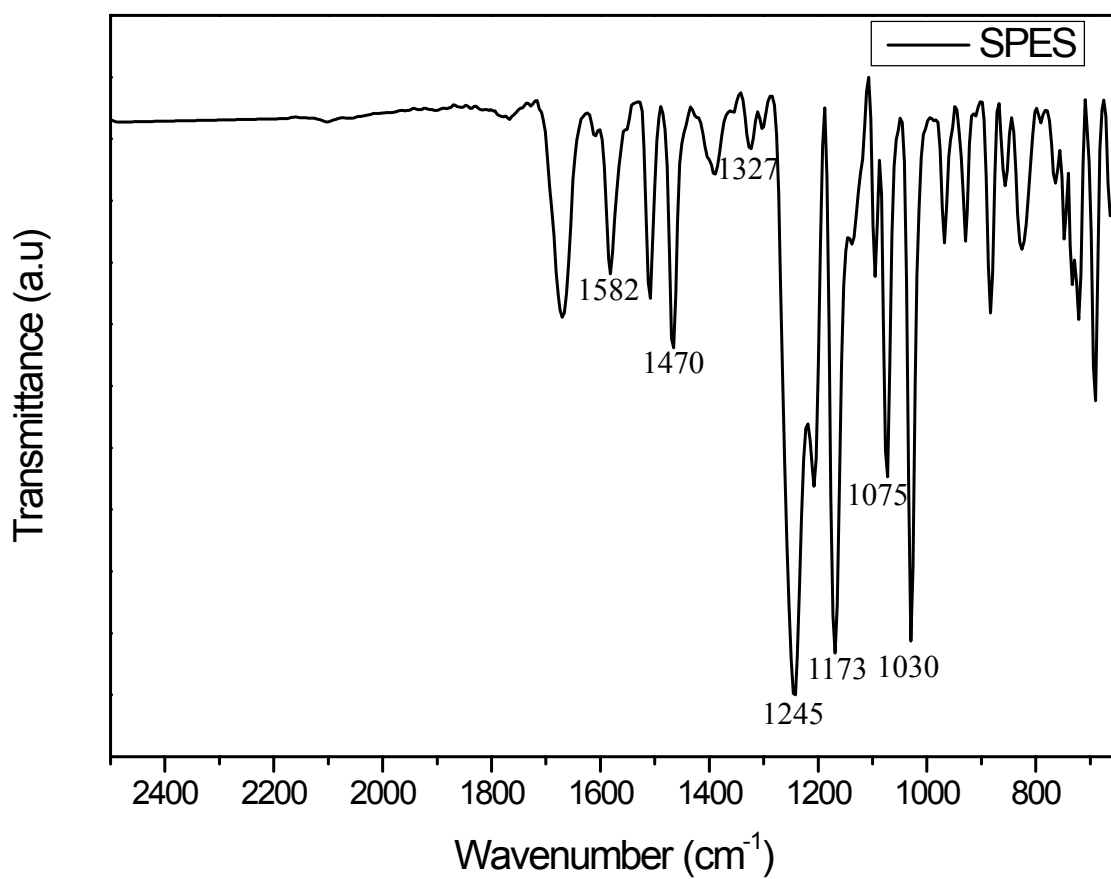
TCFs were prepared by spray-coating using the purified SWCNT solution on a polyethylene terephthalate (SH40 (PET, a thickness of 188 μm), purchased from SKC, Korea). The dispersed SWCNT solution was deposited on a substrate film (50 mm × 50 mm) using spray coater (NCS-400 manufactured from NCS, Korea) with nozzle speed 200 mm/sec at a constant rate of 1 mL/min under inert atmosphere. The distance between nozzle and the substrate was 7 mm; the temperature of the substrate was controlled at 80°C using the hot plate below the substrate. SWCNTs coated TCFs were utilized for further characterizations.



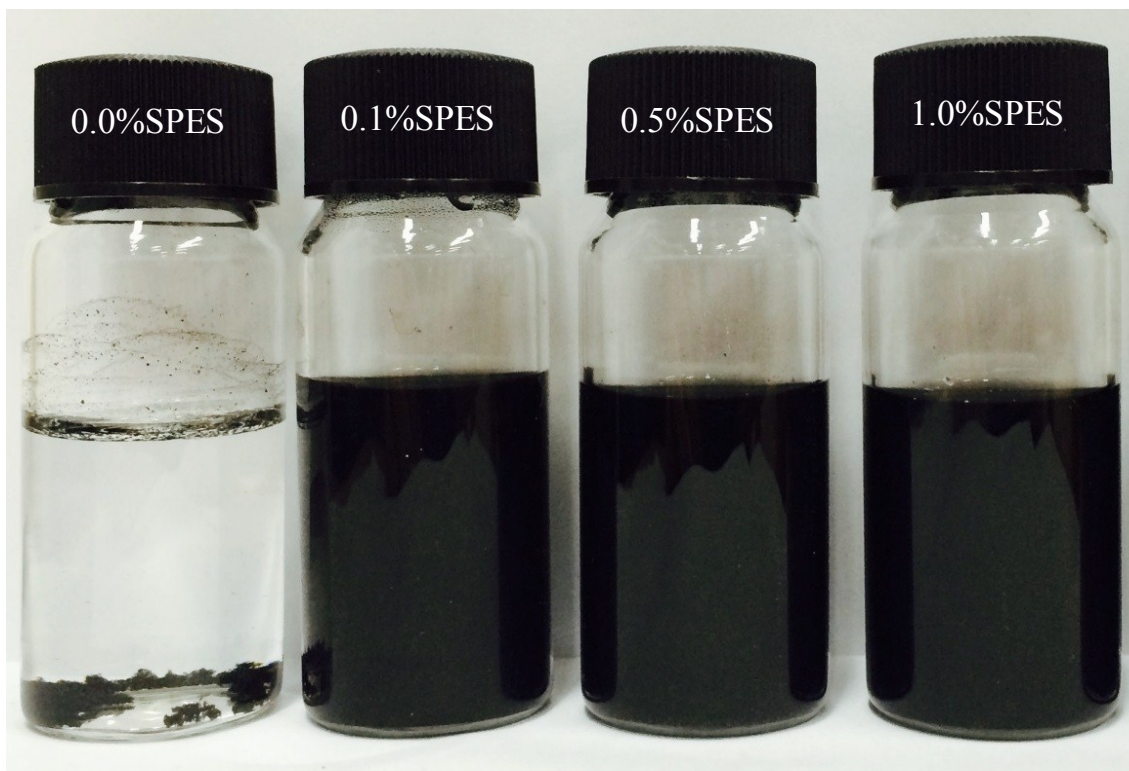
**Figure S1: Synthesis scheme of SPES**



**Figure S2:  $^1\text{H}$ NMR spectrum for SPES**



**Figure S3: FT-IR spectrum for SPES**



**Figure S4.** Photo images of SWCNT dispersions 0.0, 0.1, 0.5 and 1.0wt % SPES aqueous solution (after centrifuge)

## Reference

[S1] D. Zhang, K. Ryu, X. Liu, E. Polikarpov, J. Ly, M. E. Tompson and C. Zhou, *Nano Lett.*, 2006, 6, 1880.