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Towards High Areal Capacitance, Rate Capability and Tailorable Supercapacitor: Co_3O_4@Polypyrrole Core-Shell Nanorod Bundle Arrays Electrode

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Experiments

Synthesis of Co_3O_4 nanorods immobilized on carbon fiber cloth

In a typical synthetic process, 8 mmol of cobaltous nitrate ($Co(NO_3)_2 \cdot 6H_2O$), 23 mmol urea (CH_4N_2O) and 14 mmol ammonium fluoride (NH_4F) is dissolved in 25 mL distilled water under vigorously stirring at room temperature. After stirring for 2 h, the homogeneous solution is transferred into 25 mL hydrothermal reactor and the CFC is immersed into the solution around the reactor wall. The hydrothermal reactor is sealed and heated at 120 ^oC for 8 h in an electric oven. After the hydrothermal reactor is cooled to room temperature, the carbon clothes coated with pink precursor is picked out and washed with distilled water and ethanol for three times, respectively. After that, the carbon clothes with pink precursor is dried at 60 ^oC for 12 h. The freestanding Co_3O_4 nanorods on CFC electrode is obtained after annealing precursor at 350 ^oC for 3h. The loading mass of PPy and Co_3O_4 is evaluated by measuring the difference of mass before and after PPy and Co_3O_4@PPy growing on carbon cloth. The ratio of the mass of Co_3O_4 and PPy is 7:1 after determination. The loading mass of active materials on electrode is around 2.4 mg per square centimeter.

Fabrication of Co_3O_4 nanocone@PPy

To modify the Co_3O_4 nanorods with PPy, the freestanding Co_3O_4 nanorods immobilized on CFC electrode was immersed by mixture solution of 0.05 M pyrrole solution and 0.1 M 4-methylbenzenesulfonic acid. After that, the immersed electrode was taken out and immersed in 0.5 M ammonium persulphate aqueous solution. The electrode was subsequently left in the dark for 24 h before rinsing with methanol and deionized water successively to remove residues. Finally, freestanding Co_3O_4@PPy nanorods immobilized on CFC electrode was achieved by drying at 60°C for 24 h under vacuum.

Characterization

The crystal phase of as-synthesized products was evaluated by a Bruker D2 Phaser X-ray diffractometer with radiation from a Cu target (λ =0.154 nm) operating at 30 kV and 10 mA, respectively. The morphology of electrode materials is conducted by using field emission scanning electron microscopy (FESEM; JEOL JSM-6700F, 5 kV) and JEOL-2001F field-emission transmission electron microscopy (FESEM).

The measurement of electrochemical performance

The electrochemical performance of Co_3O_4 nanorods, Co_3O_4@PPy nanorods and porous carbon is tested using three-electrode configuration, utilizing platinum plate as counter electrode, $Hg/HgCl_2$ as reference electrode in 1 M KOH aqueous solution medium. Galvanostatic charge-discharge measurements of asymmetric supercapacitor is conducted between 0 and 1.6 V utilizing a land 2001A battery testing system with two-electrode configuration at room temperature. Cyclic voltammetry curves (CV) and electrochemical impedance spectroscopy (EIS, 100 kHz to 0.01 Hz, 5 mV amplitude) are examined using an electrochemical workstation (CHI 760D, Chenhua).

The specific capacitance of the electrode at different current densities can be calculated by the following equations:

$$C = \frac{It}{\Delta V \cdot m} \tag{1}$$

where I is the discharge current, t is the total discharge time, ΔV is the potential drop during discharging, and m is the mass of Co_3O_4 within the composite electrodes.

The power density(P)and energy density (E) can also be calculated for the ASC from the GCD results, according to the following equations:

$$E = \frac{C_m \times V^2}{2} \tag{2}$$

$$P = \frac{E}{t} \tag{3}$$

Where C_m (F/g) is the specific capacitance of the Co_3O_4@ppy//Porous carbon ASC, V (V) is the potential window during the discharge process, and t (s) is the discharging time.

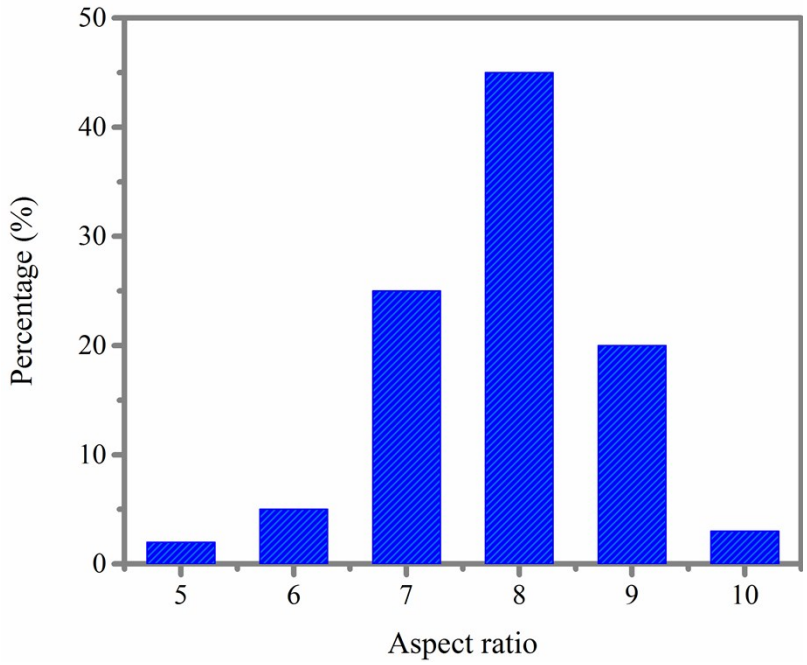

Figure S1. The distribution of the Co_3O_4@PPy nanorods aspect ratio obtained by statistical analysis of the SEM image of Figure 1g.

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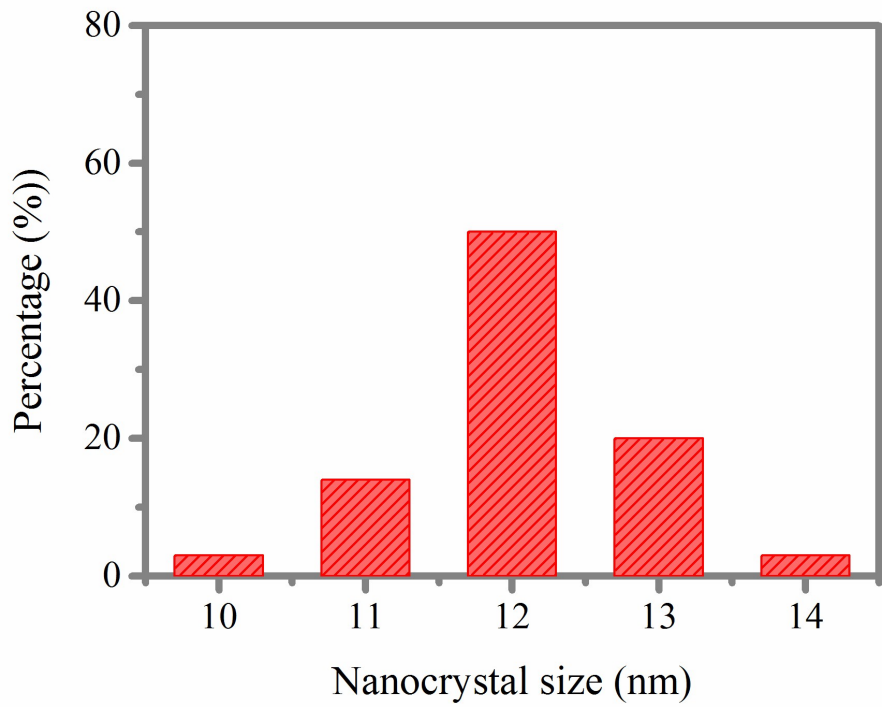

Figure S2. The nanocrystal size distribution obtained by statistical analysis of the HRTEM image of Figure 2b.

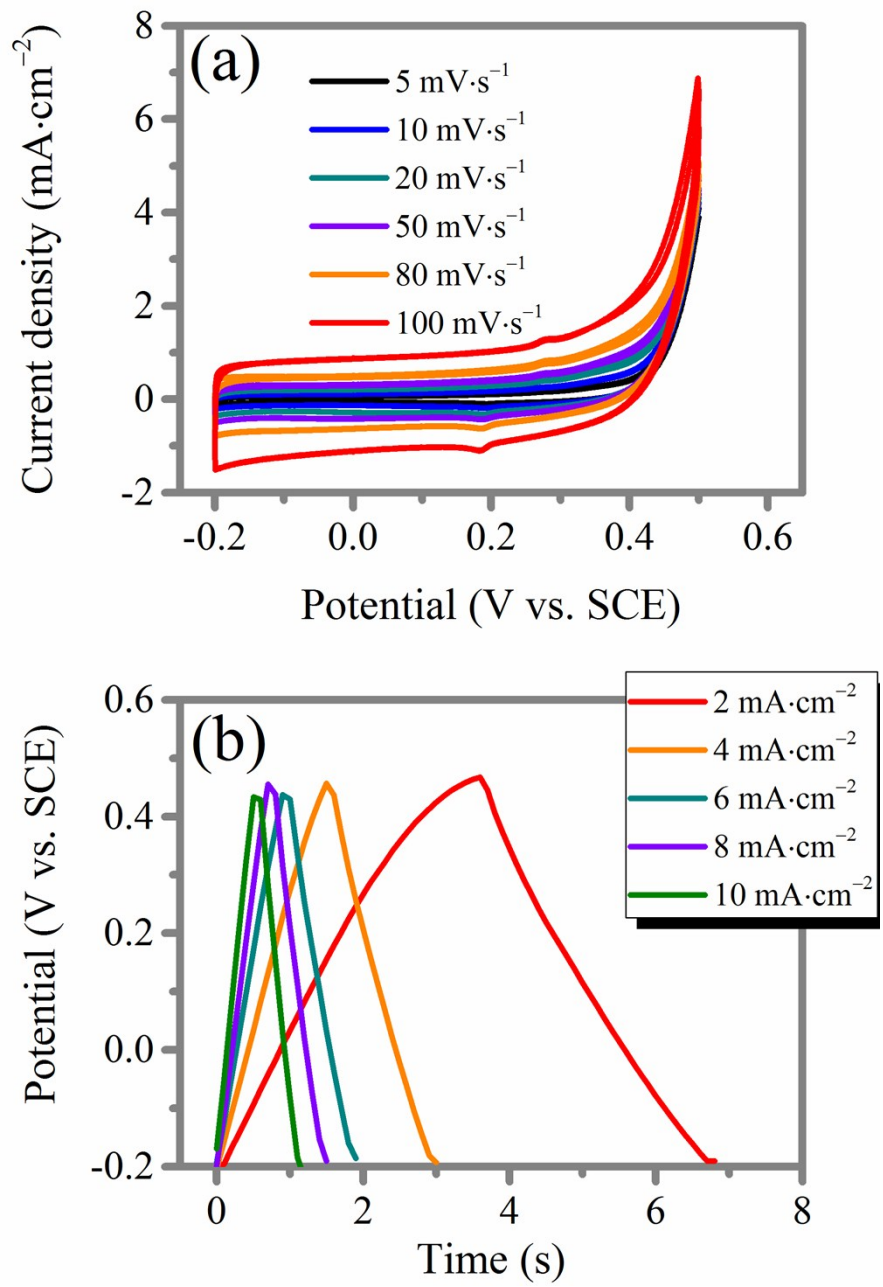

Figure S3. (a) CV and (b) charge-discharge curves of bare carbon fiber cloth.

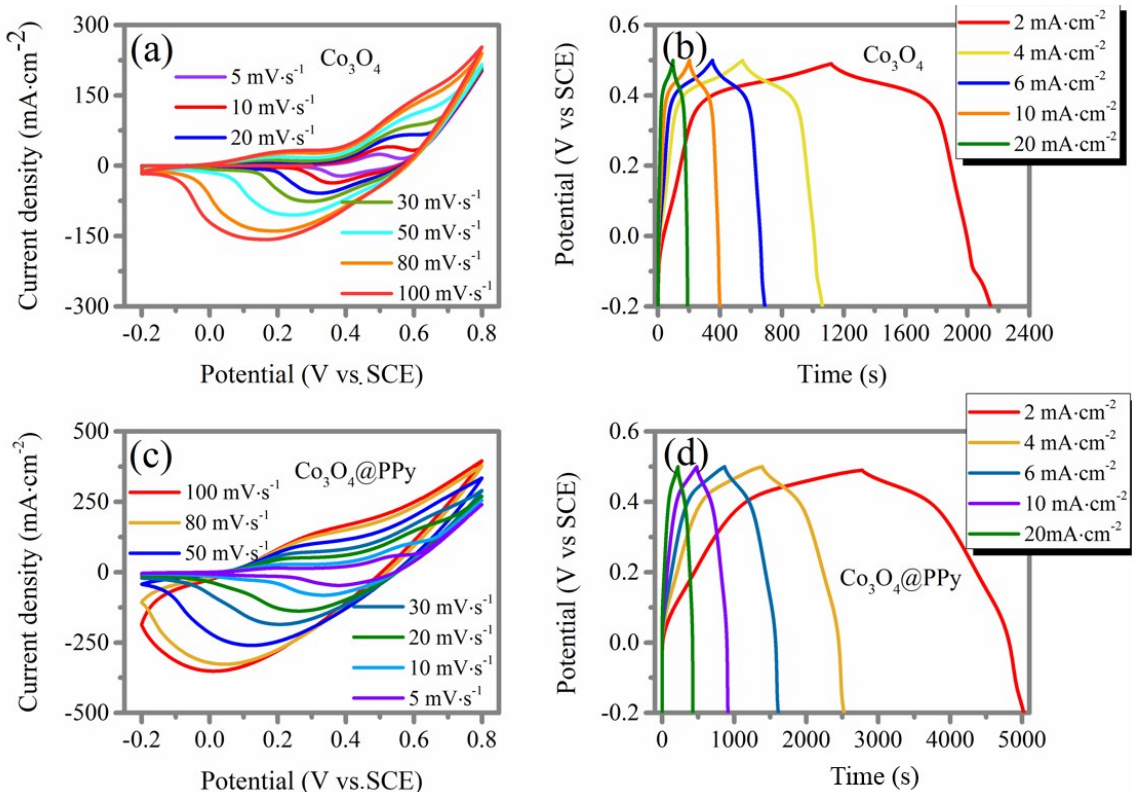

Figure S4. Co_3O_4: (a) CV and (b) charge-discharge curves. Co_3O_4 @PPy core-shell structure: (c) CV and (d) charge-discharge curves.

Table S1. Comparison of electrochemical performance with reported work

Sample	Electrolyte	Capacitance (F/cm^{-2})	Reference
Co_3O_4@PPy nanorod arrays	1 M KOH	6.67	Our work
Co_3O_4@PPy@MnO_2 nanowire arrays	1 M NaOH	1.13	Nano Energy, 2014, 7, 42.
Co_3O_4@PPy core/shell nanowire arrays	3 M KOH	4.9	Materials Letters, 2015, 157, 23.
Graphite/PEDOT/MnO_2 Composites	0.5 M Na_2SO_4	3.16	ACS Applied Materials& Interface, 2014, 6, 10506.
Co_3O_4@PPy core-shell composite nanowires	2 M KOH	3.18	Materials Research Bulletin, 2017, 96, 463.
Ni/GF/H-$CoMoO_4$	3 M KOH	5.36	ACS Applied Materials& Interface, 2017, 9, 6044.

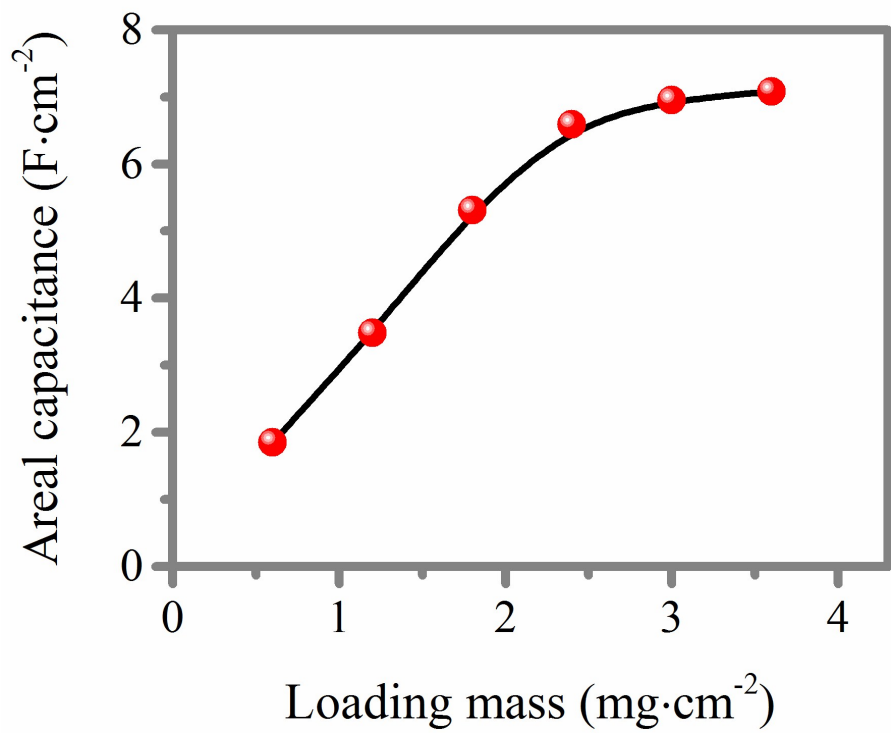

Figure S5. Capacitance changes with the increases of loading mass.

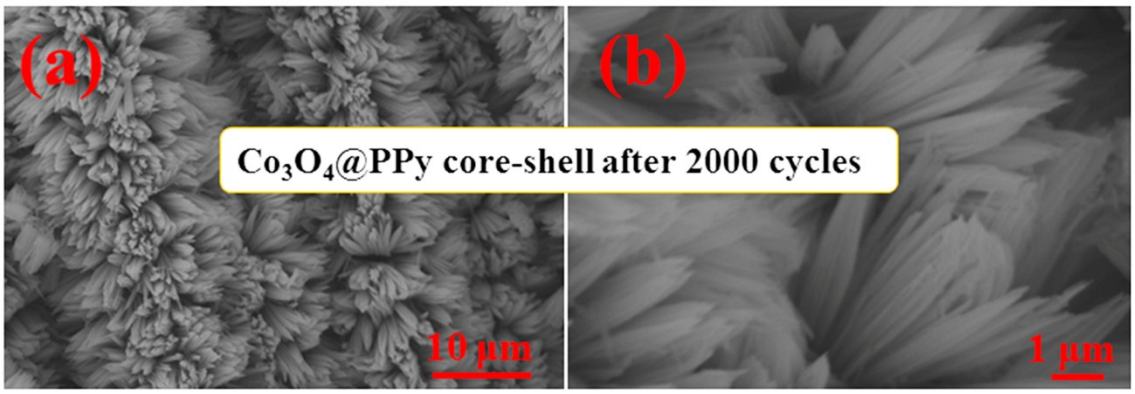

Figure S6. SEM images of Co_3O_4@PPy core-shell structure on CFC electrode after 2000 cycles charge-discharge test.

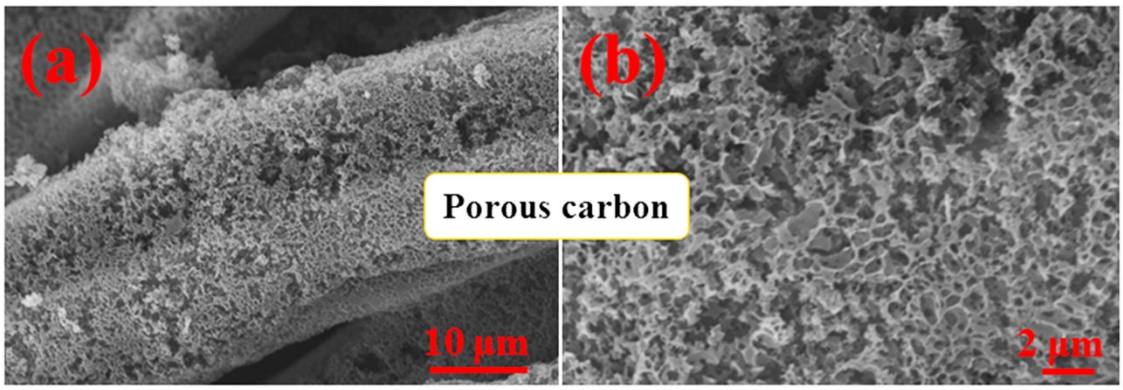

Figure S7. SEM images of porous carbon on CFC

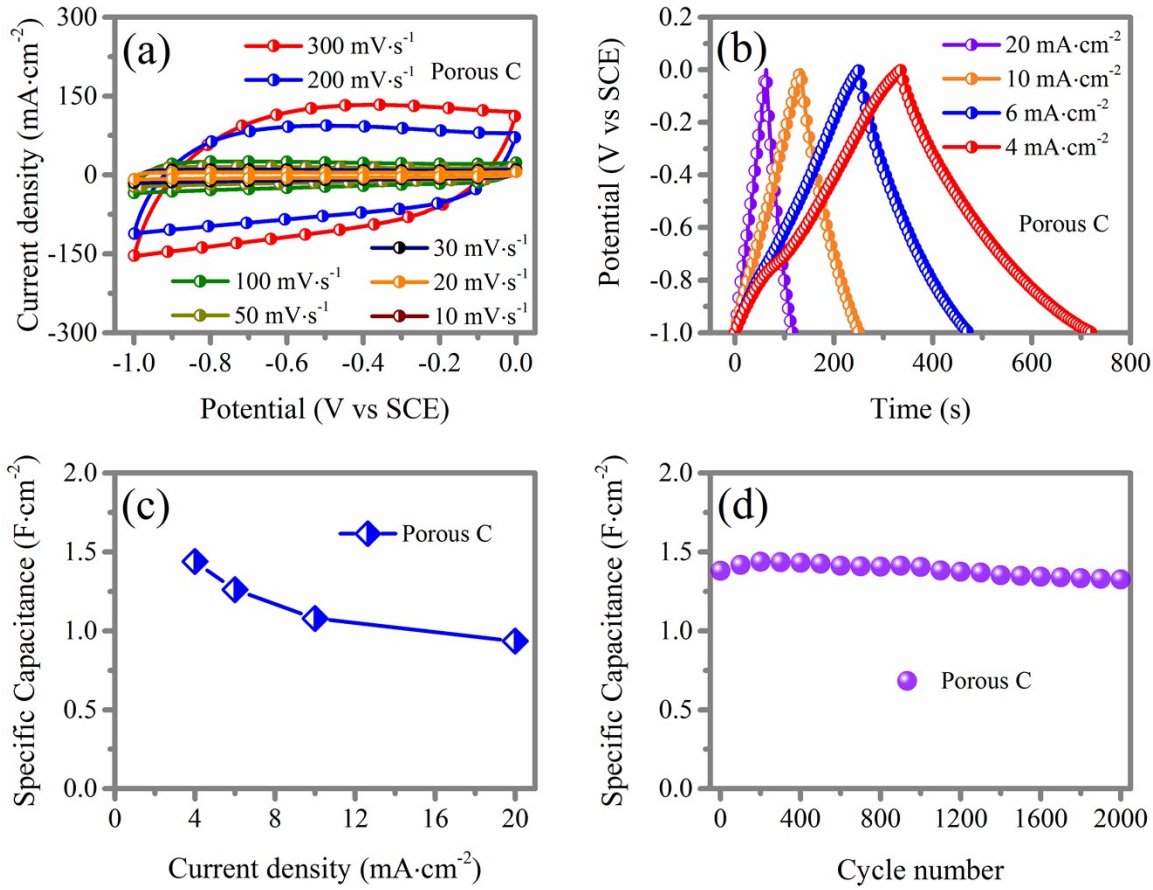

Figure S8. (a) CV and (b) charge−discharge curves of porous carbon on CFC electrode. (c) Capacitance as a function of current density for porous carbon on CFC electrodes. (d) Cycling performance of porous carbon on CFC electrodes

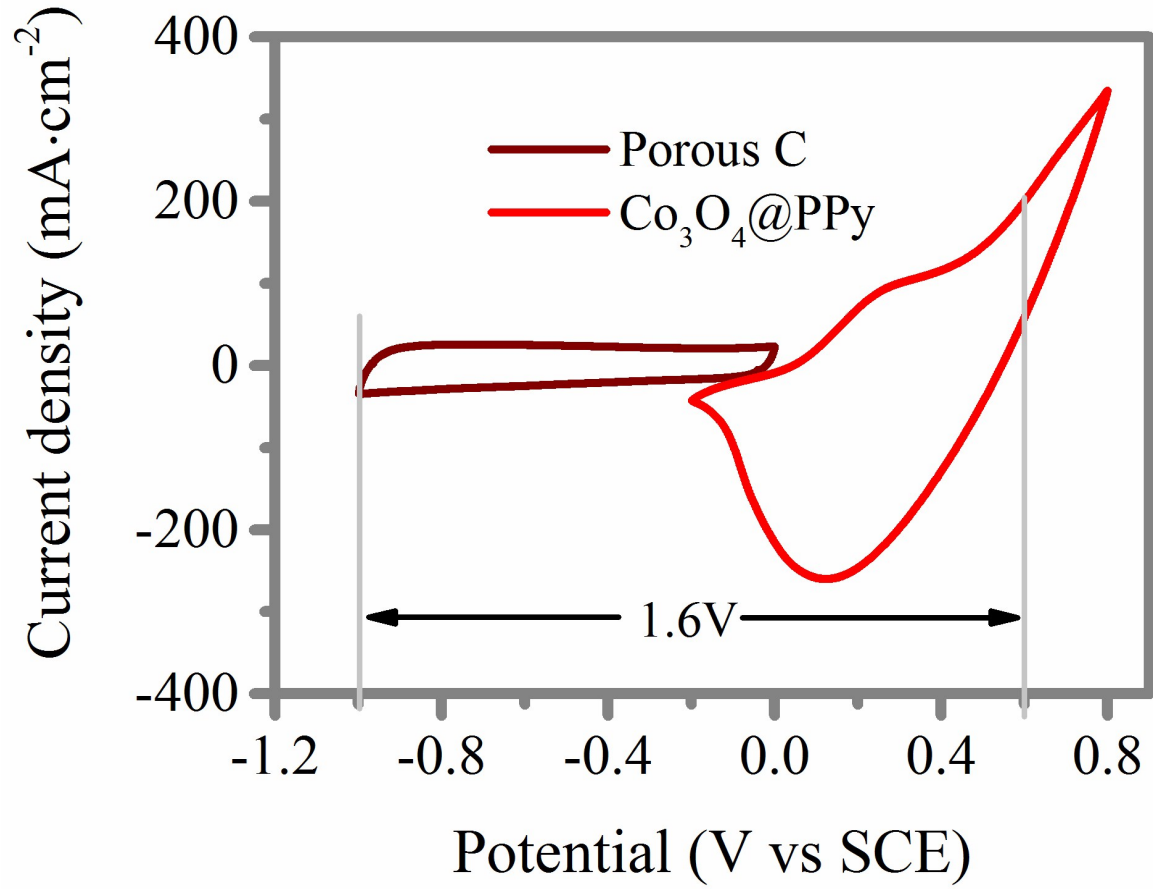

Figure S9. Comparative CV curves of Co_3O_4@PPy core-shell structure and porous carbon electrodes performed in a three-electrode configuration.

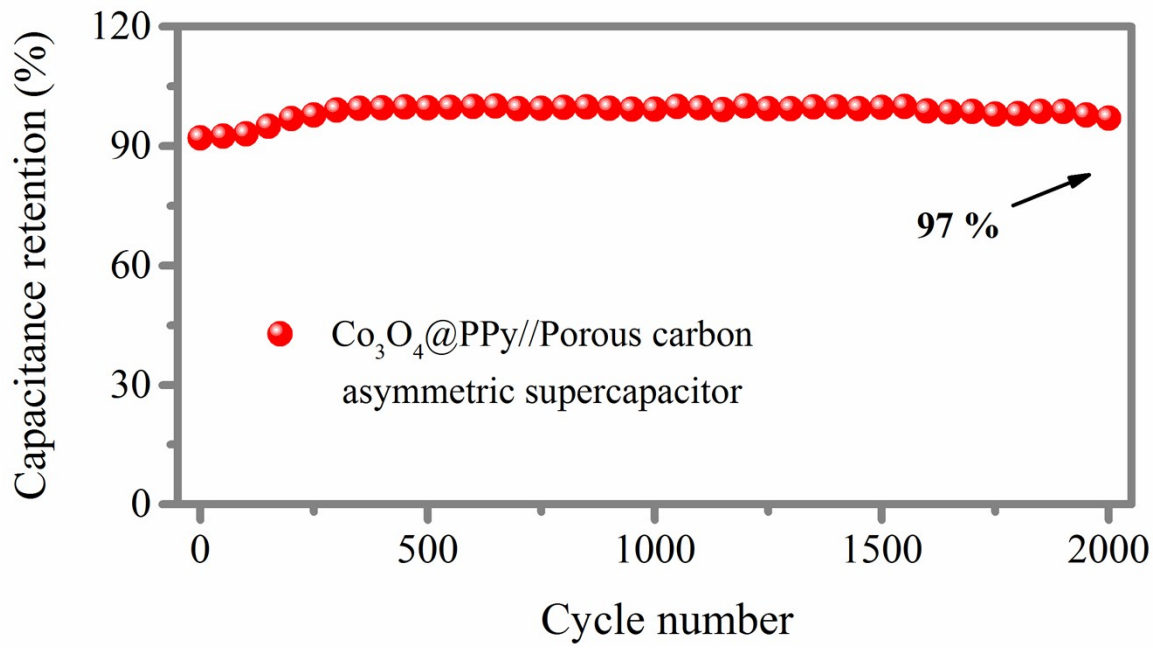

Figure S10. Cycling performance at a current density of 10 mA·cm^{-2} of an optimized Co_3O_4@PPy//Porous carbon asymmetric supercapacitor.

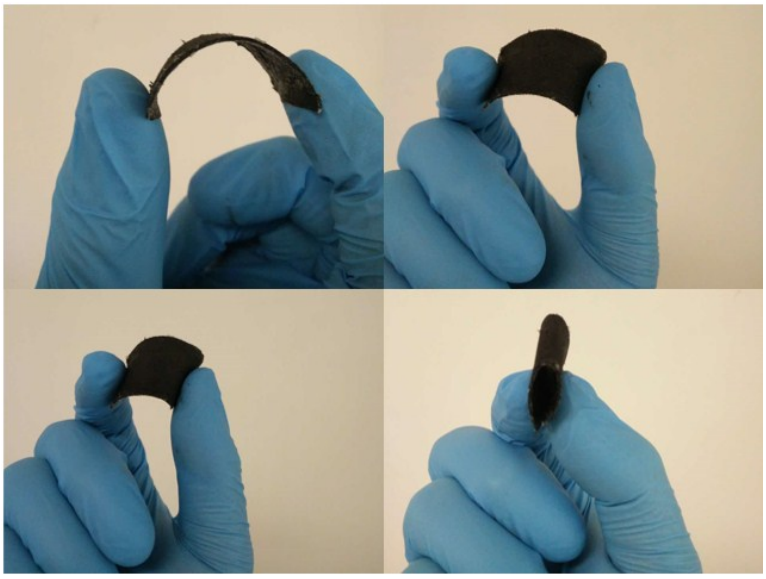

Figure S11. The photos of Co_3O_4@PPy//Porous carbon asymmetric supercapacitor in different bending degree.

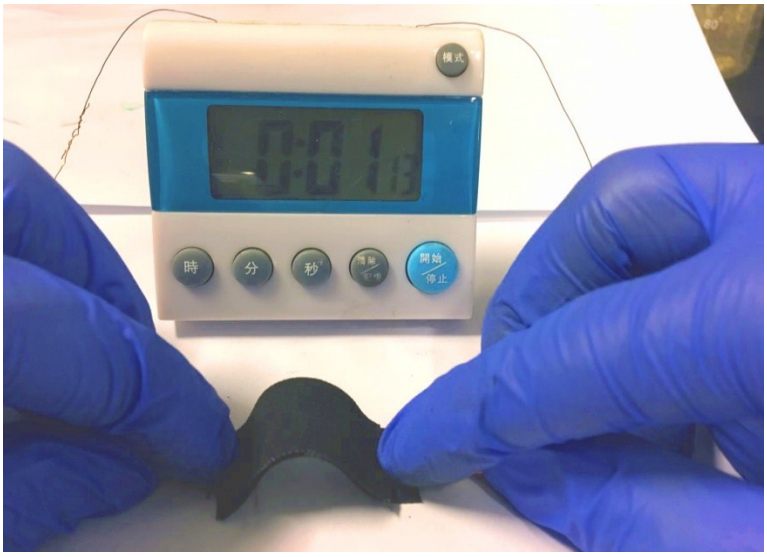

Figure S12. Powering an electronic watch when being bended.