Electronic Supporting Information

Pen-lithography for flexible microsupercapacitors with layer-by-layer assembled graphene flake/PEDOT nanocomposite electrodes

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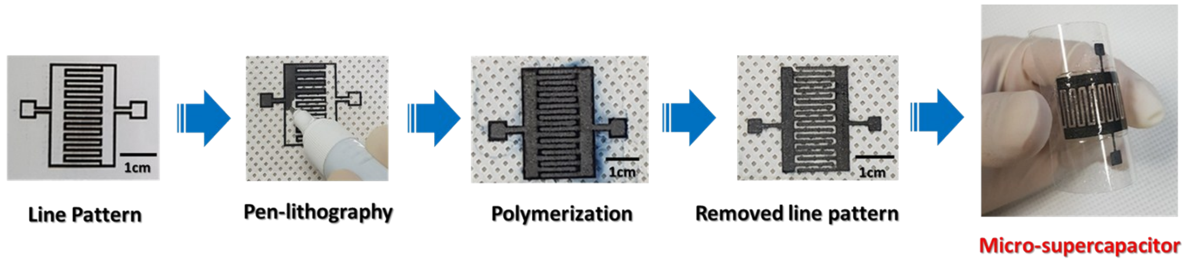

Figure S1. Schematic process of fabrication of the graphene/PEDOT microsupercapacitor (MSC) (Area: 4.68 cm^2).

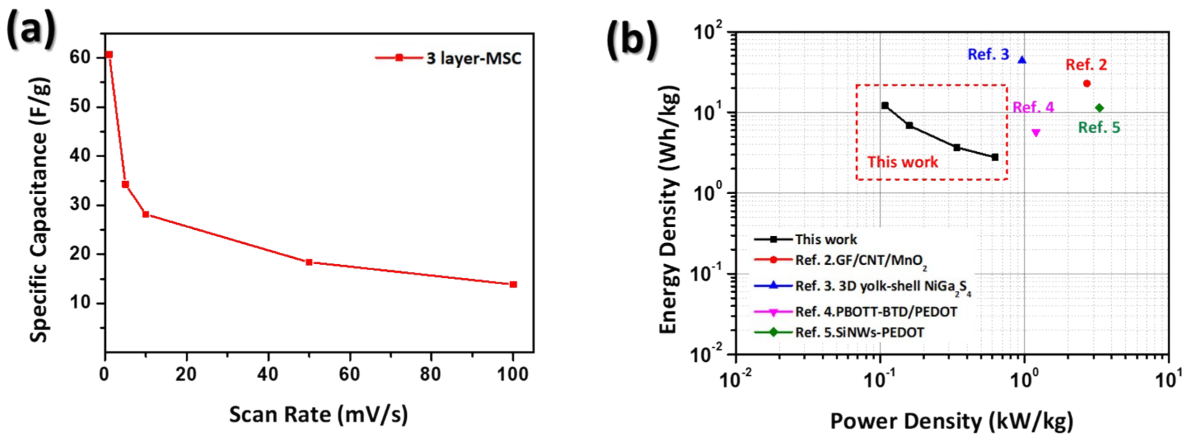

Figure S2. (a) Specific capacitance as a function of the scan rate, (b) Ragone plot of the previous literature for the mass loading of 3-layer graphene/PEDOT nanocomposite MSC.

The mass loading of the 3 layer graphene/PEDOT MSC is 1.8 mg. Using alpha step, we can measure the thickness of the 3 layer graphene/PEDOT MSC (20.7 ± 4.4 μm), as shown in Figure 2f. The area of MSC was 4.68 cm^2. According to the mass, area and the thickness of the 3 layer graphene/PEDOT MSC, we can calculate and obtain the density of graphene/PEDOT MSC (0.19 g cm^{-3}). In addition, the specific capacitances (C_{spe}) of the 3 layer graphene/PEDOT MSC could be calculated from the CV curves according to the following equations:[1]

$$C_{spe} = \frac{1}{m \cdot v \cdot \Delta V} \int i(V) dV$$

where, m is the mass of active materials, v is the potential scanrate, ΔV is the potential window in CV, $i(V)$ is the voltammetric current. The C_{spe} of graphene/PEDOT MSC was about 60.7 F g^{-1}. The calculated power and energy density were ranged from 0.11 up to 0.62 kW kg^{-1} and from 2.78 up to 12.14 Wh kg^{-1} respectively.

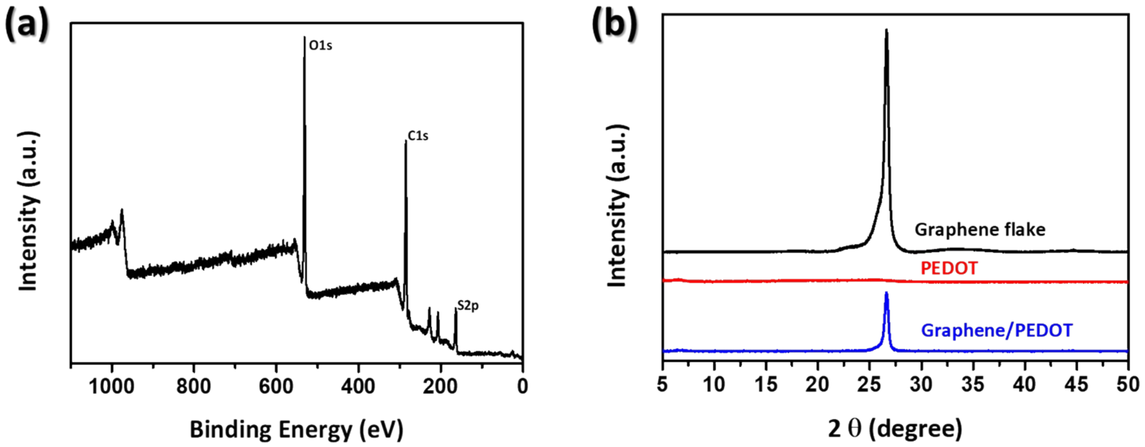

Figure S3. Properties of the graphene/PEDOT characterized by (a) XPS spectra, (b) XRD pattern.

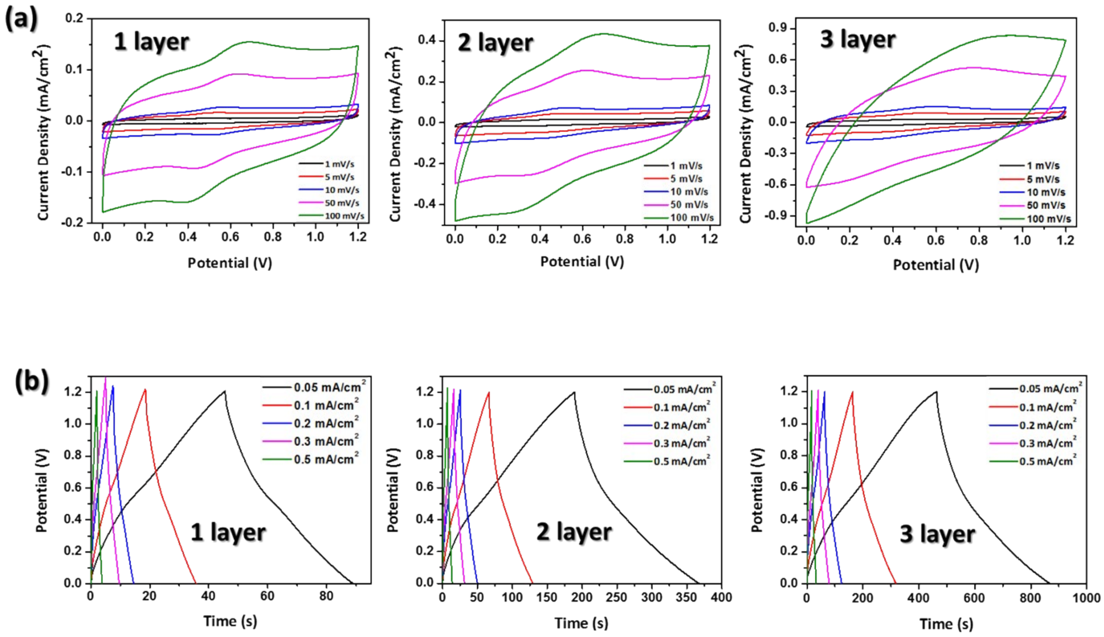

Figure S4. Electrochemical properties of the layered graphene/PEDOT MSCs, respectively (a) CV curves at scan rates from 1 to 100 $mV \cdot s^{-1}$, and (b) Galvanostatic charge-discharge curves at current densities from 0.05 to 0.5 $mA \cdot cm^{-2}$.

Calculations

The following equation was used for calculating the profile of the graphene/PEDOT microsupercapacitors:[6–8]

● The areal capacitance (C_A) / volumetric capacitance (C_V) can be calculated via the equation,

$$C = \frac{I \cdot \Delta t}{\Delta V \cdot A(or\ V)} \qquad \text{....................(1)}$$

I = Constant current used for charging and discharging

Δt = Discharge time

ΔV = The operating voltage range

A = Area of the graphene/PEDOT electrode

V = Volume of the graphene/PEDOT electrode

● The real ($C^{'}(\omega)$) and imaginary ($C^{''}(\omega)$) parts of the complex capacitance vs. frequency can be calculated via the equations:

$$C^{'}(\omega) = \frac{-Z''(\omega)}{\omega|Z(\omega)|^2}$$

$$C^{''}(\omega) = \frac{Z'(\omega)}{\omega|Z(\omega)|^2}$$

$Z^{'}(\omega)$ = The real part of the impedance

$-Z^{''}(\omega)$ = The imaginary part of the impedance

ω = The pulsation

● ω is calculated by the equation:

$$\omega = f * 2\pi$$

f = Frequency range from 100 kHz to 0.01 Hz

● The Coulombic efficiency ($\eta(\%)$) is based on the following equation:

$$\eta(\%) = \frac{t_D}{t_C} \times 100$$

t_D = The discharging times

t_C = The charging times

● The volumetric energy density E_V (Wh·cm^{-3}) and power density P_V (W·cm^{-3}) are calculated by the following equations:

$$E_V = \frac{C_V \cdot (\Delta V)^2}{7200}$$

$$P_V = \frac{EV \cdot 3600}{\Delta t}$$

C_V = The volumetric capacitance …… (1)

ΔV = The operating voltage range

Δt = The discharging times.

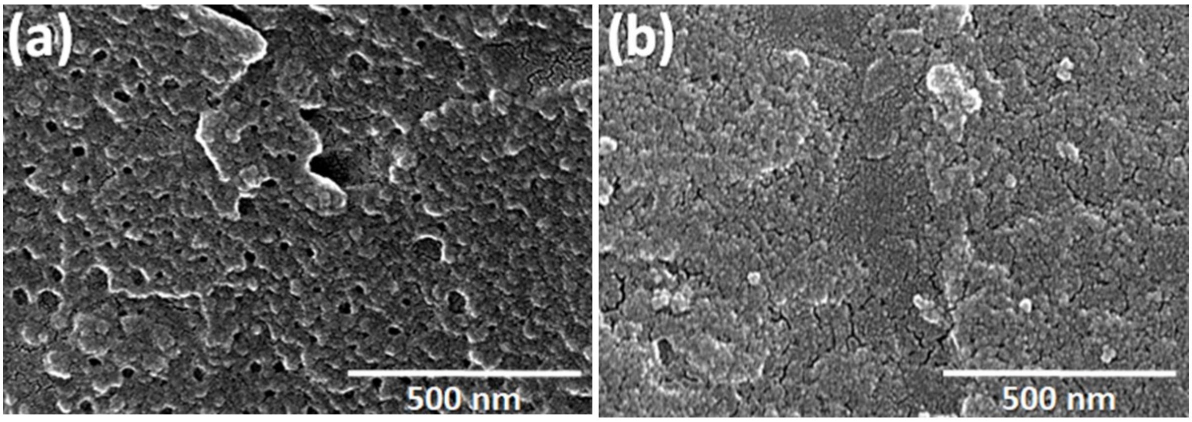

Figure S5. SEM images of 3-layers graphene/PEDOT nanocomposites MSC (a) before and (b) after 2,500 cycling test.

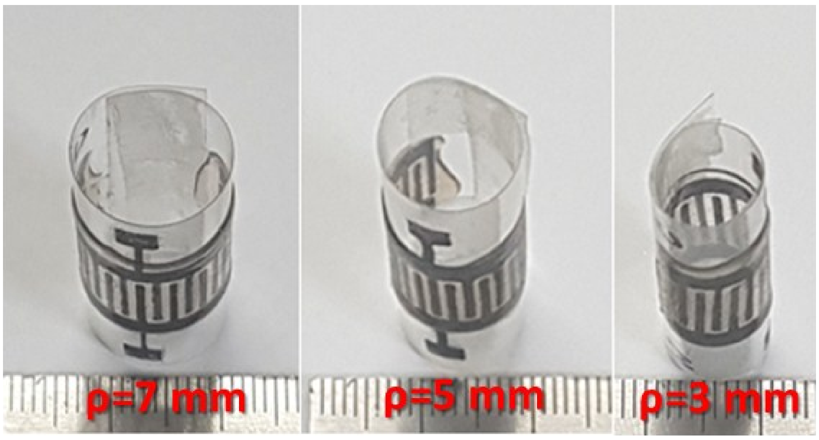

Figure S6. Digital images of the all-solid-state microsupercapacitor device at different bending radius (ρ = 7, 5, and 3 mm).

References

1. J. G. Wang, Y. Yang, Z. Huang, F. Kang, *Electrochimica Acta*, 2014, **130**, 642-649.
2. J. Liu, L. Zhang, H. B. Wu, J. Lin, Z. Shen and X. W. Lou, *Energy Environ. Sic*., 2014, **7**, 3709-3719.
3. S. Liu, K. H. Kim, J. M. Yun, A. Kundu, K. V. Sankar, U. M. Patil, C. Ray and S. C. Jun, *J. Mater. Chem. A*, 2017, **5**, 6292-6298.
4. Y. Guo, W. Li, H. Yu, D. F. Perepichka, H. Meng, *Adv. Energy Mater.*, 2017, **7**, 1601623.
5. D. Aradilla, G. Bidan, P. Gentile, P. Weather, F. Thissandier, V. Ruiz, P. Gómez-Romero, T. J. S. Schubert, H. Sahin, S. Sadki, *RSC Adv.*, 2014, **4**, 26462-26467.
6. P. L. Taberna, P. Simon and J. F. Fauvarque, *J. Electrochem. Soc.*, 2003, **150**, A292–A300.
7. C. Portet, G. Yushin and Y. Gogotsi, *Carbon*, 2007, **45**, 2511– 2518.
8. D. Yu, K. Goh, H. Wang, L. Wei, W. Jiang, Q. Zhang, L. Dai, and Y. Chen, *Nat. Nanotechnol.*, 2014, **9**, 555-562.