Electronic Supplementary Information

Co-electro-deposition of the MnO_2/PEDOT:PSS Nanostructured Composite for High Areal Mass, Flexible Asymmetric Supercapacitor Devices

To understand the interaction of MnO_2 and PEDOT:PSS on molecular level, MnO_2/PEDOT:PSS film and pure PEDOT:PSS samples were studied by Raman spectroscopy. As a powerful tool, Raman has been used for studying conducting polymers, such as PEDOT:PSS, PANI, PPy etc.[1-4] The Raman spectra of MnO_2/PEDOT:PSS and pure PEDOT:PSS are shown in **Fig S1**. The most obvious difference that was observed is of the band between 1400 and 1500 cm^{-1}, which corresponds to the stretching vibration of C_a $=C_\beta$on the ring, red-shifts and becomes narrow. The result may suggests that the resonant structure of PEDOT chain changes from a benzoid to a quinoid structure.[5] It's reported that the structure due to the coil conformation turns into linear or expanded-coil conformation can benefit the conductivity enhancement.[6] Therefore, we suppose that the interaction between MnO_2 and PEDOT:PSS is helpful to improve the electrodeproperty.

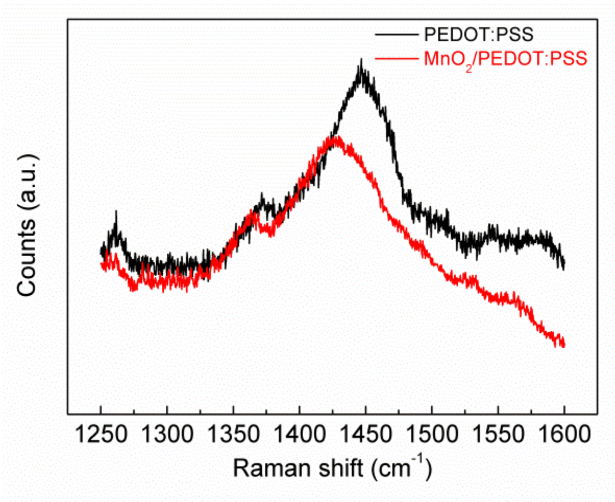

Fig. S1 Counts *vs.* Raman shift of PEDOT:PSS and MnO_2/PEDOT:PSS composite electrode.

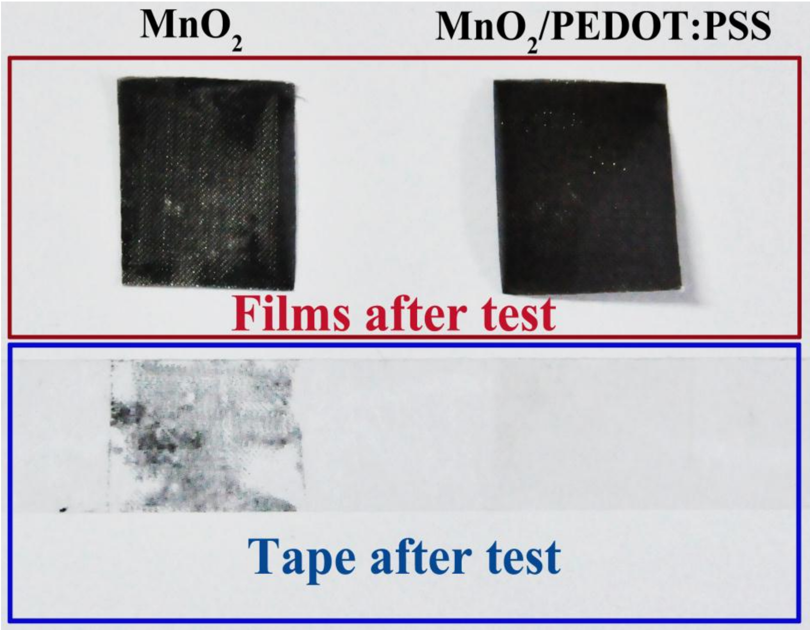

Fig. S2 Tape method is used for adhesion test. The MnO_2 films are prepared without PEDOT:PSS (left) and with PEDOT:PSS (right). The tape after the test is shown in the blue box. Tape tested for MnO_2/PEDOT:PSS electrode (right) shows no noticeable residues while that for MnO_2 electrode exhibits a significant amount of powder residues that are detached from the electrode.

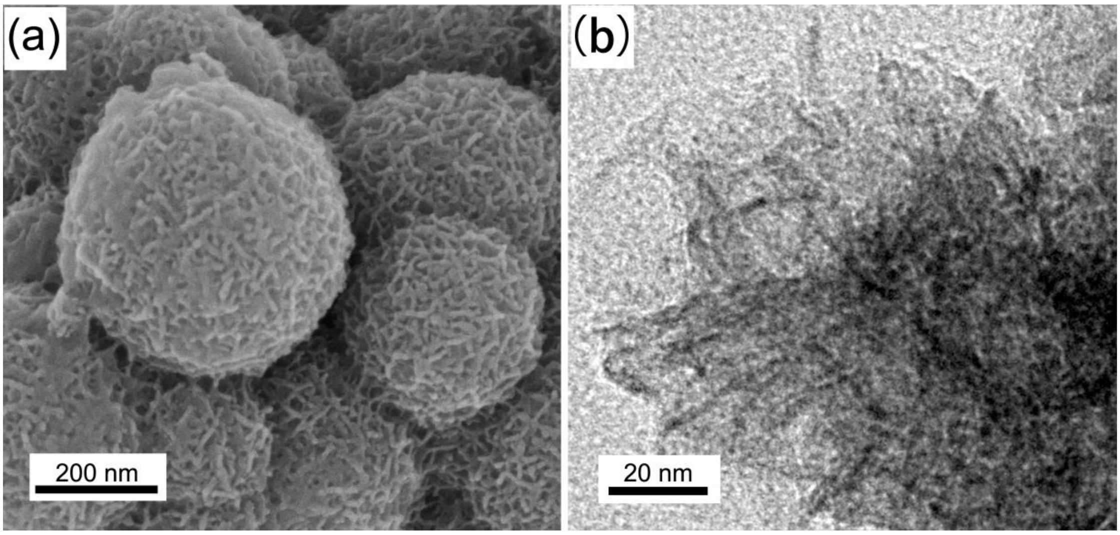

Fig. S3 (a)SEM and (b) TEM images of the MnO_2/PEDOT:PSS electrode. The MnO_2/PEDOT:PSS nanospheres have rough surface textures which increase the total surface of the active materials. Because of the water-solubility of PEDOT:PSS and MnO_2, aqueous electrolyte can be fully immersed in the active substance.

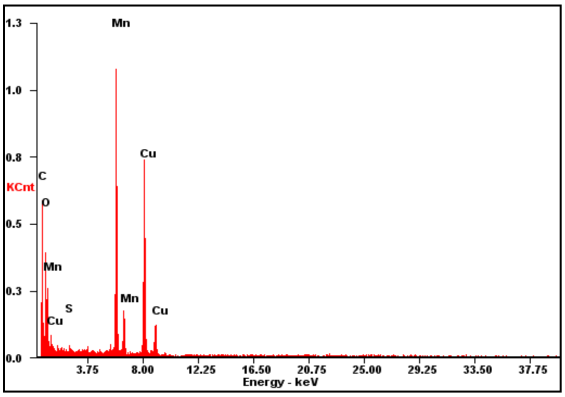

Fig. S4 EDAX spectrum of MnO_2/PEDOT:PSS. The spectrum of the nanocomposite containing signals from C, O, Mn and S further confirm the existence of MnO_2 and PEDOT:PSS.

element	Weiht(%)
C K	10.90
O K	47.14
S K	0.36
Mn K	41.60

Tab. S1 The percentage of each element provided by SEM EDS.

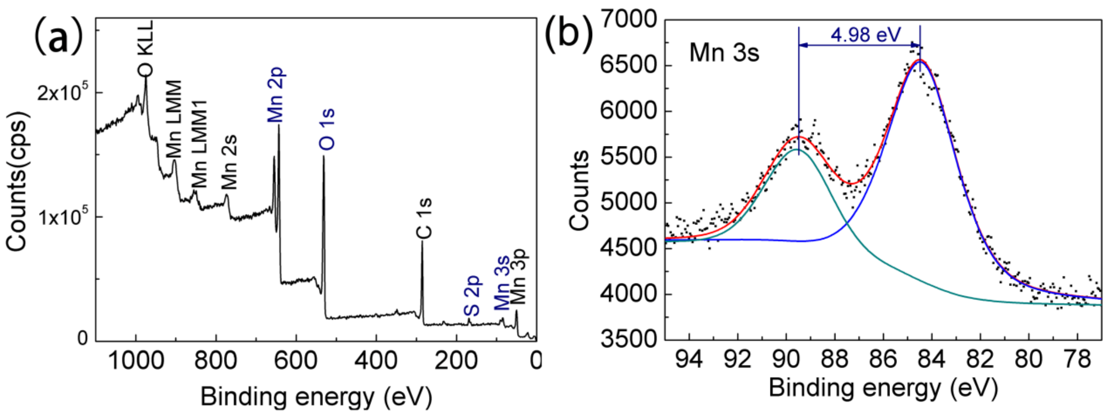

Fig. S5 (a)Surface scanning XPS full spectrum of the MnO_2/PEDOT:PSS composite. The XPS full spectrum containing signals from Mn, O, S and C elements indicates the presence of both MnO_2 and PEDOT:PSS. (b) Mn 3s core level XPS spectrum of MnO_2/PEDOT:PSS.

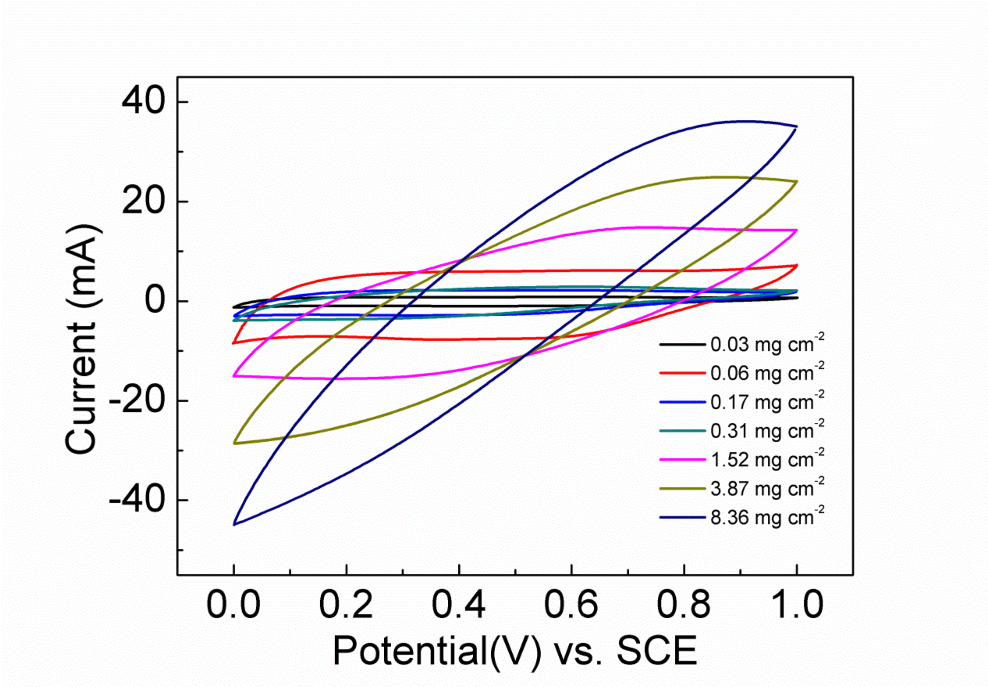

Fig. S6 CV curves of MnO_2/PEDOT:PSS with different deposition times at scan rates of 20 mV/s, respectively.

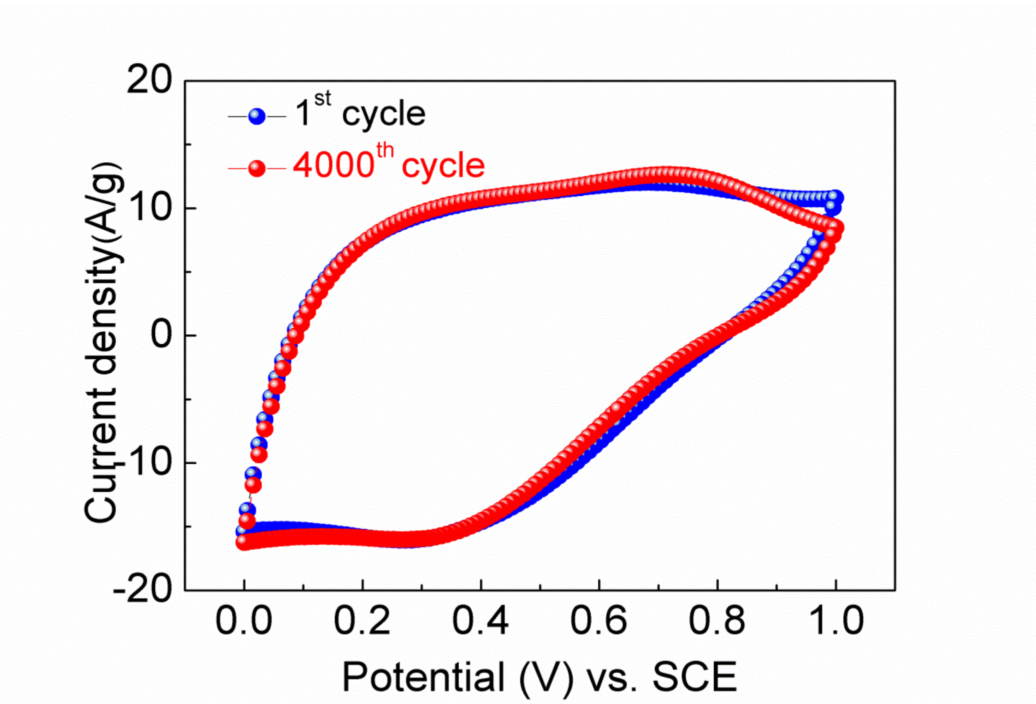

Fig. S7 The CV curves of 1st and 4000th cycles of MnO_2/PEDOT:PSS electrode at scan rate of 50mV/s. The CV curves are almost overlapped which indicates the excellent cycle performance.

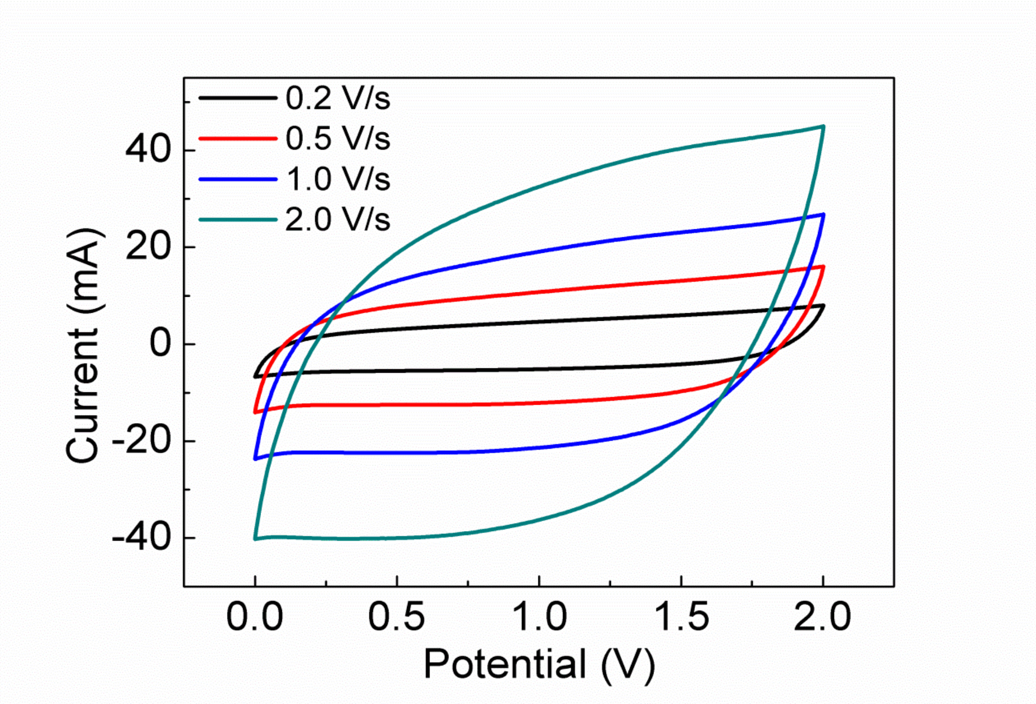

Fig. S8 CV curves of (MnO_2/PEDOT:PSS)/AC supercapacitor at scan rate of 0.2, 0.5, 1.0, 2.0V/s. Even at high scan rate of 2.0V/s, the CV curve still remains good rectangle indicates the excellent rate capability of the asymmetric supercapacitor.

Fig. S9 The electrical equivalent circuit used for fitting impedance spectra.

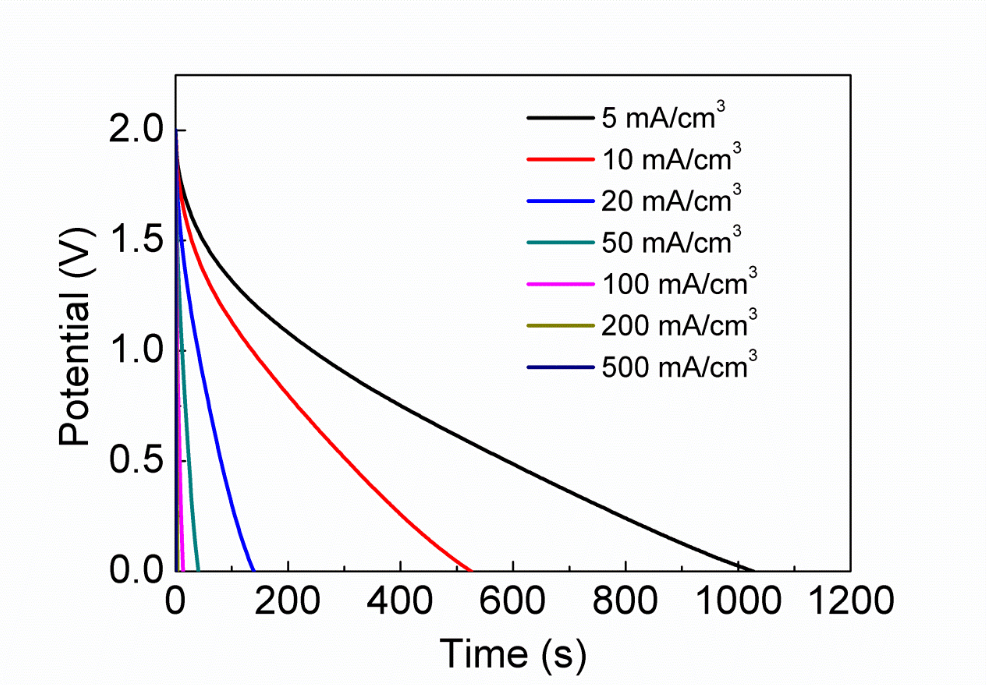

Fig. S10 Discharging curves of the MnO_2/AC asymmetric supercapacitor at different current density from 5 to 500 mA/cm^3

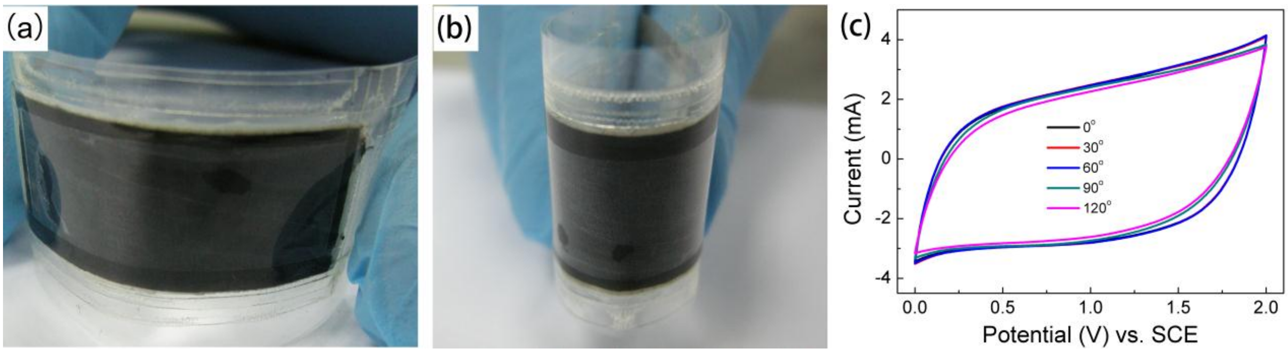

Fig. S11(a,b) Digital photographs of the as-fabricated asymmetric supercapacitor device. The images demonstrate the high flexibility of the device. Even after repeated twisting there is no obvious harm to its structural integrity. (c) CV curves of asymmetric supercapacitor under different bending angle.

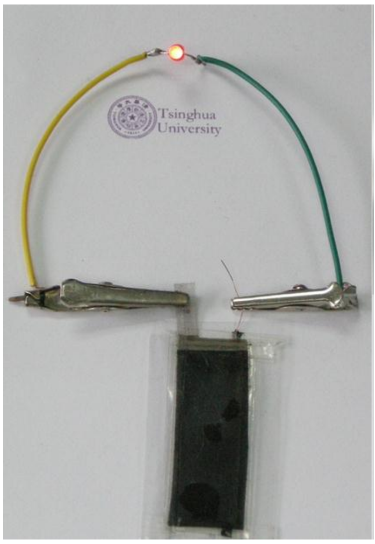

Fig. S12 A photograph showing that the asymmetric supercapacitor can lighten up a red LED indicator (1.8 V, 20 mA). After charging for 13 s, the potential can be maintained as high as 2.0V.

Fig. S13 A photograph comparing the thickness of asymmetric supercapacitor, a coin (US quarter dollar) and a credit card. The as fabricated asymmetric supercapacitor is light-weight and as thin as 0.144mm, which is much thinner than that of coin and credit card.

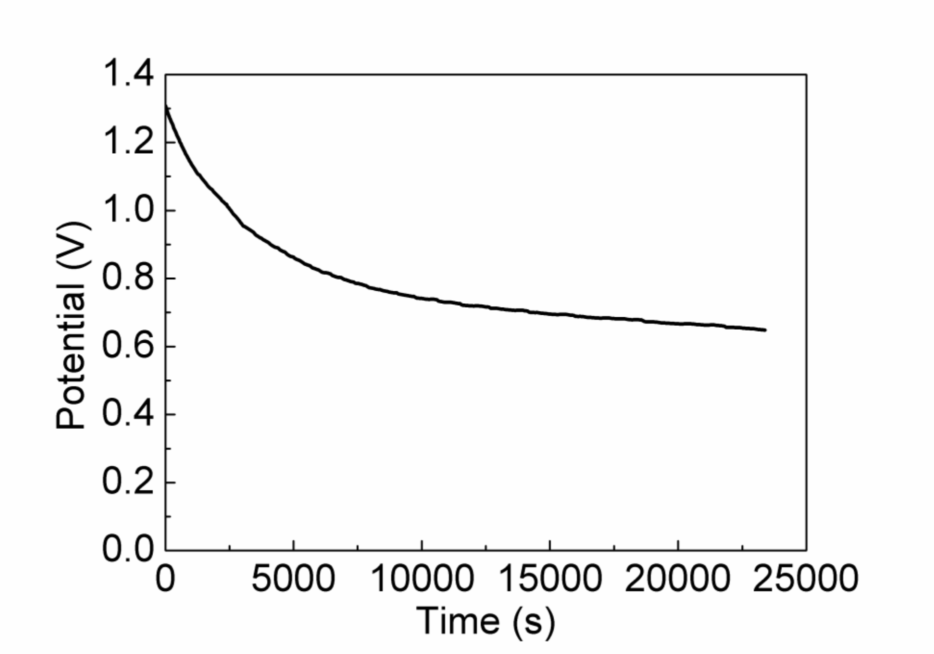

Fig. S14 Self-discharge curve of our supercapacitor device obtained immediately after charging to 1.3V. The result shows that our supercapacitor self-discharges from 1.3V to 0.65 V in a long time of 6.5 h indicating the low self-discharge property.

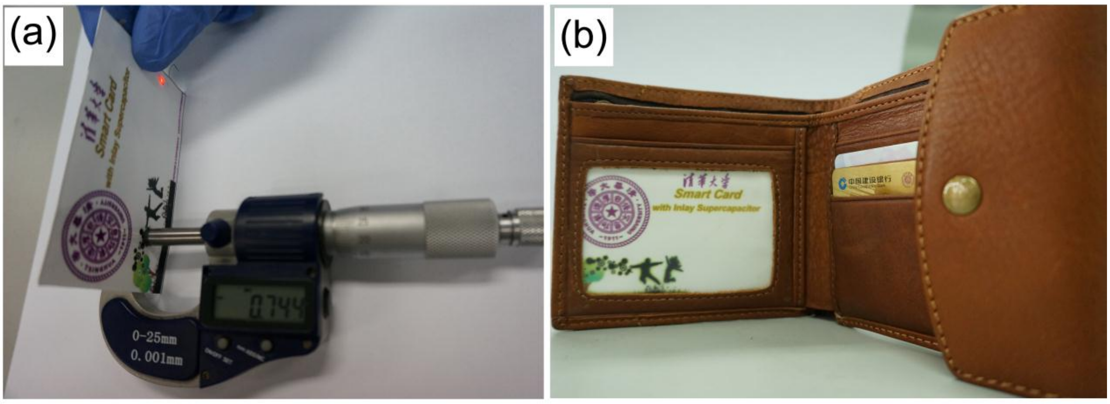

Fig.S15 (a) A photograph which shows the thicknessmeasurement of smart card with inlay supercapacitors. (b) The photograph which shows the smart card in a wallet. The total thickness is 0.77mm which is thinner than the commercial credit card. The supercapacitor based electronic can be wearable.

References:

1. B. Y. Ouyang, C. W. Chi, F. C. Chen, Q. F. Xi and Y. Yang, *Adv.Funct.Mater.*, 2005, **15**, 203-208.
2. A. Gruger, A. Novak, A. Regis and P. Colomban, *J.Mol.Struct.*, 1994, **328**, 153-167.
3. Y. C. Liu, *Langmuir*, 2002, **18**, 174-181.
4. Y. C. Liu and B. J. Hwang, *Synth.Met.*, 2000, **113**, 203-207.
5. A. J. Makinen, W. H. Kim, I. G. Hill, R. Shashidhar, N. Nikolov and Z. H. Kafafi, in *Organic Light-Emitting Materials and Devices V*, ed. Z. H. Kafafi, 2002, vol. 4464, pp. 172-177.
6. J. Ouyang, Q. F. Xu, C. W. Chu, Y. Yang, G. Li and J. Shinar, *Polymer*, 2004, **45**, 8443-8450.