Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

A super compact self-powered device based on paper-like supercapacitors

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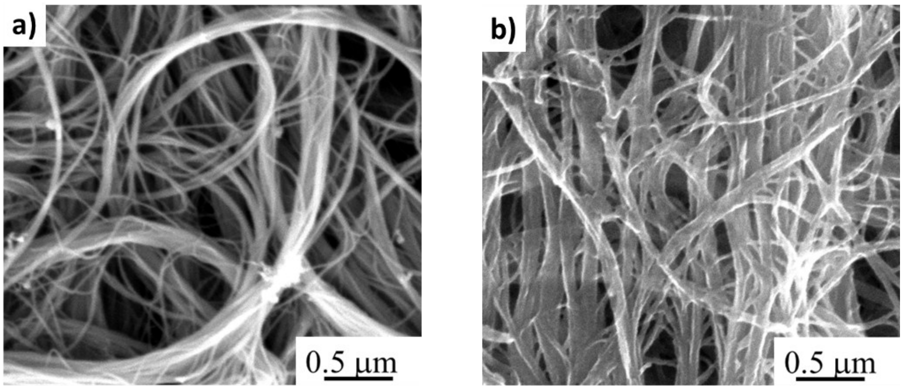

Fig. S1. High magnification SEM images of (a) CNT and (b) PANI/CNT composites. The surface of CNT became much rougher after coating with PANI which the porous structure of CNT is well preserved.

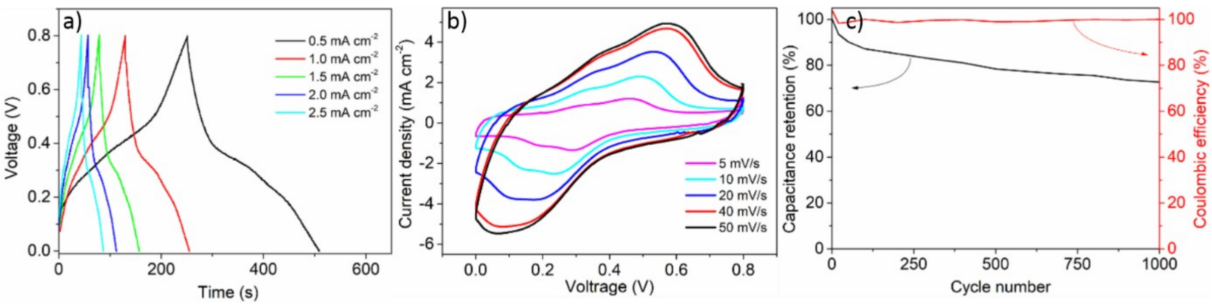

Fig. S2. Galvanostatic charge and discharge curves at various current densities (a), cyclic voltammograms at various scan rates (b), and cycling performance (c) of the paper-like supercapacitors.

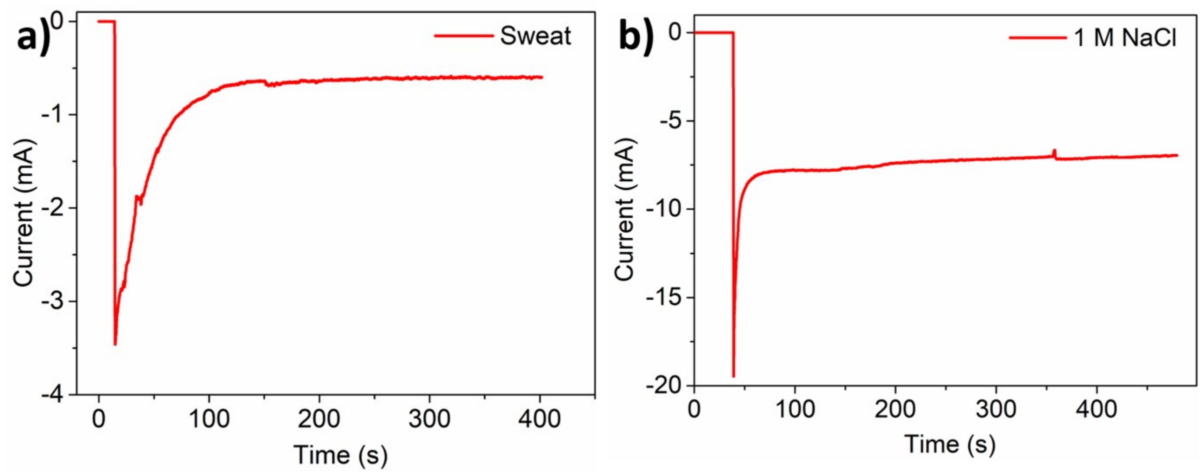

Fig. S3. Output current of the Al-air cell when PANI/CNT and Al foil were put into (a) sweat (0.5 wt% NaCl) and (b) 1 M NaCl solution. The immersed area of each electrode is 1×1 cm^2. The decrease of the current could be caused by the consumption of oxygen in cathode and the generation of $Al(OH)_3$ precipitate on the surface of Al foil.

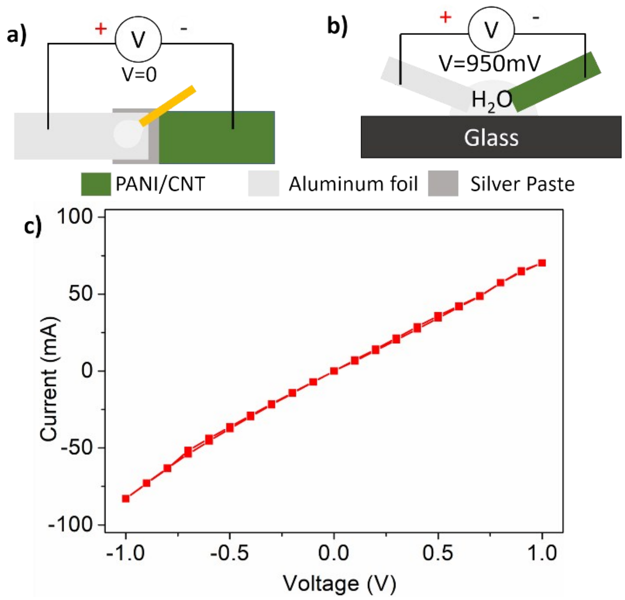

Fig. S4. Verification of the Ohmic contact and metal-air assumptions. (a) The output voltage was nearly zero when a wet swab touched the silver paste assisted Al-PANI/CNT junction. (b) The output voltage was -950 mV when Al foil and PANI/CNT electrode were bridged by a drop of water. (c) The I-V curve of the silver paste assisted Al-PANI/CNT junction, and the scanning curves in two directions are almost overlapped.

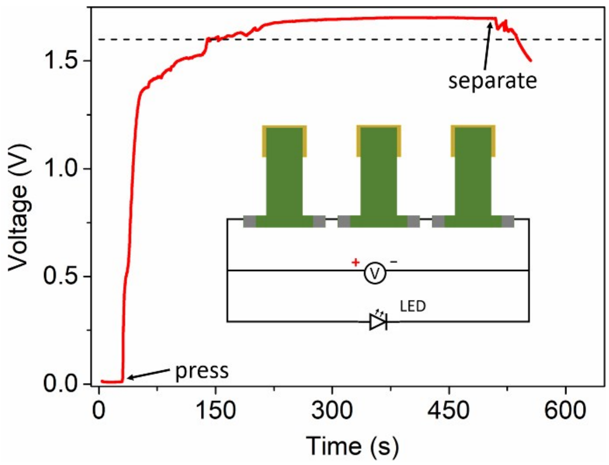

Fig. S5. Output voltage of three SPSC in series. The dash line indicates the working voltage threshold of a LED. The inset shows the measurement circuit. The three SPSCs were charged very quickly at the beginning that it only took 113 s to reach the working voltage of LED and kept at a stable value of 1.70 V. When the filter paper and the Al foil were separated, the voltage could sustain for a while to light up the LED. The longer working time and higher output voltage can be simply achieved by assembling more SPSCs.

Table S1. A comparison between different self-charging devices and the SPSC

Hybrid device	Charging voltage/time	Power density	Storage capacitance	Ref.
triboelectric generator + SC	3.0 V/117min	0.8 W·m^{-2}	10.29 mF cm^{-2}	1
	900 mV/180 min	not given	18.3 mF cm^{-2}	2
piezoelectric generator + SC	110mV/5 min	9.9 kW kg^{-2}	455 mF g^{-2}	3
	100 mV/40 s	400 mW m^{-2}	357.6 F m^{-2}	4
thermoelectric generator + SC	38 mV/350 s	2.1 W g^{-1}	1200 F m^{-2}	5
	180 mV/~ 6 min	Not given	1.03 mF cm^{-2}	6
	58mV /~ 3min	Not given	2.46 mF cm^{-2}	7
photoelectric generator + SC	0.7 V/100 s	Not Given	422 mF cm^{-2}	8
	1.2 V/3 s	487.5 μW cm^{-2}	39.1 mF cm^{-2}	9
biofuel cell + SC	0.46 V/ 10 min	0.4 mW cm^{-2}	~ 130 mF cm^{-2}	10
Al-air cell +SC	0.7 V/ 5min	2.36 mW cm^{-2}	203.7 mF cm^{-2}	This work

From the comparison, our SPSC shows a relatively satisfactory performance in many aspects, such as the large storage capacity, short self-charging time, high charging voltage and large output power. The power density is calculated based on the working condition when it powered a motor in Fig. 4b, which better reflects its application performance. Besides, the high flexibility, compact structure and easy fabrication process will promote its application field.

The chemical equations of the Al-air cell:

$$\text{Anode: } Al \rightarrow Al^{3+} + 3e^{-} \quad \text{(S1)}$$

$$\text{Cathode: } O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \quad \text{(S2)}$$

Total reaction:

$$3O_2 + 6H_2O + 4Al \rightarrow 4Al(OH)_3 \text{ in neutral solution} \quad \text{(S3)}$$

$$3O_2 + 6H_2O + 4Al + 4OH^{-} \rightarrow 4Al(OH)_4^{-} \text{ in alkaline solution} \quad \text{(S4)}$$

$$\text{Side reaction: } 2Al + 3H_2O \rightarrow 2Al(OH)_3 + 3H_2 \quad \text{(S5)}$$

All the electrochemical characters of SPSC are calculated as follows,

$$C_{\mathrm{m}} = \frac{I \cdot \Delta t}{S \cdot \Delta U} \quad \text{(S6)}$$

$$E_{\mathrm{m}} = C_{\mathrm{m}} U^2 / 2 \quad \text{(S7)}$$

$$P = UI \quad \text{(S8)}$$

Where C_m is the areal capacitance, I is the discharging current, Δt is the discharging time, S is the effective area (2.3 cm^2) and ΔU is the potential range during the discharging process. E_m is the specific energy stored in SPSC, U is the charging potential in self-powered process. P is the power of SPSC when powering a motor.

The porosity *P* of the PANI/CNT is calculated by the following formula,

$$P = 1 - \frac{\rho_{\mathrm{f}}}{\alpha\rho_{\mathrm{c}} + \beta\rho_{\mathrm{p}}}, \quad \rho_{\mathrm{f}} = \frac{m}{V} \quad \text{(S9)}$$

Where ρ_c, ρ_p and ρ_f are the density of CNT, PANI and PANI/CNT composite. The density of CNT, PANI are taken from Ref.11. α and β are the mass percentage of CNT and PANI in PANI/CNT film. m and V are mass and volume of PANI/CNT film.

Estimating the life span of SPSC

The life span of the device was mainly limited by the amout of Al in the cell part and the life span T of SPSC can be calculated as follow,

$$T = \frac{Q_{\mathrm{t}}}{Q_{\mathrm{c}}} \quad \text{(S10)}$$

$$Q_{\mathrm{t}} = \frac{3mF}{M} \quad \text{(S11)}$$

$$Q_{\mathrm{c}} = UC \quad \text{(S12)}$$

Where Q_t and Q_c are the total valence electron charge in Al foil and the charge transfer each time in the self-charging process. m and M are the mass of Al foil and the mole mass of Al. F is the Faraday constant. U and C are the self-charging voltage and capacitance of the SPSC. All the parameters are taken from the manuscript.

References:

1. J. Luo, F. R. Fan, T. Jiang, Z. Wang, W. Tang, C. Zhang, M. Liu, G. Cao and Z. L. Wang, Nano Res., 2015, **8**, 3934-3943.
2. Y. Song, X. Cheng, H. Chen, J. Huang, X. Chen, M. Han, Z. Su, B. Meng, Z. Song and H. Zhang, J. Mater. Chem. A, 2016, **4**, 14298-14306.
3. A. Ramadoss, B. Saravanakumar, S. W. Lee, Y. Kim, S. J. Kim and Z. L. Wang, ACS Nano, 2015, **9**, 4337-4345.
4. R. Song, H. Jin, X. Li, L. Fei, Y. Zhao, H. Huang, H. Lai-Wa Chan, Y. Wang and Y. Chai, J. Mater. Chem. A, 2015, **3**, 14963-14970.
5. S. L. Kim, H. T. Lin and C. Yu, Adv. Energy Mater., 2016, **6**, 1600546.
6. D. Zhao, H. Wang, Z. U. Khan, J. C. Chen, R. Gabrielsson, M. P. Jonsson, M. Berggren and X. Crispin, Energ. Environ. Sci., 2016, **9**, 1450-1457.
7. S. L. Kim, J. Hsu and C. Yu, Nano Energy, 2018, **48**, 582-589.
8. R. Liu, C. Liu and S. Fan, J. Mater. Chem. A, 2017, **5**, 23078-23084.
9. J. Liang, G. Zhu, C. Wang, P. Zhao, Y. Wang, Y. Hu, L. Ma, Z. Tie, J. Liu and Z. Jin, Nano Energy, 2018, **52**, 239-245.
10. J. Lv, I. Jeerapan, F. Tehrani, L. Yin, C. A. Silva-Lopez, J. Jang, D. Joshuia, R. Shah, Y. Liang, L. Xie, F. Soto, C. Chen, E. Karshalev, C. Kong, Z. Yang and J. Wang, Energ. Environ. Sci., 2018, **11**, 3431-3442.
11. D. Zhang, Y. Yin, C. Liu and S. Fan, Chem.Commun., 2015, 51, 322-325.