Supplementary information

Hierarchical Carbon Nanotube Hybrid Films for High-Performance All-Solid-State Supercapacitors

Susheng Zhou[a,b], Sha Zeng[b], Silan Zhang[b], Jian Qiao[b], Jiangtao Di[b], Minghai Chen[b]*, Ning Liu[a]*, Qingwen Li[b]*

[a] *School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, People's Republic of China. E-mail: liuning@hfut.edu.cn (Ning Liu)*

[b] *Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Sciences, Suzhou 215123, People's Republic of China. E-mail: jtdi2009@sinano.ac.cn (Jiangtao Di) E-mail: mhchen2008@sinano.ac.cn (Minghai Chen)*

Specific capacitance of SWNTs in hybrid films：

As compared to SWNT, MWNT have a low specific capacitance due to its low specific surface area. Besides, the specific capacitance of MWNT could be considered constant within a certain amount of content because it possess abundant macropores and could be contacted with electrolyte rapidly. In a hybrid film, the specific capacitance of MWNTs (C_m) could be considered constant according to above premise. Herein, the specific capacitance of SWNTs (C_s) in a hybrid film could be calculated by following formula: $C_h = Cs \times \alpha + C_m \times (1 - \alpha)$. Where α is the proportion of SWCNTs and C_h is the specific capacitance of hybrid film. For example, when α is 10 wt%, C_h, C_m are 35.0 F/g, 21.2 F/g respectively, $C_s = (C_h - C_m \times (1 - \alpha))/ \alpha = (35.0 - 21.2 \times 0.9) / 0.1 = 159.2$ (F/g). When α is 30 wt%, C_h, C_m are 41.6 F/g, 21.2 F/g respectively, $C_s = (C_h - C_m \times (1 - \alpha))/ \alpha = (41.6 - 21.2 \times 0.7) / 0.3 = 104.2$ (F/g).

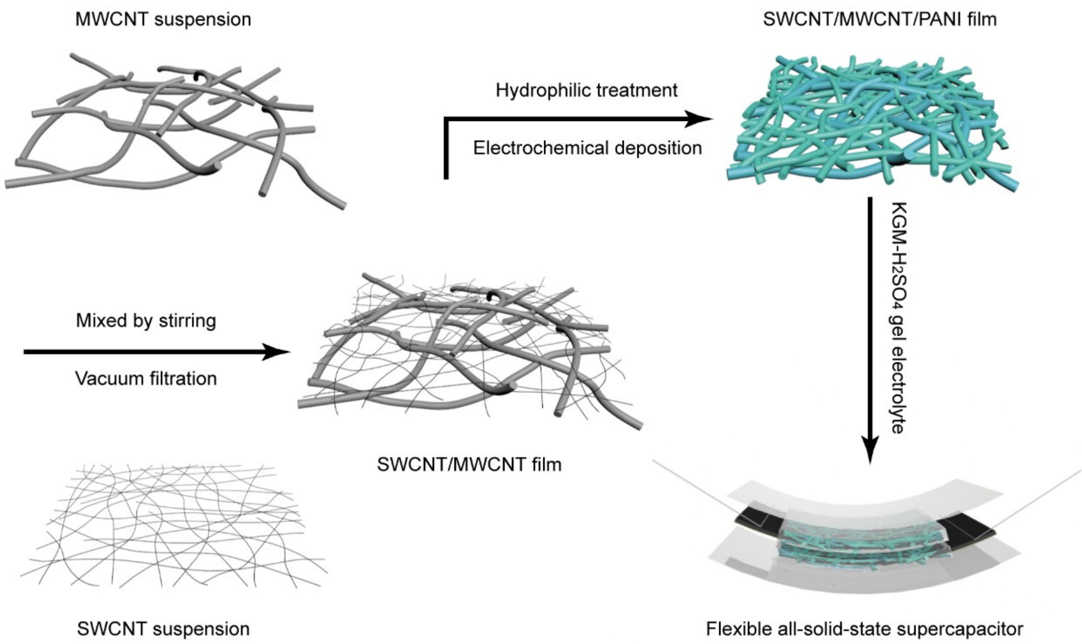

Fig. S1. Schematic illustration showing the preparation process of CNT/PANI flexible all-solid-state super-capacitor.

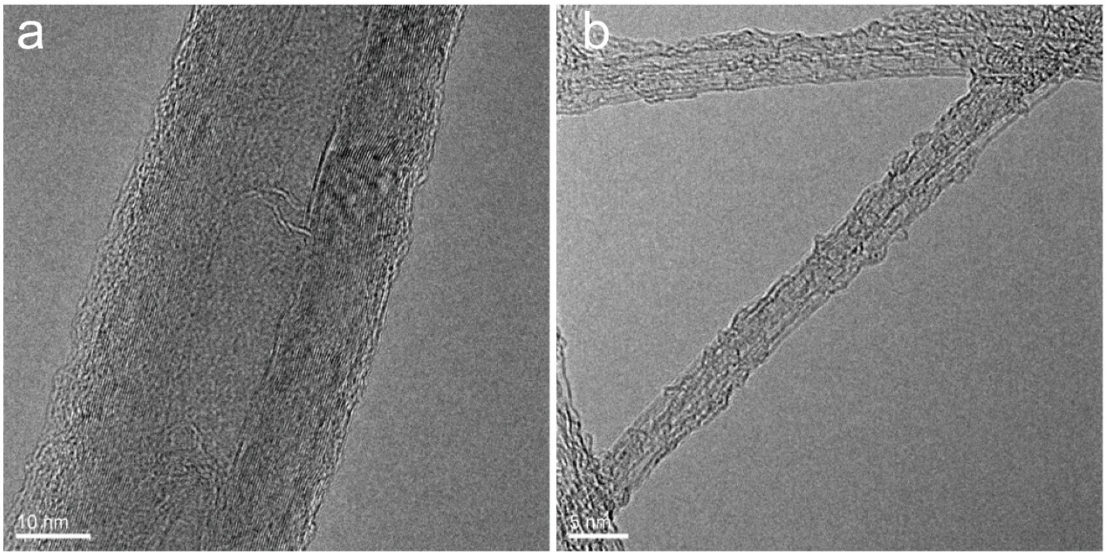

Fig. S2. TEM of MWNT (diameter of 50 nm) and SWNT (bundle diameter of 5 nm)

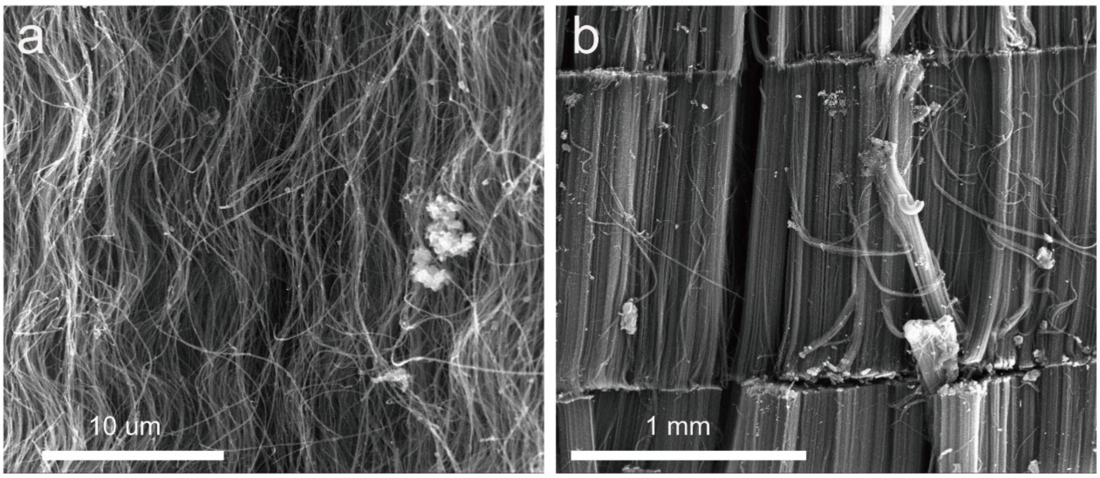

Fig. S3. SEM of vertically aligned MWNT with large porosity and its height is about 1 mm.

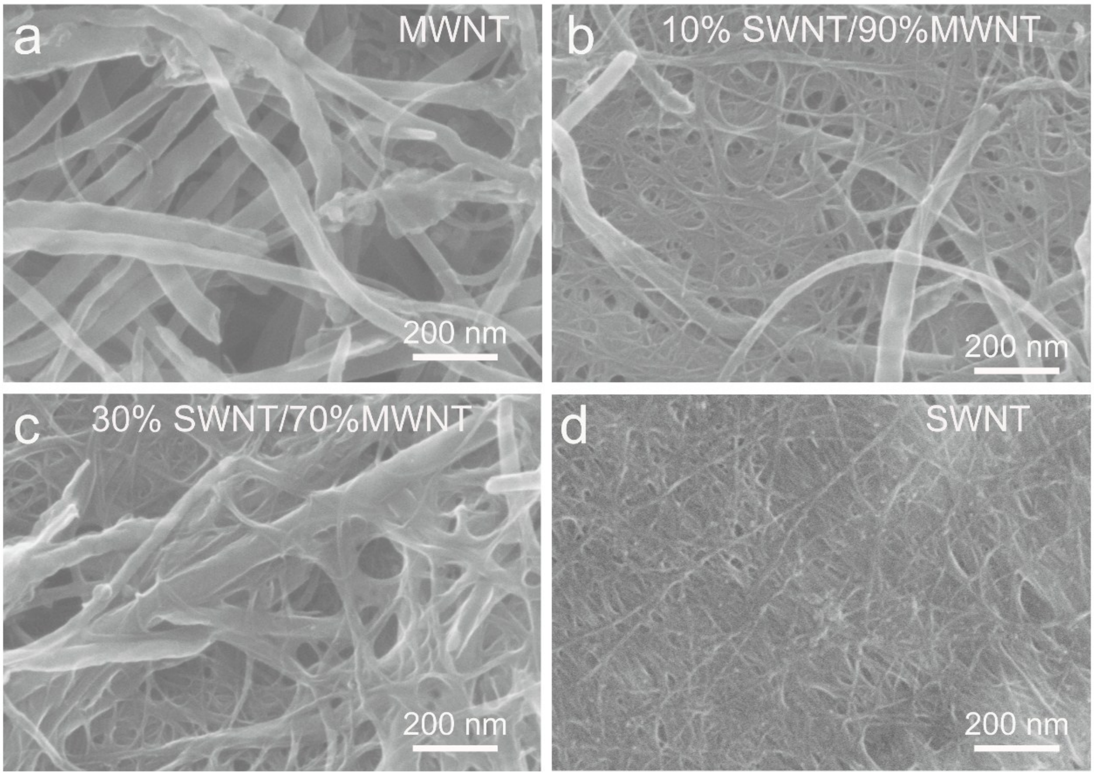

Fig. S4. SEM of pure CNT films: (a) MWNT film, (b) 10 wt% SWNT film, (c) 30 wt% SWNT film, (d) SWNT film.

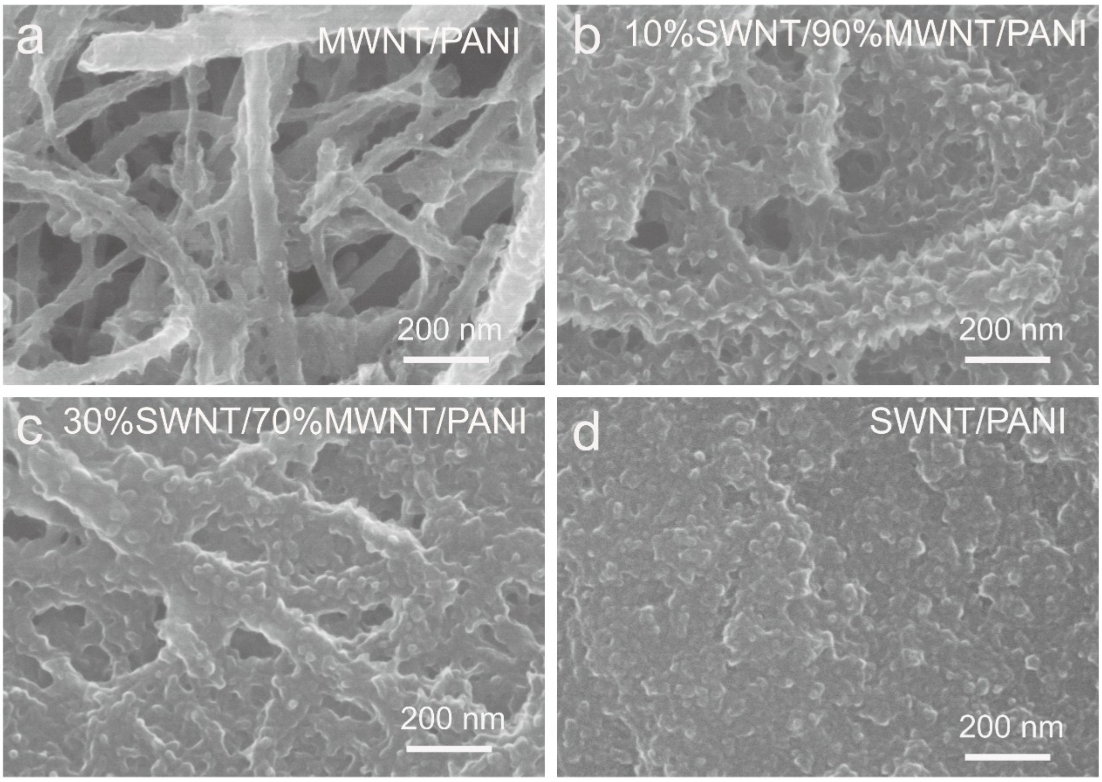

Fig. S5. SEM of CNT/PANI films: (a) MWNT/PANI film, (b) 10 wt% SWNT/PANI film, (c) 30 wt% SWNT/PANI film, (d) SWNT/PANI film.

Fig. S6. Optical Photograph of intact 30 wt% hybrid CNT film with diameter of 11.5 cm.

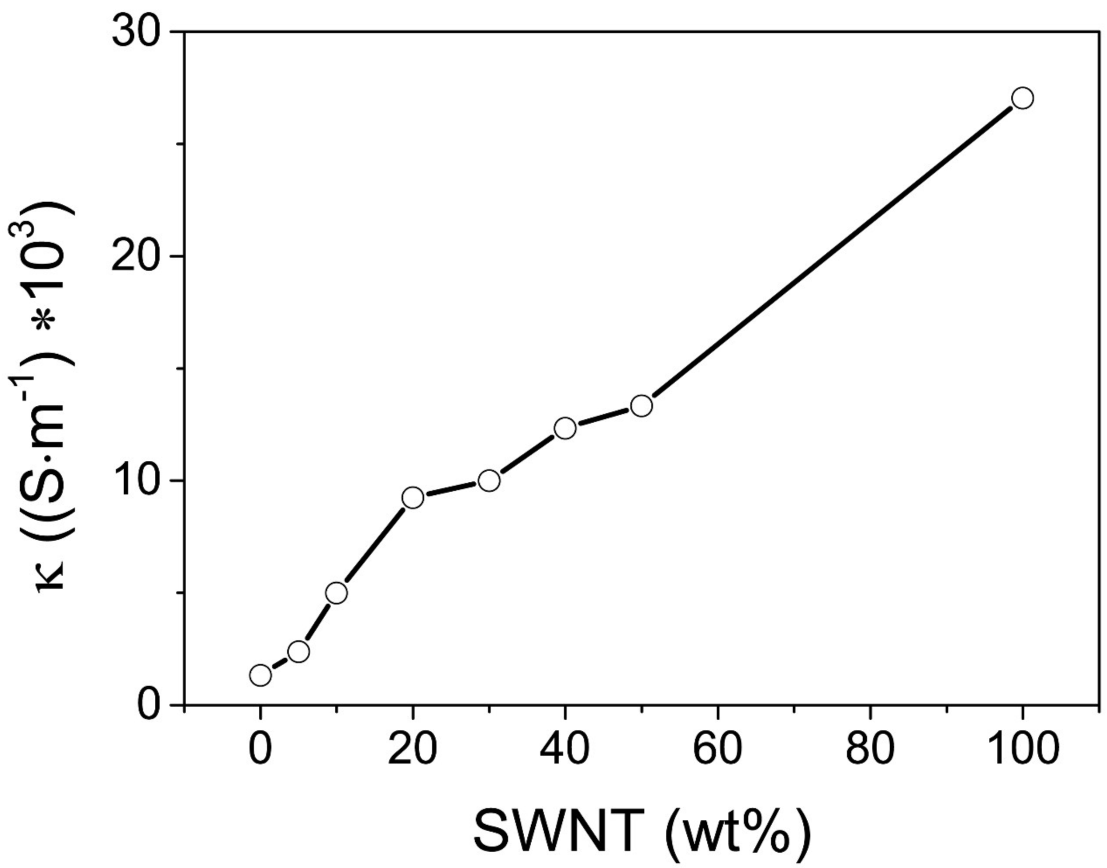

Fig. S7. Electrical conductivity of CNT films

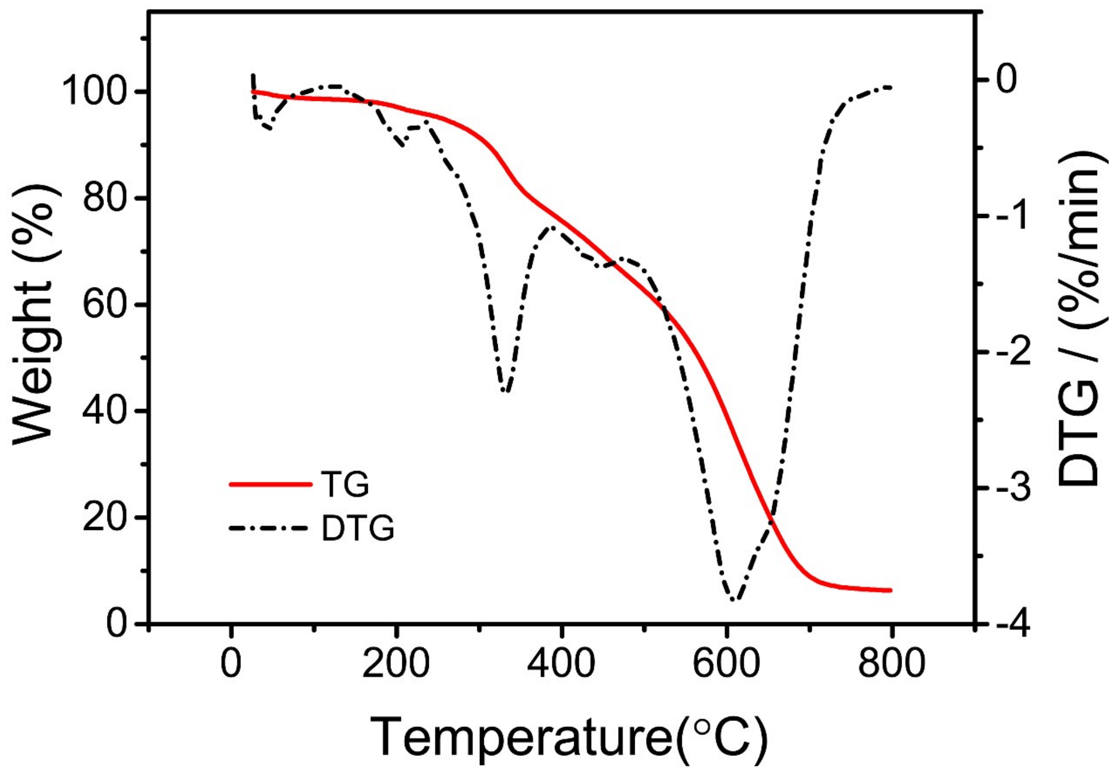

Fig. S8. TG of 30 wt% hybrid CNT film. The residual mass was no more than 5 wt%.

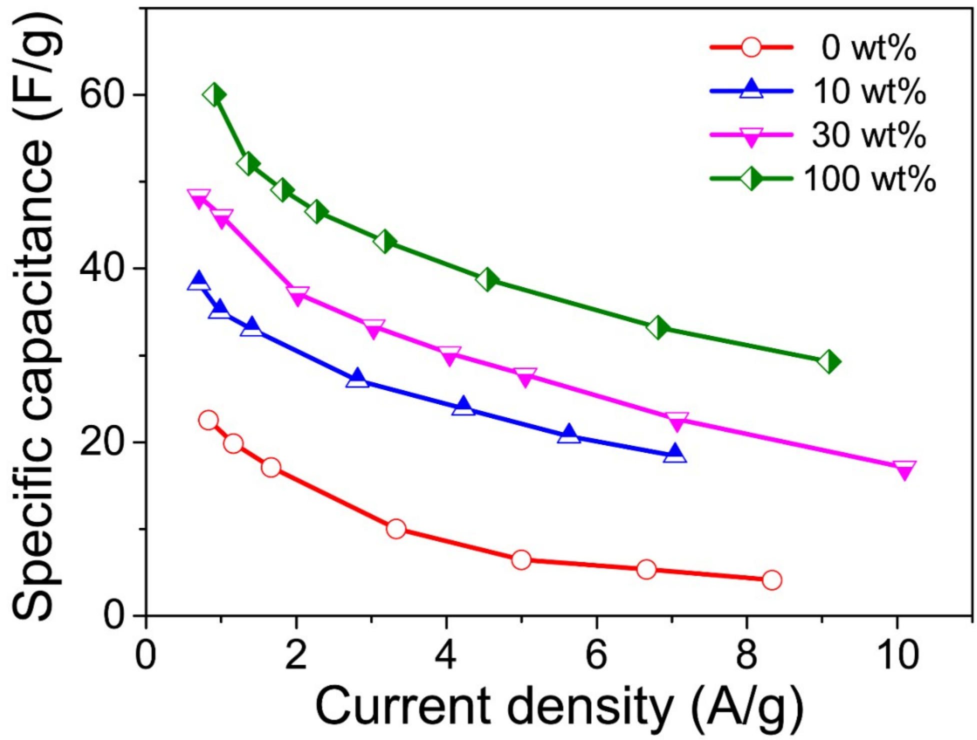

Fig. S9. Specific capacitance of pure CNT film

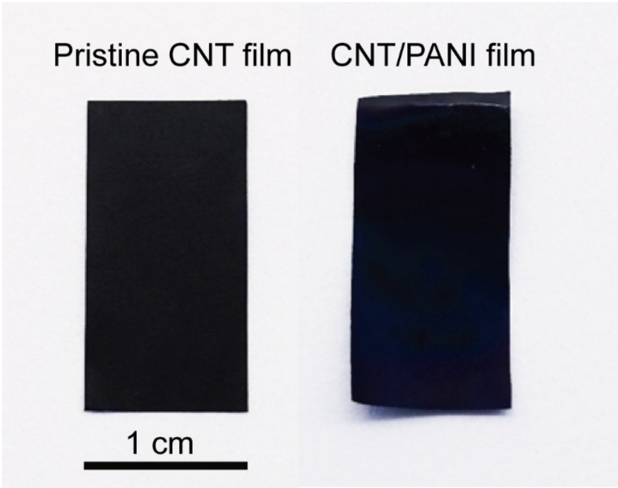

Fig. S10. Optical Photograph of 30 wt% hybrid CNT film before and after depositing PANI.

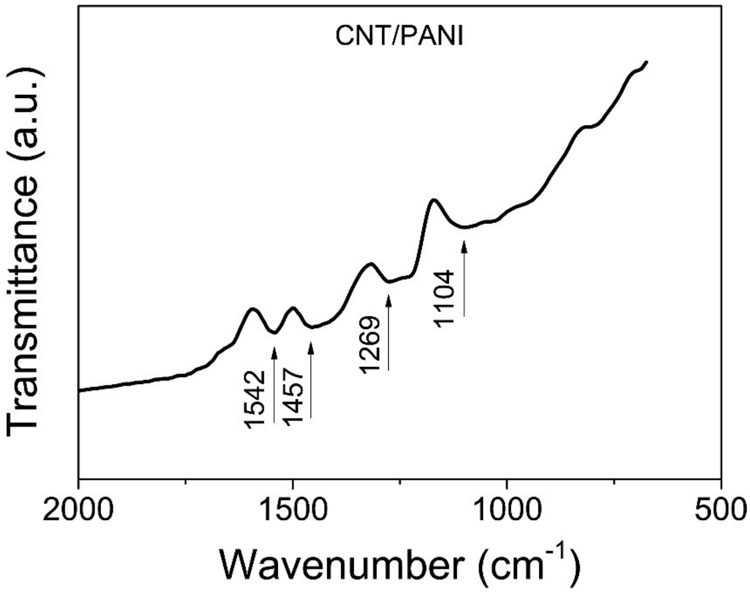

Fig. S11. FTIR spectra of CNT/PANI film.

Compared to the characteristic band (1569, 1492, 1298 and 1120 cm^{-1}) of PANI in the reference (J. Mater. Chem. A, 2016, 4, 3828–3834). The characteristic band of PANI in our CNT/PANI composite shifted to lower wavenumber direction. The bands at 1542 and 1457 cm^{-1} are assigned to C=C stretching vibrations of quinoid and benzenoid rings respectively. The bands at 1269, and 1104 cm^{-1} originate from C-N and C=N stretching vibration, respectively. The results provide evidence that PANI has been successfully deposited on the CNT film.

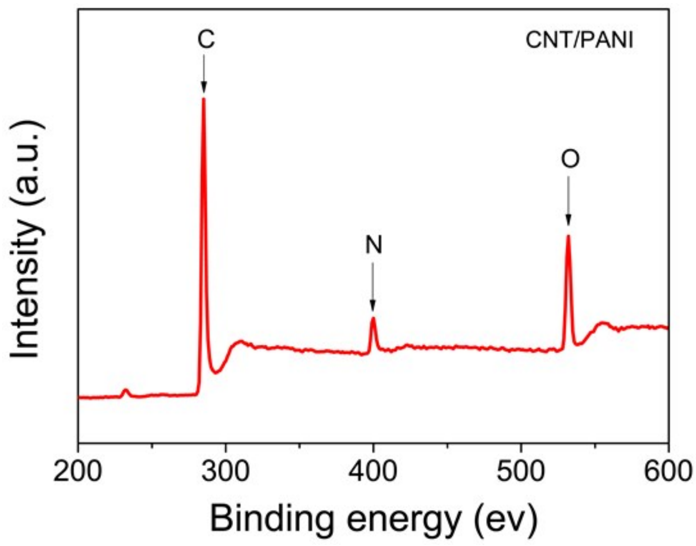

Fig. S12. XPS spectra of CNT/PANI film

Table S1. Element contents of CNT/PANI film

Sample Name	**Element contents (Atomic %)**		
	C	N	O
CNT/PANI	78.96	7.3	13.74

From XPS spectra, the atomic ratio of C: N: O is 78.96: 7.3: 13.74. The high N content might be from PANI.

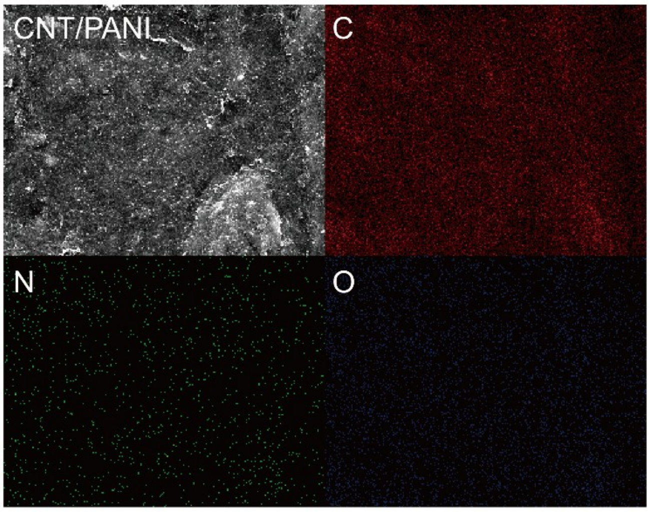

Fig. S13. EDX elemental mapping of CNT/PANI film. (SEM 5000x)

The element maps indicated that C, N, O were uniformly distributed.

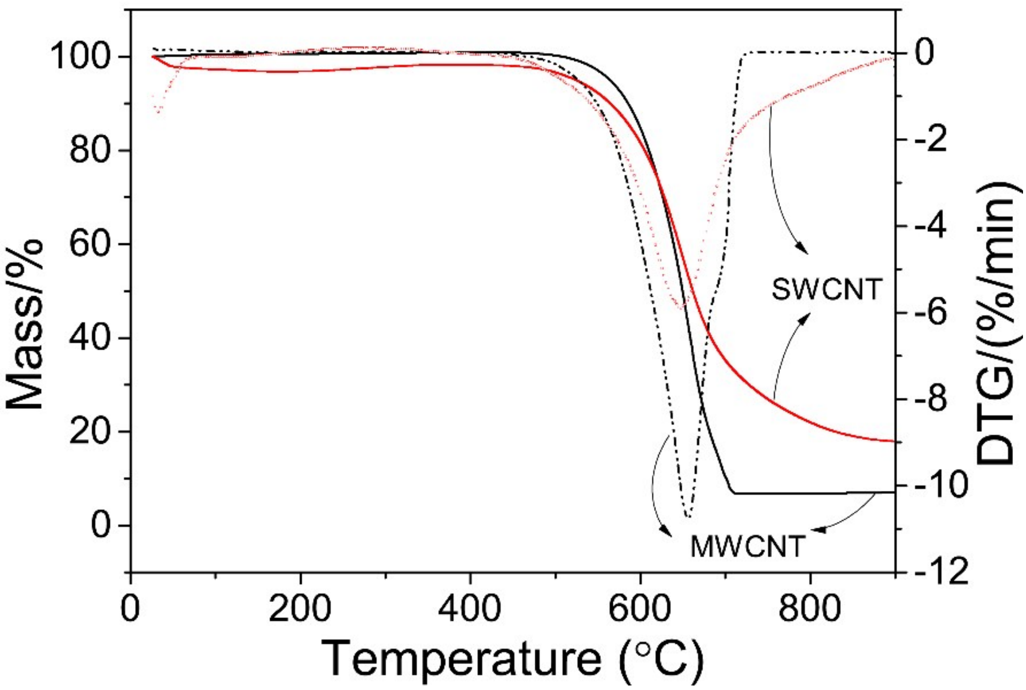

Fig. S14. TG of original SWCNTs and MWCNTs powder.

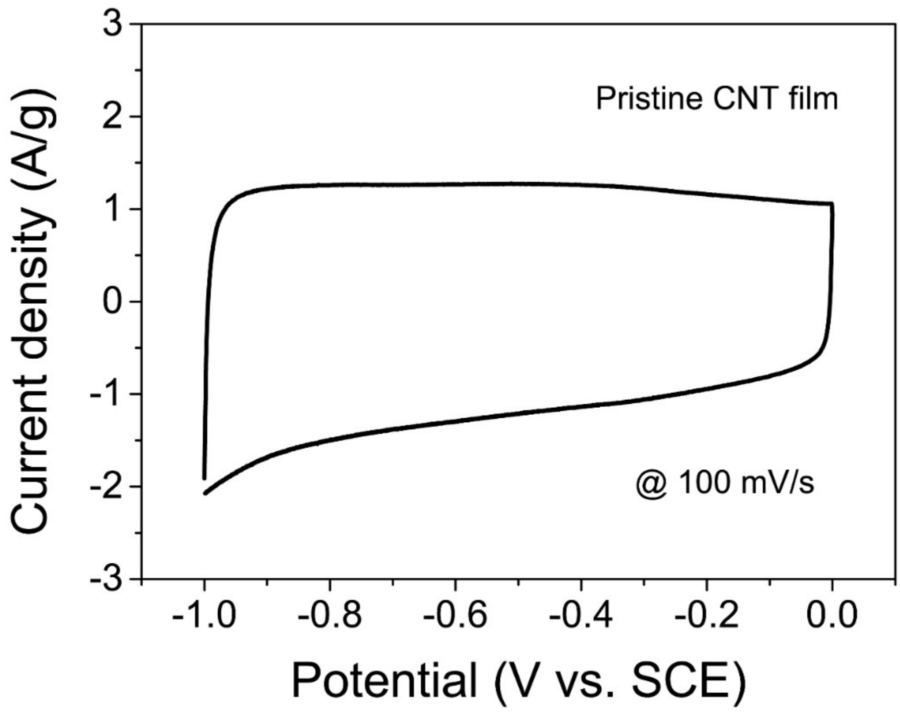

Fig. S15. The CV curve of pristine 30 wt% SWCNT CNT film.

We have performed thermogravimetric (TG) analysis on the raw carbon nanotubes we used for supercapacitors. The raw SWCNTs and MWCNTs powders have purities of 82 wt% and 93 wt%, respectively and the impurities are mainly amorphous carbon, catalyst and catalyst support. Cyclic voltammetry (CV) conducted on a hybrid film containing 30 wt% SWCNTs that was not electrochemically oxidized show a box feature that is consistent with the electrical double layer capacitance (**Fig. S15**). After electrochemical oxidation, the CV curves becomes non-box shaped (**Fig. 3a**) due to the introduction of oxygen containing functional groups on nanotube. These comparison results indicated that the impurity almost had no obvious effect on the capacitance behavior.

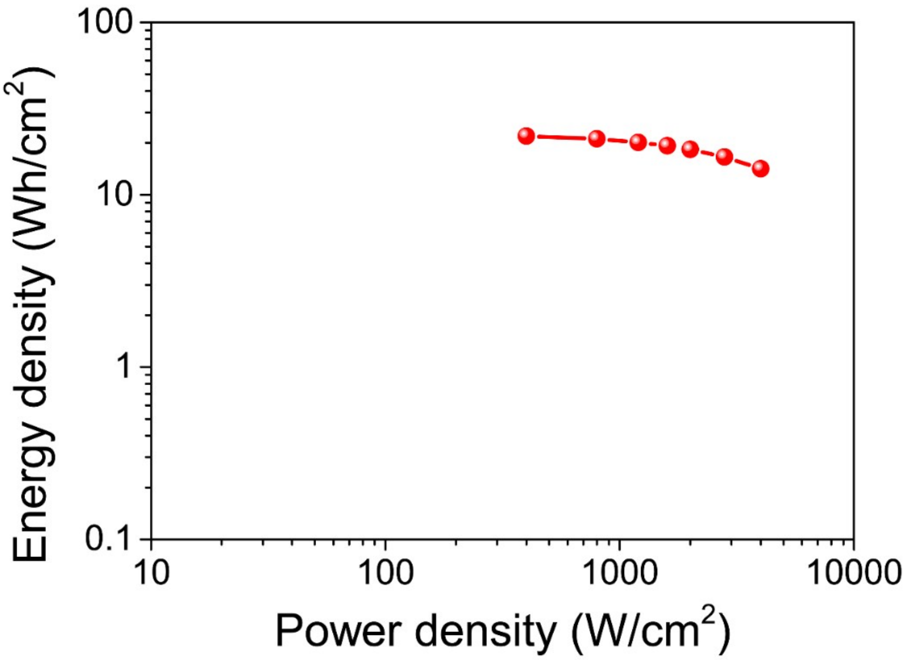

Fig. S16. Ragone plots showing the energy and power densities in area.

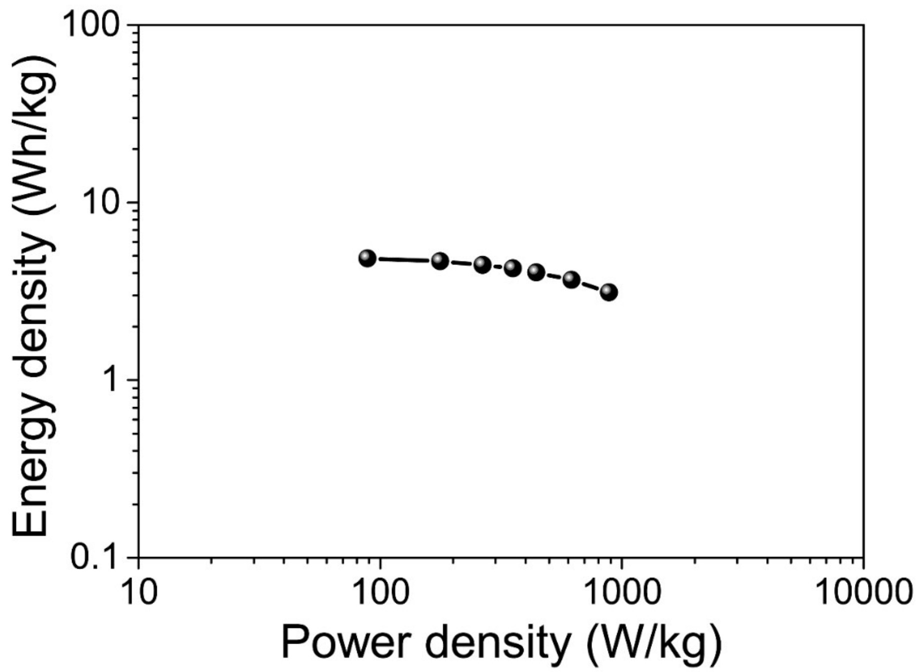

Fig. S17. Ragone plots showing the energy and power densities in mass. (The area was 1 cm^2 and mass was 4.518 mg including two electrodes)

The supercapacitor had an energy density of 21.9 Wh/cm^2 at 400 W/cm^2 and power density of 4000 W/cm^2 with an energy density of 14.1 Wh/cm^2. When it comes to mass density, the supercapacitor had an energy density of 4.7 Wh/kg at 177.1 W/kg and power density of 885.3 W/kg with an energy density of 3.1 Wh/kg.