

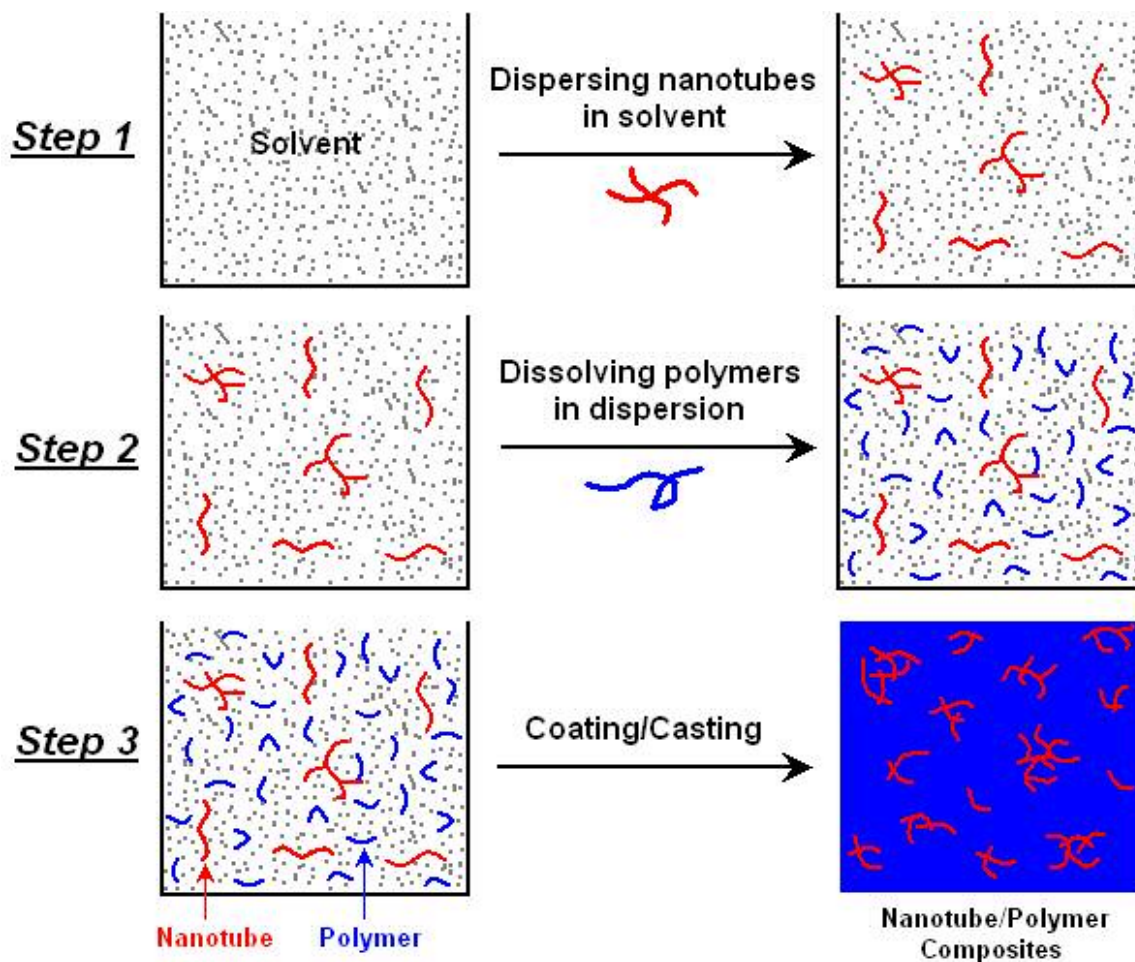
# Supporting Information

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## 1. Traditional Synthesis of Carbon Nanotube/Polymer Composites (Figure S1).

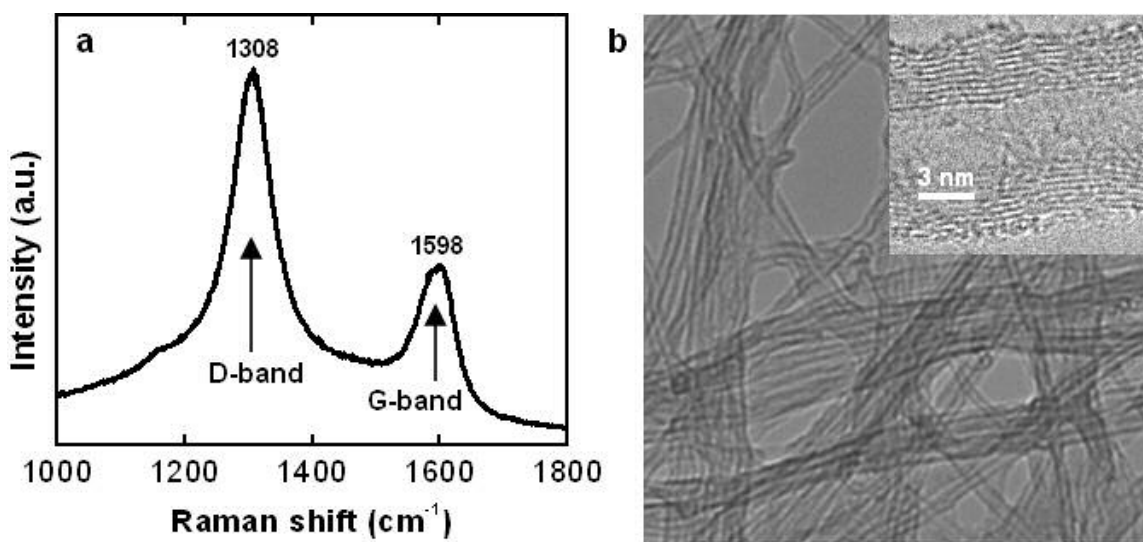
It includes three steps: 1) carbon nanotubes are dispersed in solvents; 2) designed polymers are dissolved in the carbon nanotube dispersion; 3) carbon nanotube/polymer mixture solutions are finally coated or cast on substrates, followed by evaporation of solvents. By this approach, nanotubes aggregate with each other and are randomly dispersed in the resulting composite materials.



*Figure S1.* Schematic illustration of the traditional synthesis of carbon nanotube/polymer composites.

## 2. Synthesis of Long Carbon Nanotube Arrays

Long nanotube arrays were synthesized in a quartz tube furnace with diameter of 1 inch. Pure ethylene served as the carbon source, and Ar with 6% H<sub>2</sub> was used to carry the carbon source. The catalysts used in this study were Al<sub>2</sub>O<sub>3</sub> (10 nm)/Fe (0.3–1.0 nm) on SiO<sub>2</sub> (~ 1 μm) /Si wafers. The Fe and Al<sub>2</sub>O<sub>3</sub> films were deposited by sputtering and ion-beam-assisted deposition techniques, respectively. Typically, carbon nanotube growth was carried out at 750 °C with 80 sccm ethylene and 120 sccm carrier gas for 15 min. Note that nanotube arrays are spinnable for the growth time of 30 minutes and non-spinnable for longer time. The prolonged growth results in the formation of a mixture of amorphous carbon, graphite, and nanotubes at the top surface of nanotube arrays. This carbon mixture severely hinders their spinnability.



**Figure S2.** a. Raman spectrum of the array. b. TEM image of synthesized nanotubes (inserted, high resolution TEM).

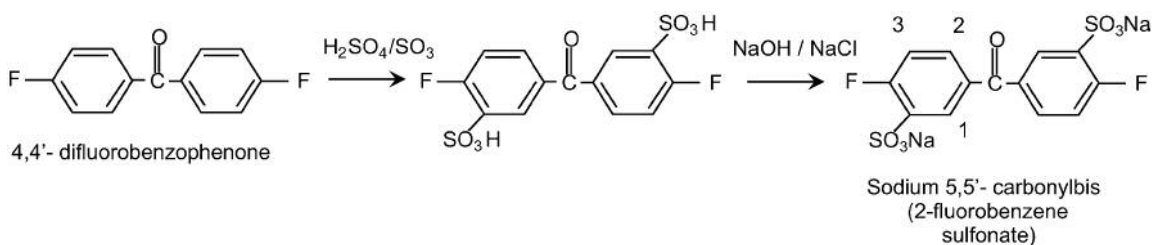
### 3. Information of Used Polymers

Polystyrene was purchased from Aldrich with  $M_n$  of  $1.4 \times 10^5$  g/mol and  $M_w$  of  $2.3 \times 10^5$  g/mol. Two poly(methyl methacrylate) samples were purchased from Aldrich with  $M_w$  of  $1.5 \times 10^4$  g/mol and  $1.20 \times 10^5$  g/mol, respectively. Poly (3-hexylthiophene-2, 5-diyl) was also purchased from Aldrich with  $M_w$  of  $8.7 \times 10^4$  g/mol. The regioregularity is greater than 98.5 % head-to-tail regiospecific conformation. All above four polymers are used as received. Polydiacetylene was synthesized by topo-chemical polymerization of 10, 12-pentacosadiynoic acid molecules under UV irradiation at the wavelength of 365 nm. It took  $\sim 20$  minutes for this polymerization process. After polymerization, the resulting materials exhibited a blue color. Sulfonated poly (ether ether ketones) was synthesized via the nucleophilic aromatic substitution reactions of sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) and 3,3',5,5'-tetramethyl-4,4'-biphenol. The synthetic details are described in the following section (Section 4).

## 4. Synthesis of S-PEEK<sup>1</sup>

### (1) Synthesis of sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate)

The synthesis of sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) was performed according to a procedure described by Wang.<sup>2</sup> As shown in Figure S4, 21.8 g (0.1 mol) of 4,4'-difluorobenzophenone was dissolved in 30% fuming sulfuric acid (50 ml). The solution was stirred at 110 °C for 6 h, cooled to room temperature, and poured into ice water. Excess NaOH was added to the mixture to neutralize the solution. The mixture was then incubated to room temperature and NaCl was added to precipitate the sulfonated monomer. The sulfonated monomer was finally filtered and dried in an ambient condition. The monomer was then re-crystallized for three times using a mixture of methanol and water. The yield of the sulfonation reaction is around 85% (35.87 g of sulfonated monomer were produced when 21.8 g of 4,4'-difluorobenzophenone was used). The chemical structure of sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) was confirmed by Fourier transform infrared (FTIR) and <sup>1</sup>H NMR spectroscopies. The FTIR spectrum (KBr substrate, cm<sup>-1</sup>) shows intense absorption bands at 1664 (C=O stretching), 1259 and 1093 (asymmetric and symmetric stretching vibrations of sodium sulfonate groups), and 624 (stretching vibrations of C=S). The <sup>1</sup>H NMR spectrum (500 MHz, DMSO) shows peaks at  $\delta_{H1} = 8.0$  ppm (dd, 2.5, 4.5 Hz),  $\delta_{H2} = 7.7$  ppm (m, 2.5, 2.0, 8.5 Hz), and  $\delta_{H3} = 7.3$  ppm (t, 8.5 Hz), where H<sup>1</sup>, H<sup>2</sup>, and H<sup>3</sup> respectively represent the hydrogen atoms of the sulfonated monomer labeled in Figure S3. These spectroscopic results confirm the formation of the sulfonated monomer.<sup>2</sup>

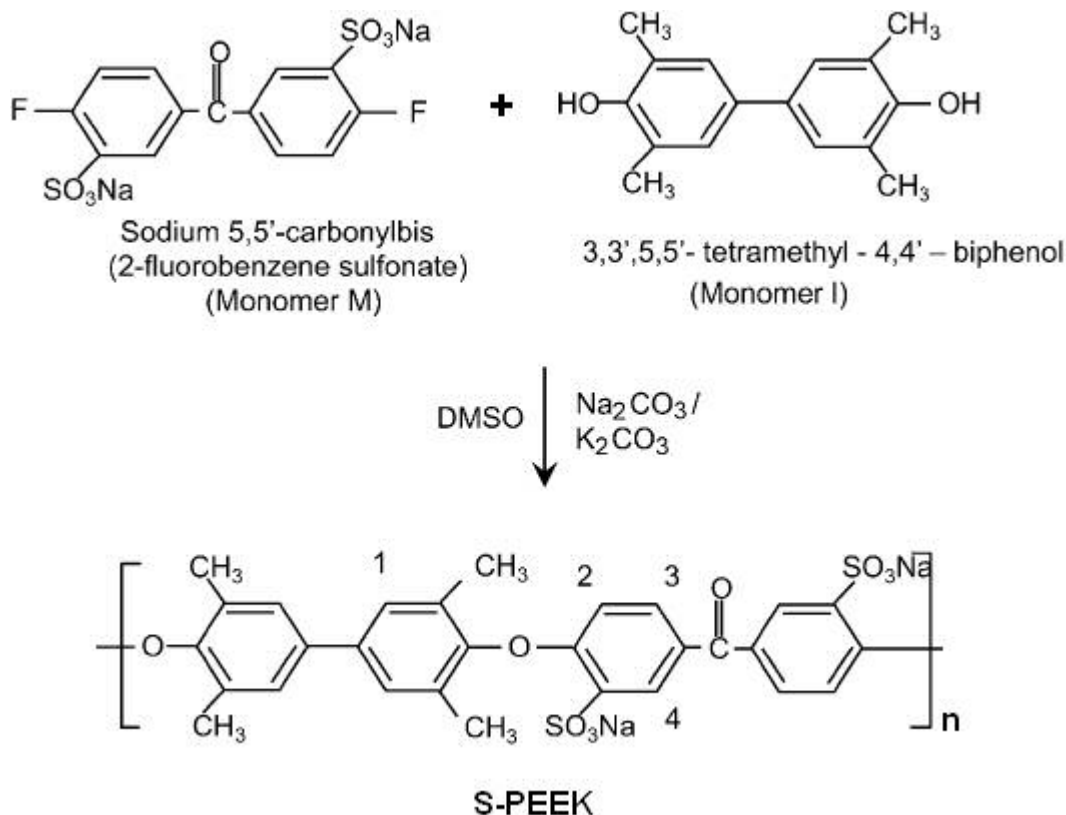


**Figure S3.** Synthesis of the sulfonated monomer.

### (2) Synthesis of the sulfonated polymers

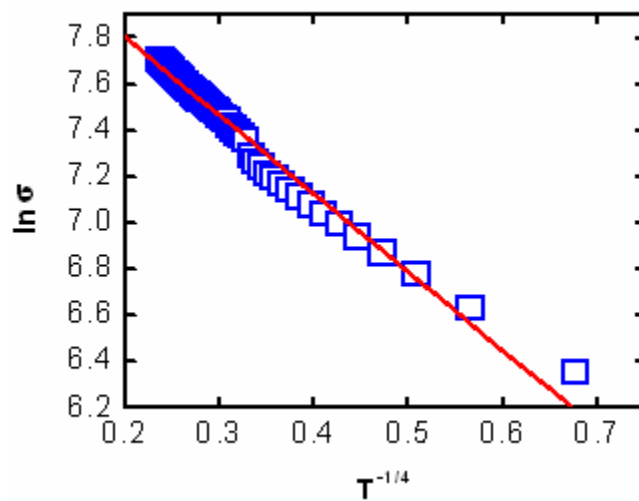
As shown in Figure S4, sulfonated aromatic poly (ether ether ketones) (S-PEEK) were synthesized via the nucleophilic aromatic substitution reactions of sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) (monomer 1) and 3,3',5,5'-tetramethyl-4,4'-biphenol (monomer 2). Monomer 1 and monomer 2 were first dissolved in DMSO with equal molar ratio. Polymerization was conducted sequentially at 140 °C for 4 h and at

170 °C for 6 h using anhydrous potassium carbonate as catalyst. The products were precipitated using a mixture of water and methanol.

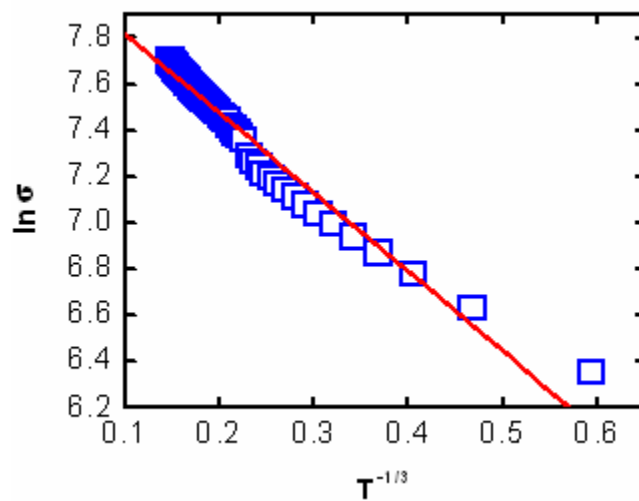


**Figure S4.** Synthesis of the S-PEEK through co-condensation reaction.

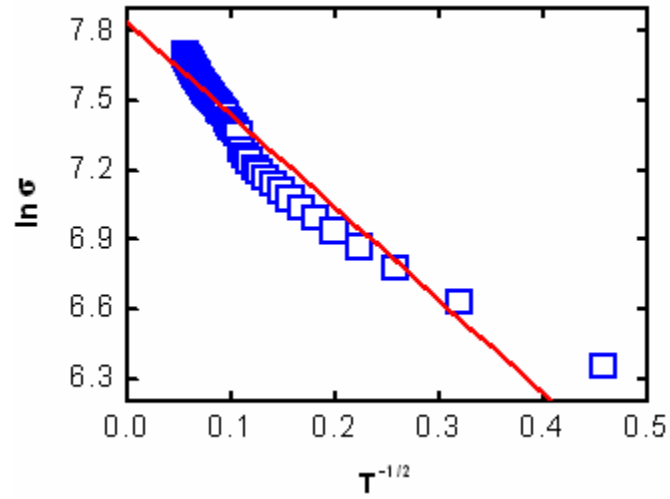
The polymer structure was confirmed by <sup>1</sup>H NMR and FTIR spectroscopic studies. The <sup>1</sup>H NMR spectrum (500 MHz, DMSO) of the polymers shows peaks at δ<sub>H1</sub> = 7.54 ppm, δ<sub>H2</sub> = 6.46 ppm, δ<sub>H3</sub> = 7.64 ppm, and δ<sub>H4</sub> = 8.23 ppm, where H<sup>1</sup>, H<sup>2</sup>, H<sup>3</sup> and H<sup>4</sup> respectively represents the hydrogen atoms of the sulfonated polymers labeled in Figure S5, confirming the formation of polymer. For the typical FTIR spectrum of the S-PEEK, the absorption bands at 1241, 1085, and 1027 cm<sup>-1</sup> can be assigned to the asymmetric and symmetric stretching vibrations of the sodium sulfonate groups. The absorption band at 685 cm<sup>-1</sup> can be assigned to the stretching of the sodium sulfonate groups. The absence of aromatic-sulfone group vibrations in the range of 1140–1110 cm<sup>-1</sup> indicates a copolymerization without significant cross-linking. The molecular weights of S-PEEKs were characterized by gel permeation chromatography. *M<sub>n</sub>* of S-PEEK samples used in this study is 4992 g/mol. S-PEEK can be dissolved in DMF and H<sub>2</sub>O. In this study, H<sub>2</sub>O was used as its solvent.



**Figure S5.** The plot of  $\ln \sigma$  vs.  $T^{-1/4}$  based on the Mott's variable range hopping model as  $\sigma \propto \exp(-A/T^{1/(d+1)})$ , where  $\sigma$  is the electrical conductivity,  $A$  is a constant,  $T$  is the temperature, and  $d$  is the dimensionality. For this plot,  $d=3$ , i.e. three-dimensional hopping mechanism.



**Figure S6.** The plot of  $\ln \sigma$  vs.  $T^{-1/3}$  based on the Mott's variable range hopping model as  $\sigma \propto \exp(-A/T^{1/(d+1)})$ , where  $\sigma$  is the electrical conductivity,  $A$  is a constant,  $T$  is the temperature, and  $d$  is the dimensionality. For this plot,  $d=2$ , i.e. two-dimensional hopping mechanism.



**Figure S7.** The plot of  $\ln \sigma$  vs.  $T^{-1/2}$  based on the Mott's variable range hopping model as  $\sigma \propto \exp(-A/T^{1/(d+1)})$ , where  $\sigma$  is the electrical conductivity,  $A$  is a constant,  $T$  is the temperature, and  $d$  is the dimensionality. For this plot,  $d=1$ , i.e. one-dimensional hopping mechanism.



**Reference:**

1. Gil, M.; Ji, X.; Li, X. F.; Na, H.; Hampsey, J. E.; Lu, Y. *J. Membr. Sci.* **2004**, *234*, 75-81.
2. Wang, F.; Chen, T. L.; Xu, J. P. *Macromol. Chem. Phys.* **1998**, *199*, 1421–1426.

**Full list of references:**

- (1b) Rogers, J. A.; Bao, Z.; Baldwin, K.; Dodabalapur, A.; Crone, B.; Raju, V. R.; Kuck, V.; Katz, H.; Amundson, K.; Ewing, J.; Drzaic, P. *Proc. Natl. Acad. Sci. U. S. A.* **2001**, *98*, 4835-4840.
- (6) Li, Q.; Zhang, X.; DePaula, R. F.; Zheng, L.; Zhao, Y.; Stan, L.; Holesinger, T. G.; Arendt, P. N.; Peterson, D. E.; Zhu, Y. T. *Adv. Mater.* **2006**, *18*, 3160-3163.
- (8a) Li, Q.; Li, Y.; Zhang, X.; Chikkannanavar, S. B.; Zhao, Y.; Dangelewicz, A. M.; Zheng, L.; Doorn, S. K.; Jia, Q.; Peterson, D. E.; Arendt, P. N.; Zhu, Y. *Adv. Mater.* **2007**, *19*, 3358-3363.