

## Synthesis of vertical aligned TiO<sub>2</sub>@polyaniline core-shell nanorods for high-performance supercapacitors

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### Experiment section

#### The perparation of vertical aligned TiO<sub>2</sub> nanorods

A rutile TiO<sub>2</sub> nanorods array was grown on the FTO substrates by the reported hydrothermal method with some modification. In a typical preparation, 1 mL of tetrabutyl titanate, 30 mL of deionized water and 30 mL of concentrated hydrochloric acid with a volume ratio of 1: 30: 30 was mixed together under stirring. After 10 min of stirring, the homogeneous solution prepared above was transferred into 100 mL Teflon-lined stainless autoclaves. Then, two pieces of clean FTO substrates were immersed into the reaction solution upright in autoclaves. After that, the autoclave was sealed and maintained at 150 °C for 12h and allowed to cool down to room temperature spontaneously, the FTO substrates were taken out of the autoclaves and rinsed with distilled water, dried in air.

#### The preparation of TiO<sub>2</sub>@MnO<sub>2</sub> nanorods

The vertical aligned TiO<sub>2</sub> nanorods on the FTO substrates were immersed into a 30 mL of glucose (0.3 mol L<sup>-1</sup>) aqueous solution for 12 h. The free space between neighboring nanorods would allow adsorption of glucose molecules onto the nanorods surface. Then the FTO substrates were taken out, dried at 50 °C for 12 h, and further annealed in Ar gas at 500 °C at a rate of 5 °C min<sup>-1</sup> and remained 5 h to allow the carbonization of glucose. A thin layer carbon could be painted homogenously on the

surface of the TiO<sub>2</sub> nanorods.<sup>1</sup> To fabricate TiO<sub>2</sub>@MnO<sub>2</sub> nanorods, TiO<sub>2</sub>@C nanorods were immersed into a 12 mL of KMnO<sub>4</sub> (0.03 mol L<sup>-1</sup>) aqueous solution and sealed in a Teflon-lined stainless steel autoclave at 160 °C for 5 h. Due to the interfacial reaction between C and KMnO<sub>4</sub>, the TiO<sub>2</sub>@MnO<sub>2</sub> core-shell nanorods were obtained. The TiO<sub>2</sub>@MnO<sub>2</sub> core-shell nanorods was rinsed with distilled water and dried at 50 °C for 8h.

### **The preparation of TiO<sub>2</sub>@PANI nanorods**

Firstly, 0.2 mL of aniline was added into the 30 mL of HCl (1 mol L<sup>-1</sup>) solution with stirring for 5 min, then, the FTO with TiO<sub>2</sub>@MnO<sub>2</sub> core-shell nanorods was immersed into the above solution. The MnO<sub>2</sub> served as the oxidant for the synthesis of PANI. After reacting for 12 h at 0-5 °C, the product on the surface of the FTO substrates turn green, then taken it out, the TiO<sub>2</sub>@PANI core-shell nanorods was washed with distilled water and absolute ethyl alcohol, after that dried at 50 °C.

### **The preparation of pure PANI**

In our experiment, the pure PANI was obtained from the well-known chemical oxidation polymerization method. Firstly, 0.2 mL aniline was added into a 30 mL of HCl (1 mol L<sup>-1</sup>) solution, and then 0.2 g ammonium persulfate (APS) was added into the above solution with magnetic stirring for 10 min, after that a piece of FTO glass was placed into the solution. The final solution was immobilized for 24h at 0-5 °C. Then, the product on the surface of the FTO substrates turn green, then taken it out, the PANI was washed with distilled water and ethyl alcohol, after that dried at 50 °C.

## Characterization

SEM images were obtained by using a XL-30 ESEM FEG scanning electron microscope operated at 20 KV with gold sputtered on samples. TEM images were obtained using a Philips JEM-2010 transmission electron microscopy at an acceleration voltage of 200 KV. The samples for TEM observation were prepared by dispersing some products in ethanol. Then, deposition of a drop of the dispersion onto a carbon-coated copper grid. The XRD was measured with a D/max 2200 PC spectrometer with a Cu K $\alpha$  source. Scans were made from 3 to 90° (2 $\theta$ ) at the speed of 2° min<sup>-1</sup>. FT-IR spectrum was measured on an Alpha-Centauri 650 spectrometer with a KBr pellet. The frequency range was 4000-400 cm<sup>-1</sup>.

Electrochemical performance Measurement: The cyclic voltammetry (CV) and the galvanostatic charge-discharge (GCD) electrochemical experiments were all performed with a CHI660C electrochemical workstation in a three-electrode electrochemical cell at room temperature. EIS measurements were conducted with PARSTAT 2273 electrochemical station. EIS measurements were performed by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 Hz at open circuit potential. The FTO glass supported nanostructure materials TiO<sub>2</sub>, polyaniline (PANI), TiO<sub>2</sub>@C, TiO<sub>2</sub>@MnO<sub>2</sub> and TiO<sub>2</sub>@PANI. (~1 cm<sup>2</sup> area; TiO<sub>2</sub> mass: 0.39 mg; PANI mass: 0.10 mg, TiO<sub>2</sub>@C mass: 0.44 mg; TiO<sub>2</sub>@MnO<sub>2</sub> mass: 0.58 mg, and TiO<sub>2</sub>@PANI mass: 0.51 mg ) acted directly as the working electrode. A platinum wire and Ag/AgCl were used as counter electrode and reference

electrode, respectively. For the TiO<sub>2</sub>, TiO<sub>2</sub>@C and TiO<sub>2</sub>@MnO<sub>2</sub> electrodes with electrolyte of 1M Na<sub>2</sub>SO<sub>4</sub>; and for both PANI and TiO<sub>2</sub>@PANI electrodes with electrolyte of 1M H<sub>2</sub>SO<sub>4</sub>. FTO glass was employed as the current collector for all materials.

### **Calculation:**

For the hybrid electrode, the specific capacitance (F g<sup>-1</sup>) was calculated using the following equations:

$$C_s = I \cdot t / (\Delta V \cdot m) \quad (1)$$

where  $I$  is the constant discharge current,  $t$  is the discharging time,  $\Delta V$  is the voltage drop upon discharging (excluding the IR drop),  $m$  is the total mass of the electrode material.<sup>2</sup>

The area specific capacitances were calculated using the equations:

$$C_a = \int I \cdot dv / (v \cdot \Delta V \cdot S) \quad (2)$$

Where  $\int I \cdot dv$  is the integral area of cyclic voltammogram loop,  $v$  is the scan rate,  $S$  is the geometrical area of the active electrode, and  $\Delta V$  is the sweep potential window.

The energy density ( $E$ ) of a supercapacitor is calculated using the equation:

$$E = 1/8 C_s V^2 \quad (3)$$

Where  $C_s$  is the specific capacitance, and  $V$  is the windows of voltage.

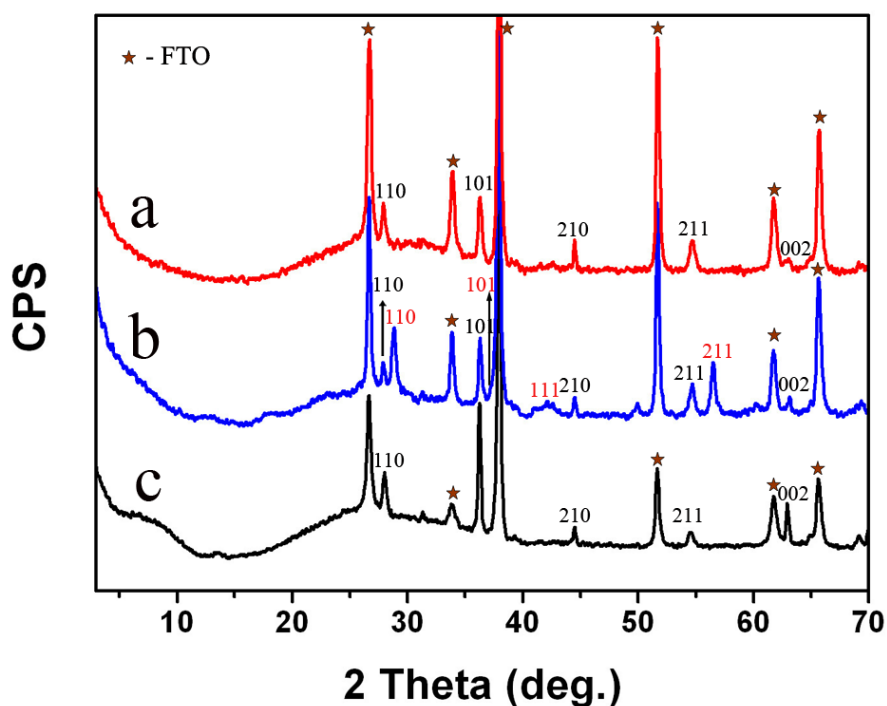
The power density ( $P$ ) was calculated by the following equation:

$$P = V^2/4Rm \quad (4)$$

Here  $V$  is the cutoff voltage,  $m$  is the total mass of the electrode, and ( $R = \Delta V_{IR}/I$ ) with  $\Delta V_{IR}$  being the voltage drop between the first two points in the voltage drop at its top cutoff.

The  $C_s$ , energy and power densities of the  $\text{TiO}_2@\text{PANI}$  electrodes were all calculated based on the total mass of both  $\text{TiO}_2$  and PANI excluding the current collector.

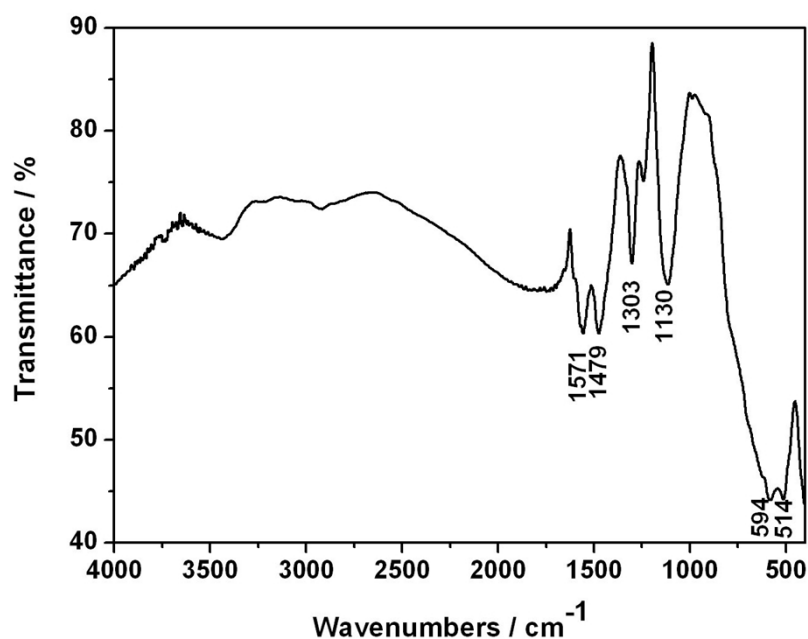
All used chemicals were of analytical grade. Aniline (Beijing Chemical Co.) was distilled twice under vacuum before use. HCl was purchased from Beijing chemical factory as the oxidant without further purification. Glucose and  $\text{KMnO}_4$  were purchased from Beijing chemical factory without further purification. Tetrabutyl titanate and ammonium persulfate (APS) were purchased from Sigma-Aldrich Corporation without further purification.



**Figure S1** XRD patterns of the TiO<sub>2</sub> (a), TiO<sub>2</sub>@MnO<sub>2</sub> (b) and TiO<sub>2</sub>@PANI nanocomposite (c). (peaks from the FTO substrate are indicated with star symbol)

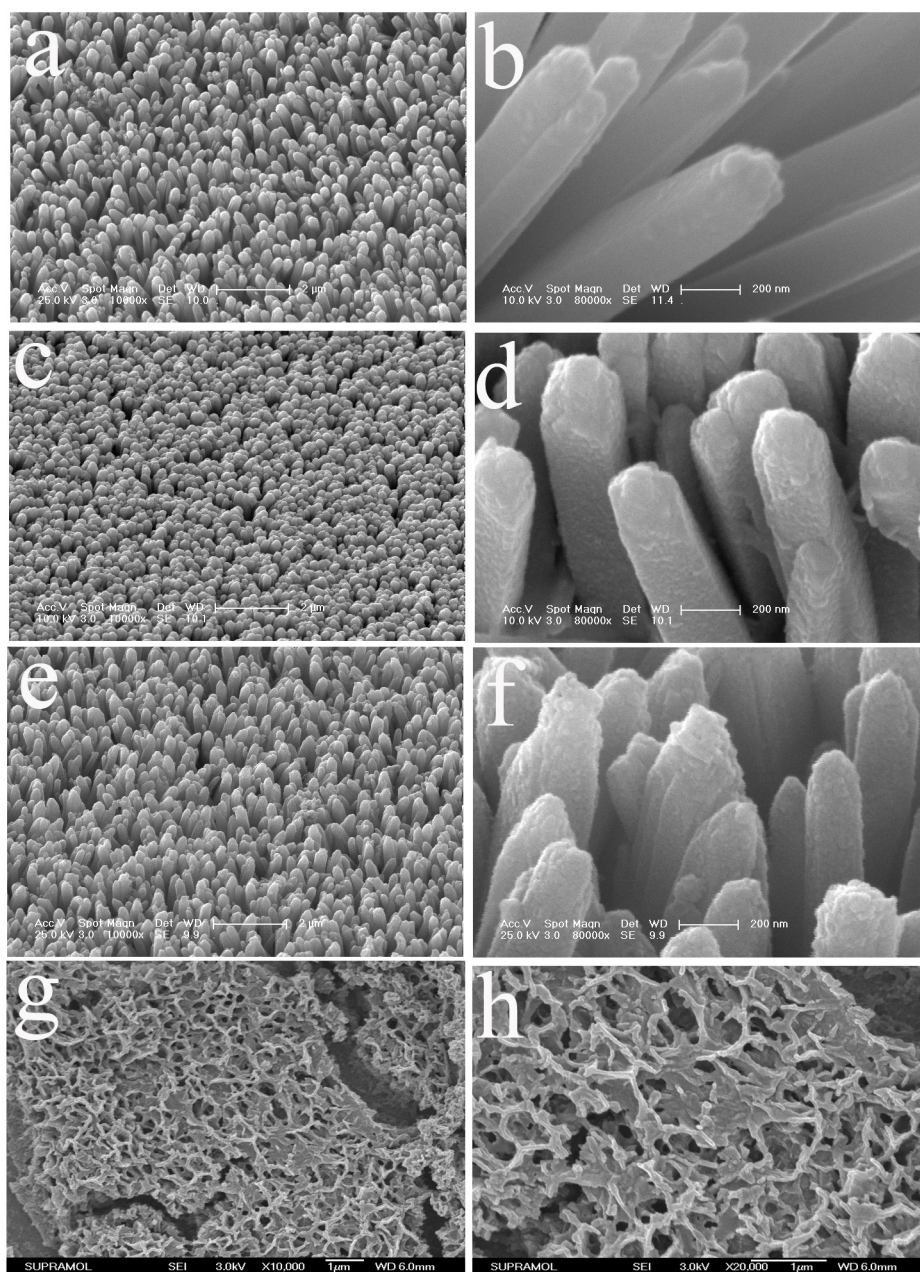
The XRD patterns of the TiO<sub>2</sub>, TiO<sub>2</sub>@MnO<sub>2</sub> and TiO<sub>2</sub>@PANI nanocomposite films on FTO substrates are presented in Figure S1. After subtracting the diffraction peaks of FTO glass (the star mark, JCPDS Card, No. 46-1088), the diffraction peaks in the lines (a, b and c) can be indexed as rutile TiO<sub>2</sub> (with the cell constants of a=4.517 Å, b =4.517 Å, c =2.940 Å, black peak value), and for the line (b) of TiO<sub>2</sub>@MnO<sub>2</sub>, subtracting the diffraction peaks of FTO glass and rutile TiO<sub>2</sub>, the diffraction peaks can be indexed as MnO<sub>2</sub> (with the cell constants of a=4.404 Å, b =4.404 Å, c =2.876 Å, red peak value), the test results of TiO<sub>2</sub> and MnO<sub>2</sub> are consistent with the values in the literature (JCPDS Card, No. 88-1175 and JCPDS Card, No. 81-2261). XRD pattern of the TiO<sub>2</sub>@PANI nanocomposite shows a wide

peak around  $2\theta \approx 25^\circ$  which is caused by the periodicity perpendicular to the polymer chains of PANI.



**Figure S2** FT-IR spectrum of the TiO<sub>2</sub>@PANI core-shell nanorods.

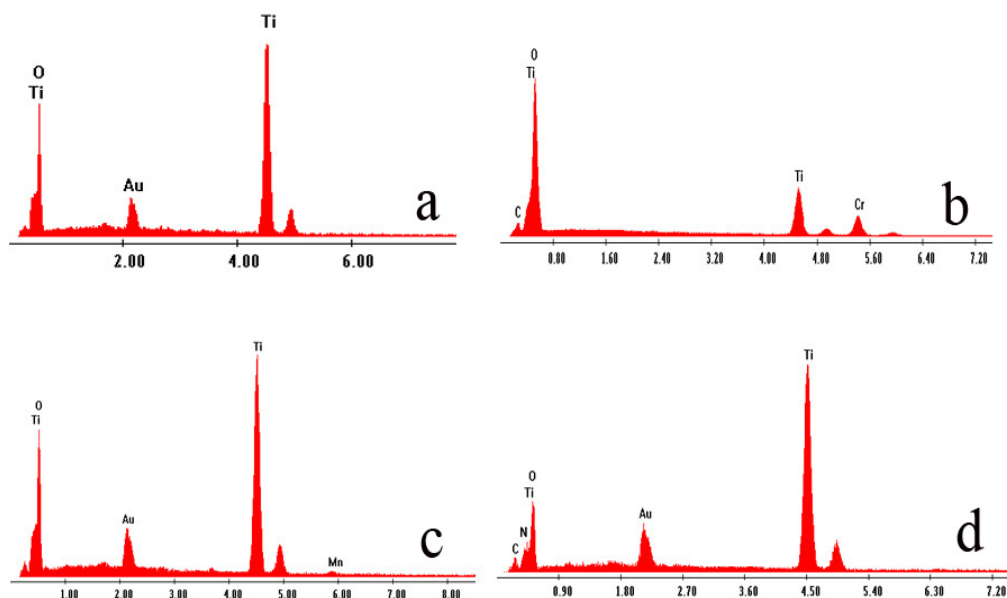
The well-resolved peaks at 1571 cm<sup>-1</sup> and 1479 cm<sup>-1</sup> correspond to the C=C stretching vibration of benzenoid and quinoid rings, respectively. The peak at 1303 cm<sup>-1</sup> relates to the C-N stretching vibration with aromatic conjugation. The peak at 1130 cm<sup>-1</sup> assigned to the characteristic of Q=NH<sup>+</sup>-B (where Q and B denote quinoid ring and benzene ring, respectively) is also observed. The broad characteristic peak of TiO<sub>2</sub> is found within 400-700 cm<sup>-1</sup>. FT-IR spectrum of the TiO<sub>2</sub>@PANI nanorods exhibits characteristic bands of PANI as well as TiO<sub>2</sub>, which confirms the presence of both components in the nanocomposite.



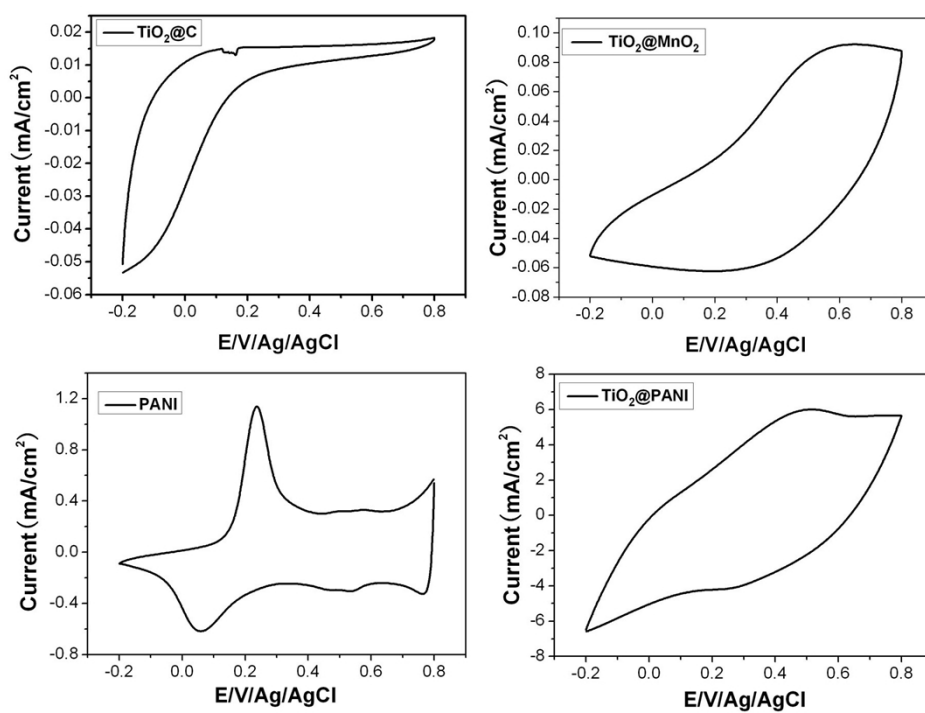
**Figure S3** FE-SEM image of the TiO<sub>2</sub>@C (a, b), TiO<sub>2</sub>@MnO<sub>2</sub> (c, d), TiO<sub>2</sub>@PANI (e, f) and PANI (g, h).

The field emission scanning electron microscope (FE-SEM) image (Figure S3) of the different materials of the TiO<sub>2</sub>@C (a, b), TiO<sub>2</sub>@MnO<sub>2</sub> (c, d), TiO<sub>2</sub>@PANI (e, f) and PANI (g, h). The low magnification SEM images (a, c, e, g) are the top portion of the nanosize materials, and we can find that from the high magnification SEM mages (b, d, f, h), the surface morphology of the different step of the materials are different.



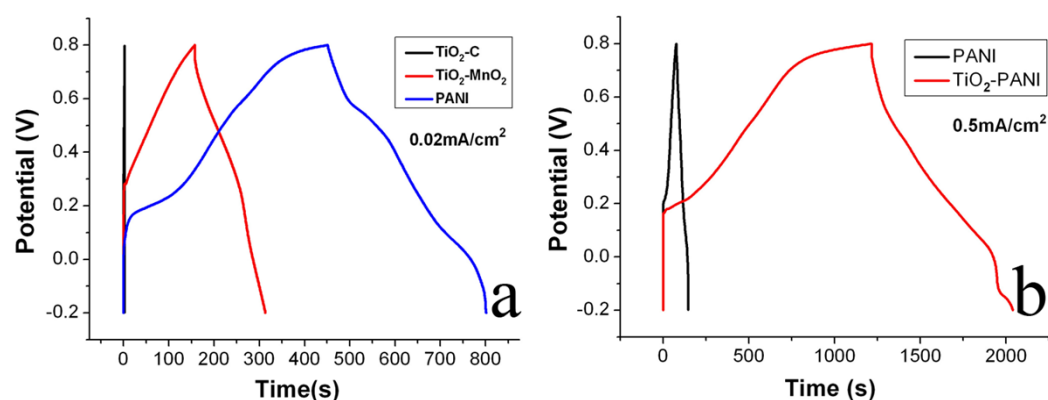


**Figure S4** EDX patterns of the  $\text{TiO}_2$  (a),  $\text{TiO}_2@\text{C}$  (b),  $\text{TiO}_2@\text{MnO}_2$  (c) and  $\text{TiO}_2@\text{PANI}$  nanocomposite (d).



**Figure S5** CV curves of  $\text{TiO}_2@\text{C}$ ,  $\text{TiO}_2@\text{MnO}_2$ , PANI and  $\text{TiO}_2@\text{PANI}$  core-shell nanorods. (scan rate of  $20 \text{ mV s}^{-1}$ , with the same geometrical area is  $1 \text{ cm}^2$ ).

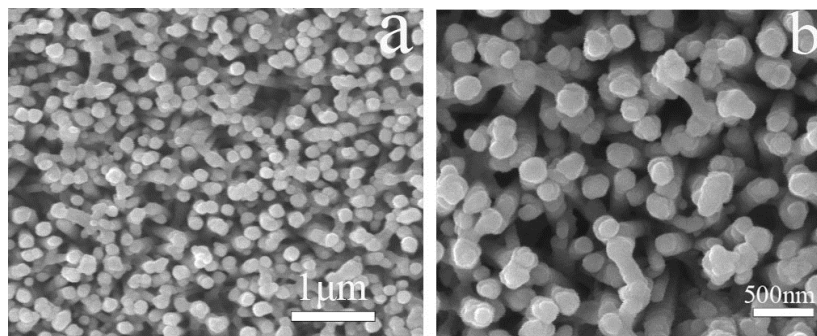
Figure S5 shows the CV curves of  $\text{TiO}_2@\text{C}$ ,  $\text{TiO}_2@\text{MnO}_2$ , PANI and  $\text{TiO}_2@\text{PANI}$  core-shell nanorods at a scan rate of  $20 \text{ mV s}^{-1}$ . From the CV curves,  $\text{TiO}_2@\text{PANI}$  nanorods has the largest integral area of all the electrodes, suggesting the highest capacitance. In our experiment, the area specific capacitance of  $\text{TiO}_2@\text{PANI}$  is  $0.367 \text{ F / cm}^2$  at the scan rate of  $5 \text{ mV s}^{-1}$ .



**Figure S6** The GCD curves of  $\text{TiO}_2@\text{C}$ ,  $\text{TiO}_2@\text{MnO}_2$  and PANI (a: at the current density of  $0.02 \text{ mA / cm}^2$ ) and PANI,  $\text{TiO}_2@\text{PANI}$  nanomaterials.(b: at the current density of  $0.5 \text{ mA / cm}^2$ ) (all them are with the same geometrical area is  $1 \text{ cm}^2$ )

The electrochemical performance of different samples was further studied by GCD measurement. Figure S6a shows the typical GCD curves of  $\text{TiO}_2@\text{C}$  (black),  $\text{TiO}_2@\text{MnO}_2$  (red) and PANI (blue) at a current density of  $0.02 \text{ mA / cm}^2$ . The GCD curve of PANI was much prolonged over the  $\text{TiO}_2@\text{C}$  and  $\text{TiO}_2@\text{MnO}_2$  electrodes. Figure S6b shows the GCD curves of PANI (red) and  $\text{TiO}_2@\text{PANI}$  at the same

current density of 0.5 mA / cm<sup>2</sup>. The GCD curve of TiO<sub>2</sub>@PANI was much prolonged over the PANI electrode. From the comparison, TiO<sub>2</sub>@PANI electrode has the highest area specific capacitance in all materials, the result is agree with that of CV curve analysis conclusion.



**Figure S7** SEM image of the top view of the TiO<sub>2</sub>@PANI electrode after 1000 cycles of charge-discharge test. (a, b different magnification, at the current density of 10 A g<sup>-1</sup>)

**REFERENCE:**

- (1). X. Sun, Q. Li, Y. N. Lu and Y. B. Mao, *Chem. Commun.*, 2013, **49**, 4456.
- (2). C. Zhou, Y. W. Zhang, Y. Y. Li and J. P. Liu, *Nano Lett.*, 2013, **13**, 2078-2085.