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Exploiting High Quality PEDOT:PSS/SWNT Composite Formulations for Wet-Spinning Multifunctional Fibers

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The supplementary information

Increasing the SWNT loading

Achieving SWNT loadings higher than 0.02 V_f, was possible only by increasing the SDS-SWNT stock dispersion concentrations. Therefore, a second SDS-SWNT stock concentration of 2.2 mg ml^{-1} (after centrifugation of a 3 mg ml^{-1}) was made up to prepare formulations with SWNT loadings greater than 0.02 V_f. The mass ratio of the surfactant (SDS) to SWNT was critical for the formation of a good dispersion at such a high concentration. We experimentally found the optimum mass fraction of SDS to the SWNT to be around 3 to 5. When the concentration of SDS was lower, stabilization was inadequate. Table S1 lists a summary of all the dispersions and spinning formulations used to prepare fibers reported here.

Table S1. Summary of the PEDOT:PSS/ SWNT spinning solution composition and the calculated SWNT loading in the resultant fiber.

SDS-SWNT [ml]	Water [ml]	PEDOT:PSS [mg]	total solid content [mg ml^{-1}]	SDS Mass fraction	PEDOT:PSS mass fraction	SWNT Volume fraction [c]
0	1	20	20.0	0	100	0
1[a]	1.5	70	30.2	6.6	92.7	0.005
1[a]	0.5	32	25	13.3	85.3	0.01
1[a]	0.27	20	25.5	19.6	78.4	0.015
1[a]	0	15	20.5	24.4	73.2	0.018
1[a]	0	12.5	18	27.7	69.4	0.020
1[b]	1.2	34	20.5	19.9	75.2	0.037
1[b]	0.5	19.5	20.5	29.3	63.5	0.054
1[b]	0.2	11	20.1	40.5	49.5	0.074
1[b]	0	6.5	17.7	50.8	36.7	0.092
1[b]	0	3.9	15.1	59.6	25.8	0.11

[a] The SDS-SWNT stock dispersion concentration used is 0.5 mg ml^{-1} and is obtained after a mild centrifugation (3000 g, 90 min) of a dispersion containing 1 mg SWNT, 5 mg SDS and 1 ml water.

[b] The SDS-SWNT stock dispersion used is 2.2 mg ml^{-1} and is obtained after a mild centrifugation (3000 g, 90 min) of a dispersion containing 3 mg SWNT, 9 mg SDS and 1 ml water.

[c] This SWNT volume fraction is calculated based on mass fraction of SWNT/PEDOT:PSS in spinning solution and with the assumption that no SWNT, SDS and PEDOT:PSS were lost in the wet spinning process (EQ S1). The densities of SWNT, SDS and PEDOTPSS were assumed to be ~1.5, ~1.01 and ~1.1-1.2 mg cm^{-3}, respectively.

$$\text{SWNT volume fraction} = \left(\frac{V_{SWNT}}{V_{Total}}\right) = \left[\frac{\left(\frac{m_{SWNT}}{\rho_{SWNT}}\right)}{\left(\left(\frac{m_{SWNT}}{\rho_{SWNT}}\right)+\left(\frac{m_{SDS}}{\rho_{SDS}}\right)+\left(\frac{m_{PEDOT:PSS}}{\rho_{PEDOT:PSS}}\right)\right)}\right] \qquad \text{(EQ S1)}$$

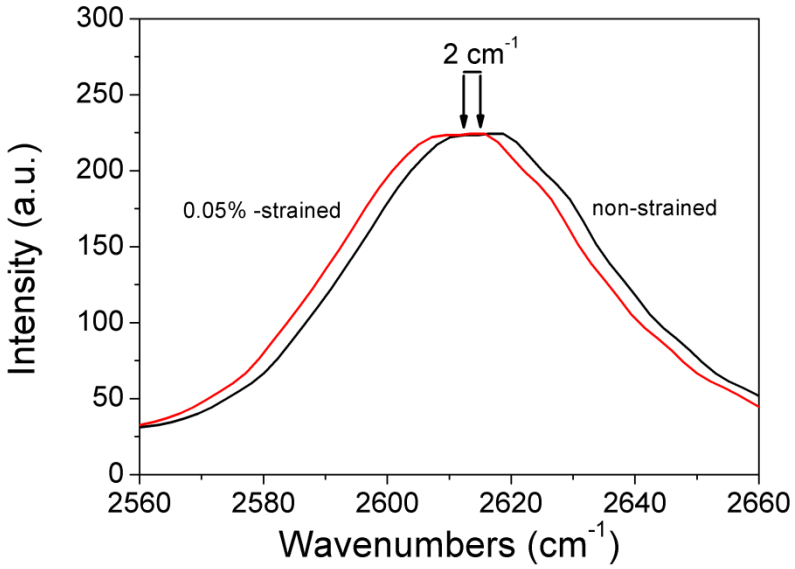

Fig S1. Variation of G' band of the Raman spectra of composite fibers under 0.05% strain.

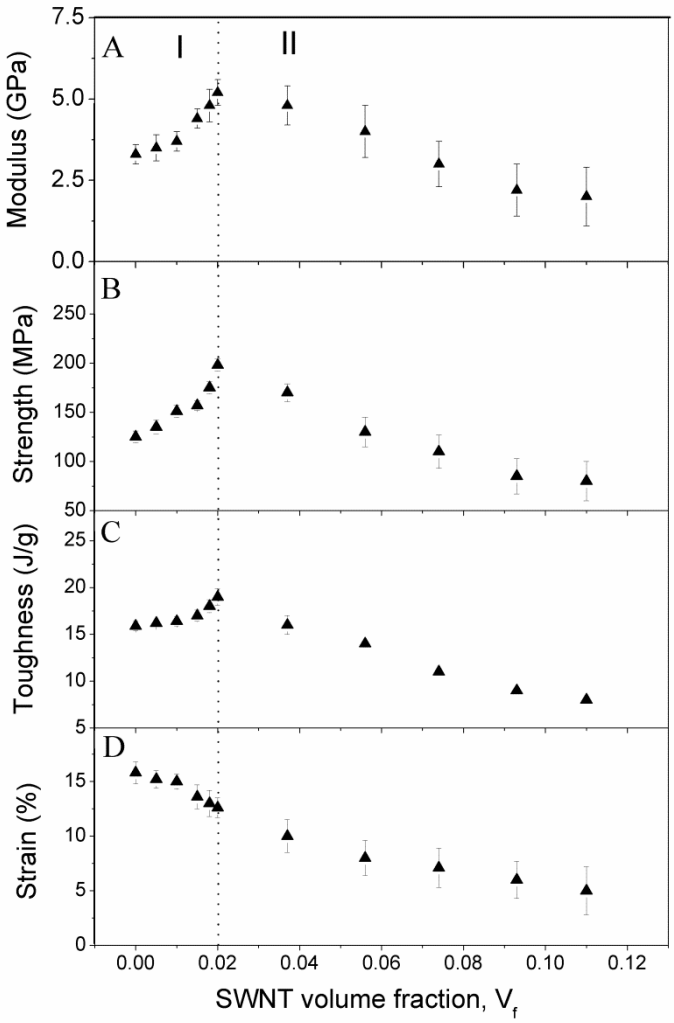

Fig. S2 Comparison of the mechanical properties of PEDOT:PSS/SWNT composite fibers as a function of SWNT loading.

The addition of SWNT up to the loading of 0.02 V_f resulted in a linear increase in modulus up to 5.2 GPa; however, the modulus decreased with SWNT loadings of more than 0.02 V_f using the second SDS-SWNT stock dispersion.

As with modulus, reinforcement in strength occurred at two distinct SWNT loading regions. Addition of SWNT to more than 0.02 V_f decreased the strength to ~80 MPa at $d\sigma/dV_f$ of -1.4 GPa. The strength of fibers showed an extremely structure-sensitive property. In addition to bundling effects, we suggest that the non-covalently bound SDS and its significantly increased concentration in region II contributed to the observed distinct phase segregation with adversely affected the strength of the fiber at high SWNT loadings.

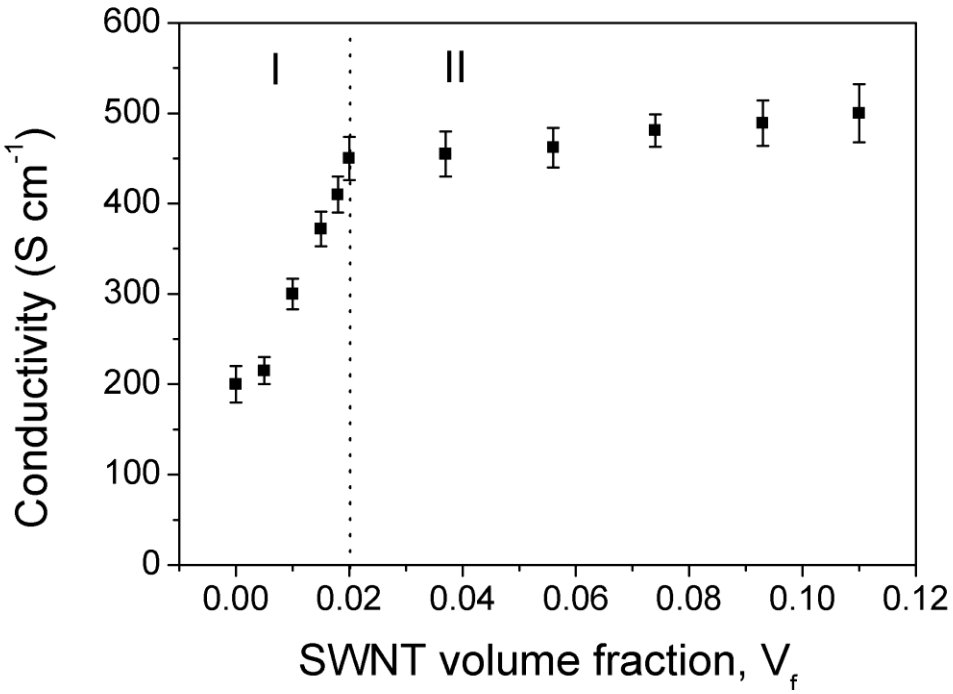

Fig. S3 Comparison of the electrical properties of PEDOT:PSS/SWNT composite fibers as a function of SWNT loading. Region I is $V_f \leq 0.02$ and II is $V_f > 0.02$.

Unlike the mechanical properties, electrical conductivities were found to increase with increasing volume fraction of SWNT in the first and second region. There was a sharp increase in conductivity (reaching up to 450 S cm^{-1}) achieved at SWNT loading of 0.02 V_f followed by a slower linear increase in conductivity of up to ~500 S cm^{-1} at 0.11 V_f. Structural defects and a much higher concentration of surfactant lowered the conductivity enhancement rate from dS/dVf =13300 to 500 S cm^{-1} from the first to the second region.

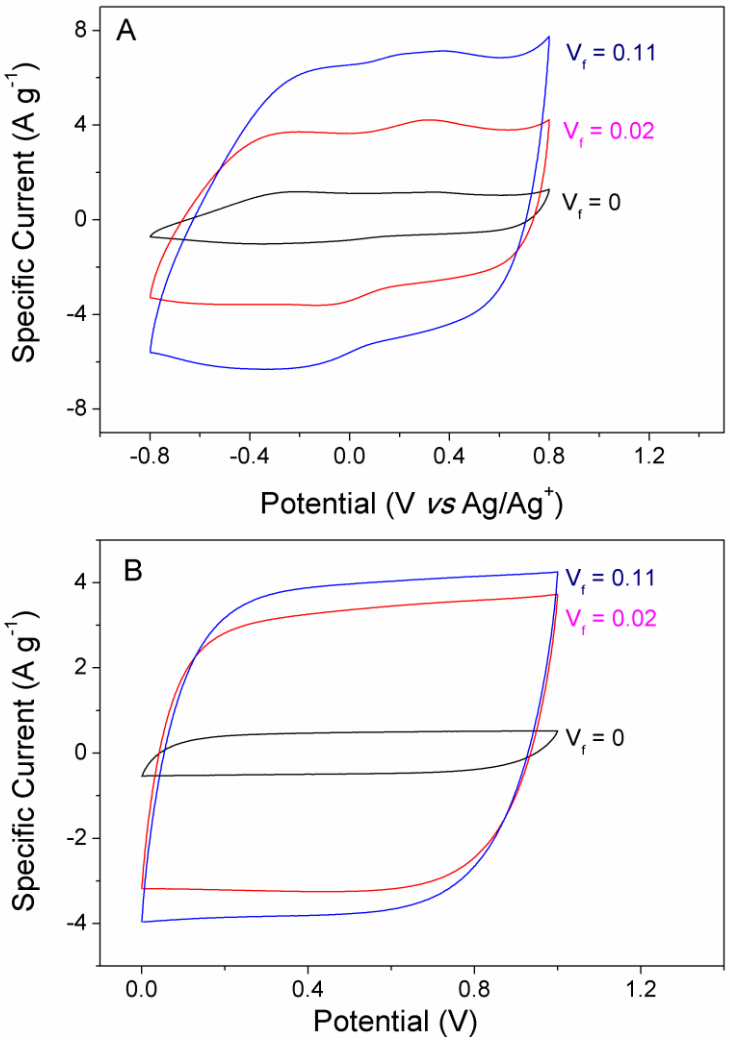

Fig. S4 CV of PEDOT:PSS/SWNT composite fibers as a function of SWNT loading in 0.1 M $TBABF_4$/acetonitrile taken at a scan rate of 50 mV s^{-1}. A) three-electrode cell system when potential measured vs $Ag/AgNO_3$. B) two-electrode (symmetric) cell.

Significant improvement in the specific capacitance that also was dependent on SWNT loading was observed. In comparison to the specific capacitance (two-electrode cell) of pure PEDOT:PSS fibers (10 F g^{-1}), values of V_f 0.02 and the highest SDS-SWNT loading resulted in approximately six-fold (59 F g^{-1}) and eight-fold (77 F g^{-1}) increases in the specific capacitance for composite fibers, respectively. Fiber from the first SDS-SWNT stock dispersion showed in a much higher rate of capacitance enhancement ($dC_{esp}/dV_f = 2450$ F g^{-1} *vs* $dC_{esp}/dV_f = 700$ F g^{-1}) consistent with the higher rate of electrical conductivity.

Table S2. Comparison of some of the most successful CNT based composite fiber properties with presented work.

Processing Details	Reference	SWNT loading	Comments	Mechanical properties						Electrical Conductivity		Specific Capacitance
				Modulus [GPa]	dY/dV_f [GPa]	Strength [MPa]	$d\sigma/dV_f$ [GPa]	Strain [%]	Toughness [J g^{-1}]	[S cm^{-1}]	dS/dV_f [S cm^{-1}]	[F g^{-1}]
Wet-spinning of PEDOT:PSS/SDS-SWNT composite	This report	Vf=0.02 ~ 3 wt %	ethylene glycol treatment	5.2	89	200	3.2	12.6	19	455	13300	59 (2 cell) 67 (3 cell)
Wet-spinning of PAni-SWNT fibers	[2]	0.76 wt%	Chemical doping of PAni	7.3		255		4		716		
Wet-spinning of HA-SWNT fibers	[3]	67 wt%	coagulated in acid	13		110			6-10	537		44
Wet-spinning of DNA-SWNT fibers	[3]	50 wt%								150		
Wet-spinning of CHT-SWNT fibers	[3]	33 wt%								21		
Wet-spinning of DNA-SWNT-PVA fibers	[4]	50 wt%	Annealed at 350 °C	14.5		101				166.7		0.1
Wet-spinning of SWNT-PVA fibers	[5]	60 wt%								0.2		
Wet-spinning of SWNT-PVA fibers then remove polymer	[5]	100 wt%	Annealed at 1000 °C to remove PVA							140		100
Wet-spinning of HA-SWNT fibers	[6]	65 wt%	CIH coagulation bath	4		20		4.1		135		33.3
PEDOT:PSS/ SWNT paper	[7]	20-50 wt%										35-104 at 0.2 A g^{-1}

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