

Electronic Supplementary Information

Titanium dioxide @ polypyrrole core-shell nanowires for all solid-state flexible supercapacitors

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1. Experimental

1.1. Synthesis of TiO₂ and TiO₂@PPy NWs

TiO₂ NWs were grown on carbon cloth substrate by a seed-assisted hydrothermal method reported elsewhere.^{1, 2} Detailed synthetic process of TiO₂ NWs on carbon cloth can be referred to the literature that Zheng et al recently reported.² A white TiO₂ NW film on the carbon cloth surface was obtained after hydrothermal method, and then was annealed at 550 °C for 1 h in air. Anodic deposition of PPy shell on the surface of TiO₂ NWs was performed in a solution of 0.01 M pyrrole and 0.1 M H₂SO₄ with a current density of 1 mA cm⁻² for 20 min at 50 °C.

1.2. Fabrication of Solid-State Device

The solid-state device was assembled by separating two identical TiO₂@PPy NW electrodes with a separator (NKK separator, Nippon Kodoshi Corporation) and polyvinyl alcohol (PVA)/H₂SO₄ gel electrolyte. PVA/H₂SO₄ gel electrolyte was prepared by dissolving PVA (3 g) into 30 ml 1 M H₂SO₄ aqueous solution at 85 °C under vigorously stirring for 1 h. Before the assembling, electrodes and the separator were immersed in PVA/H₂SO₄ gel electrolyte for 10 min and then allowed to solidify at room temperature for 3 h. Finally, they were assembled together and kept at 45 °C for 12 h to remove excess water in the electrolyte.

1.3. Characterization

The morphology, microstructure, and compositions of the products were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6330F), transmission electron microscopy (TEM, JEM2010-HR), X-ray diffractometry (XRD, D8 ADVANCE), Infrared-ray spectrometer (FT-IR, Nicolet 330), and laser Micro-Raman Spectrometry (Renishaw inVia). The surface area of the product was calculated from nitrogen adsorption/desorption isotherms at 77 K that were conducted on an ASAP 2020 V3.03 H instrument. Cyclic voltammetry (CV) and galvanostatic charge/discharge measurements were conducted using an electrochemical workstation (CHI 660D, Chenhua, Shanghai). The electrochemical studies of the individual electrode were performed in a three-electrode cell, with a Pt wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The electrolyte is 1 M H₂SO₄ aqueous solution.

References

- 1 X. H. Lu, G. M. Wang, T. Zhai, M. H. Yu, S. L. Xie, Y. C. Ling, C. L. Liang, Y. X. Tong and Y. Li, *Nano letters*, 2012, **12**, 5376-5381.
- 2 H. M. Zheng, T. Zhai, M. H. Yu, S. L. Xie, C. L. Liang, W. X. Zhao, S. Wang, Z. S. Zhang and X. H. Lu, *Journal of Materials Chemistry C*, 2013, **1**, 225-229.

2. Calculations:

2.1. Single Electrode :

Specific capacitances of the TiO₂@PPy electrodes were calculated from their CVs according to the following equation:

$$C_A = \frac{Q}{\Delta V \times S} = \frac{\int |I| dt}{2\Delta V \times S} = \frac{\int |I| dU}{2\Delta V \times S \times v} \quad (1)$$

where C_A (F/cm²) is the areal capacitance, Q (C) is the average charge during the charging and discharging process, ΔV (V) is the potential window, S (cm²) is the area of TiO₂@PPy electrodes, I (A) is the current value in CV curves, t (s) is the sum of charging time and discharging time, U (V) is the potential value in CV curves, v (V s⁻¹) is the applied scan rate.

Alternatively, specific capacitances of the TiO₂@PPy electrodes were estimated from their slopes of the discharge curves according to the following equation:

$$C_A = \frac{I \times \Delta t}{\Delta V \times S} \quad (2)$$

where I is the applied current, S (cm²) is the area of TiO₂@PPy electrodes, Δt is the discharging time, ΔV (V) is the voltage window.

2.2. TiO₂@PPy -based Devices:

The cell (device) capacitance (C_{cell}) and volumetric capacitance of the TiO₂@PPy-based devices were calculated from their CVs according to the following equation:

$$C_{cell} = \frac{Q}{\Delta V} = \frac{\int |I| dt}{2\Delta V} = \frac{\int |I| dU}{2\Delta V \times v} \quad (3)$$

$$C_V = \frac{C_{cell}}{V} = \frac{\int |I| dU}{2V \times \Delta V \times \nu} \quad (4)$$

where Q (C) is the average charge during the charging and discharging process is the applied current, V is the volume (cm^3) of the whole device (The area and thickness of our $\text{TiO}_2@PPy$ -based device are about 1 cm^2 and 0.08 cm . Hence, the whole volume of our $\text{TiO}_2@PPy$ -based device is about 0.08 cm^3), ΔV (V) is the voltage window, I (A) is the current value in CV curves, t (s) is the sum of charging time and discharging time, U (V) is the potential value in CV curves, ν (V s^{-1}) is the applied scan rate. It is worth mentioning that the volumetric capacitances were calculated taking into account the volume of the device stack. This includes the active material, the flexible substrate and the separator with electrolyte.

Alternatively, the cell (device) capacitance (C_{cell}) and volumetric capacitance of the electrode (C_V) were estimated from the slope of the discharge curve using the following equations:

$$C_{cell} = \frac{I \times \Delta t}{\Delta V} \quad (5)$$

$$C_V = \frac{C_{cell}}{V} = \frac{I \times \Delta t}{V \times \Delta V} \quad (6)$$

where I is the applied current, V is the volume (cm^3) of the whole device (the whole volume of our $\text{TiO}_2@PPy$ -based device is about 0.08 cm^3), Δt is the discharging time, ΔV (V) is the voltage window.

Volumetric energy density of the devices were obtained from the following equations:

$$E = \frac{1}{2 \times 3600} C_V \Delta V^2 \quad (7)$$

where E (Wh cm^{-3}) is the energy density, C_V is the volumetric capacitance obtained

from Equation (6) and ΔV (V) is the voltage window.

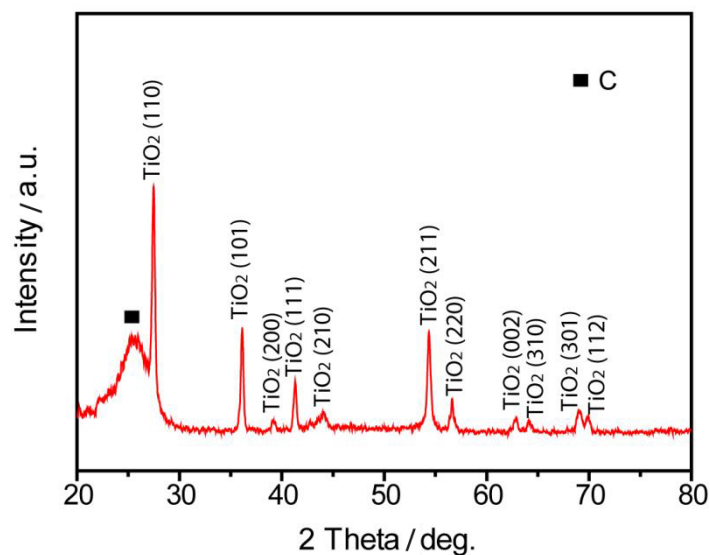


Figure S1. XRD pattern of the TiO_2 @PPy core shell NWs

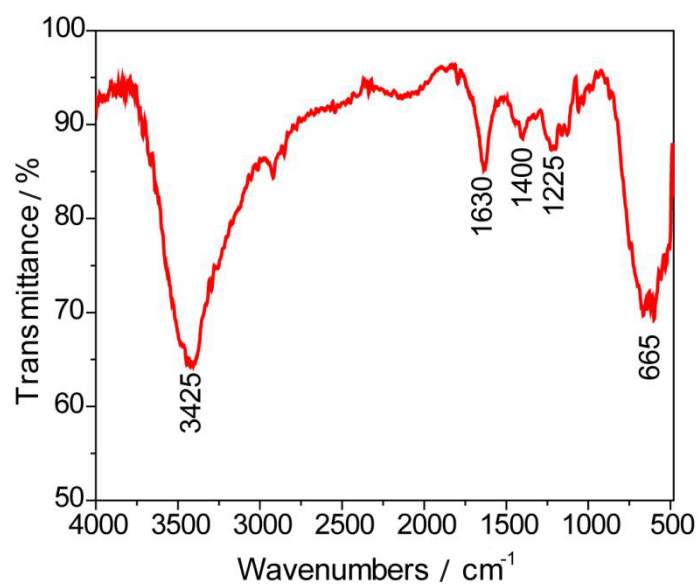


Figure S2. FT-IR absorption spectrum of the TiO_2 @PPy core shell NWs

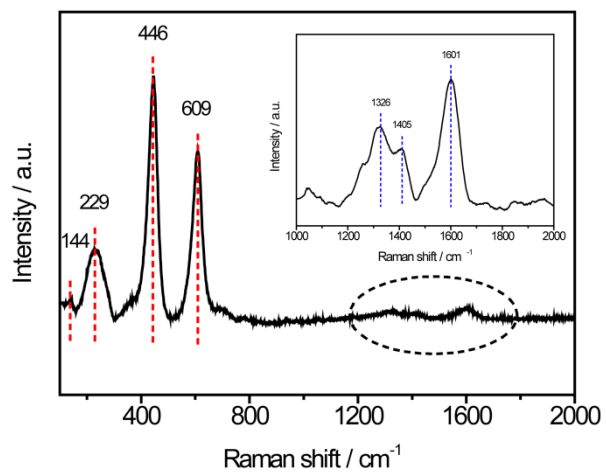


Figure S3. Raman spectra of the TiO₂@PPy core shell NWs

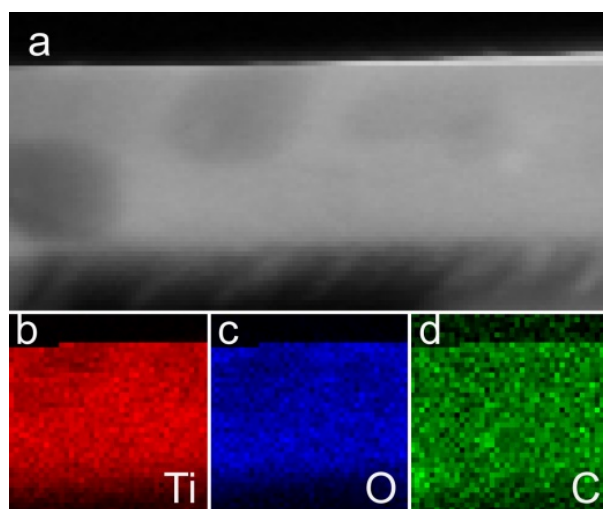


Figure S4. STEM image (a), and titanium (b), oxygen (c), and carbon (d) element mapping images of TiO₂@PPy core shell NWs.

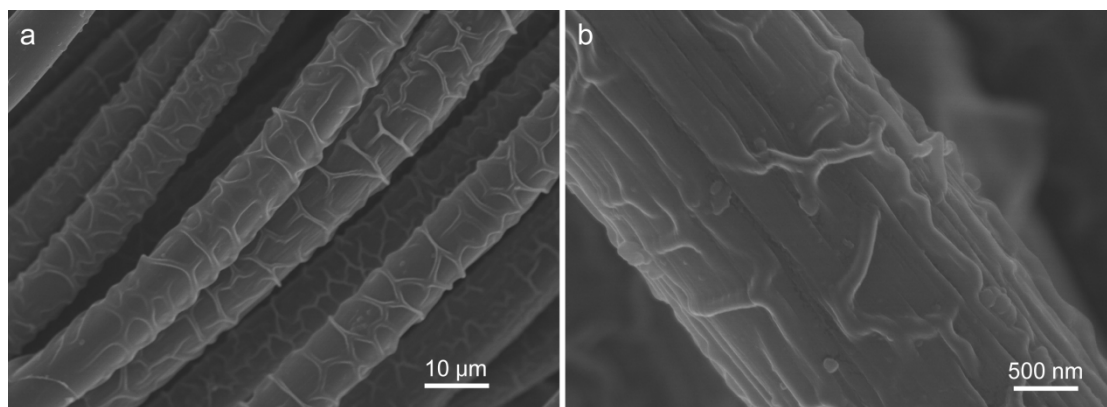


Figure S5. SEM images of the PPy directly on surface of carbon cloth prepared under the same condition as TiO₂@PPy NWs.

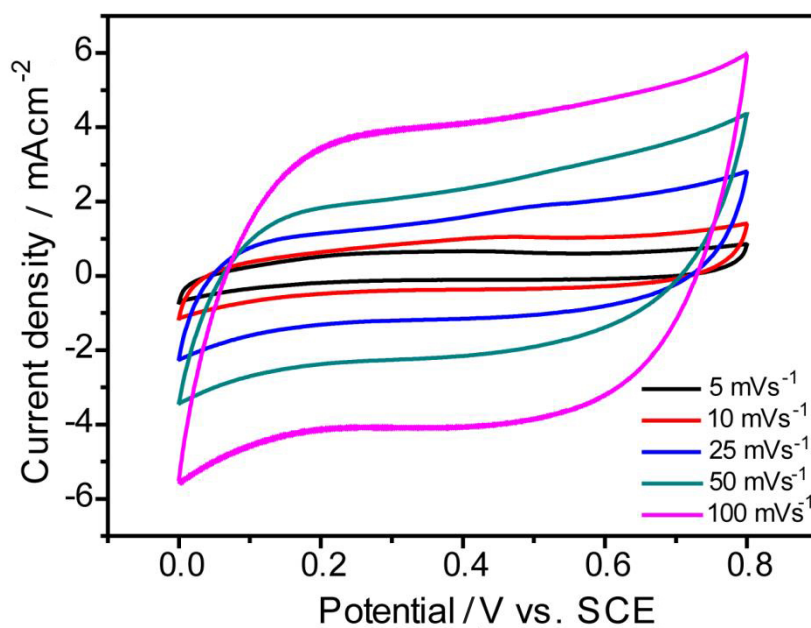


Figure S6. CV curves of TiO₂@PPy core shell NW electrode collected at different scan rates

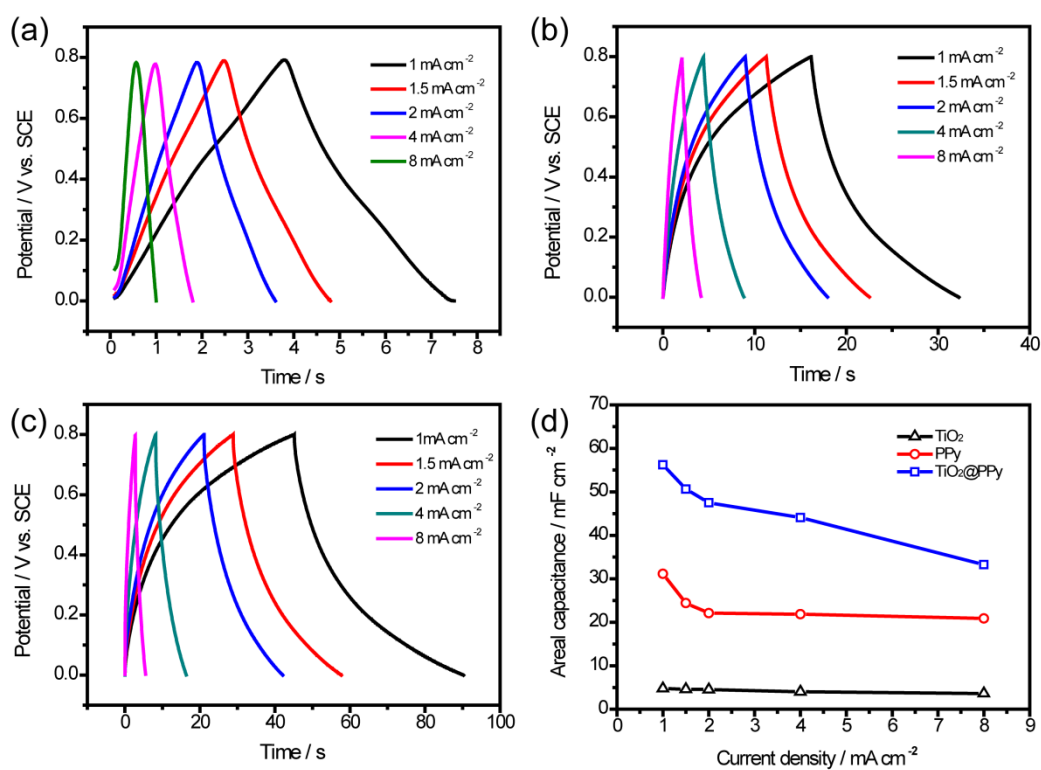


Figure S7. Galvanostatic charge/discharge curves of the TiO_2 (a), PPy (b), and $\text{TiO}_2@PPy$ (c) electrodes collected at different current densities. (d) Areal capacitance as a function of current density of the TiO_2 , PPy and $\text{TiO}_2@PPy$ electrodes.

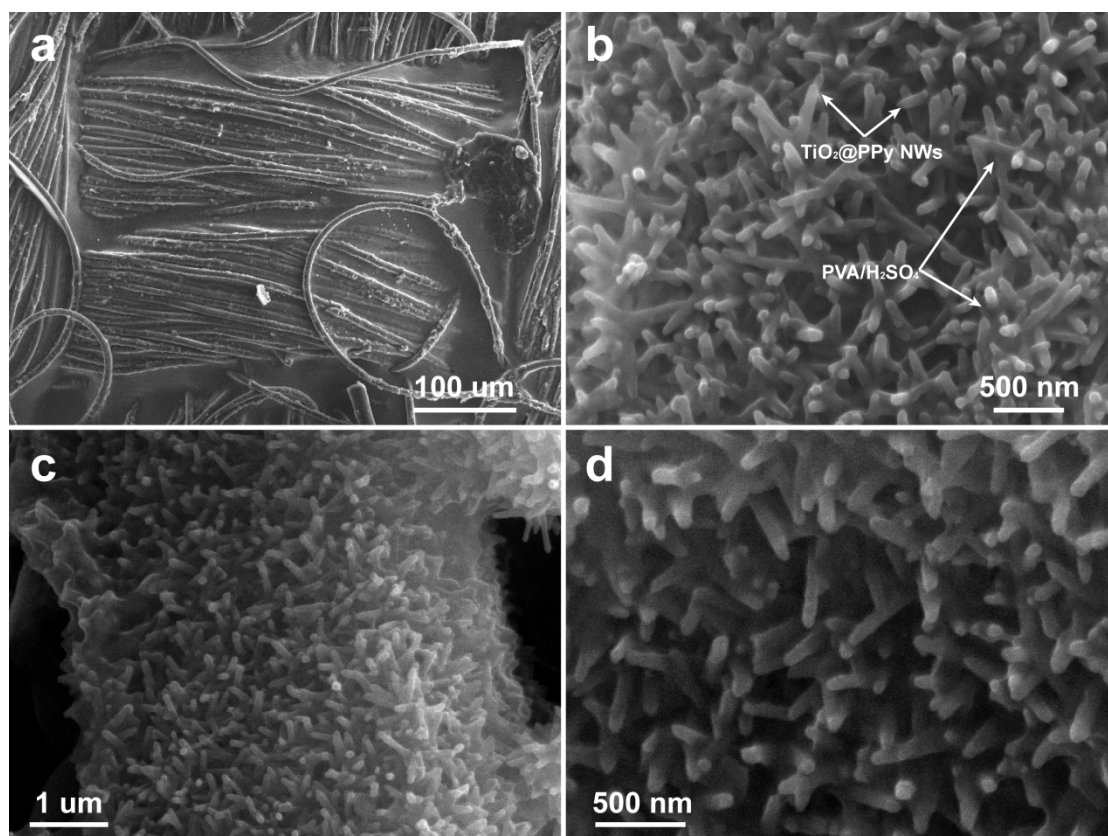


Figure S8. SEM images of TiO₂@PPy nanowires coated carbon on cloth wrapped by PVA/H₂SO₄ polymer gel before (a, b) and after (c, d) bending these TiO₂@PPy-SC devices.

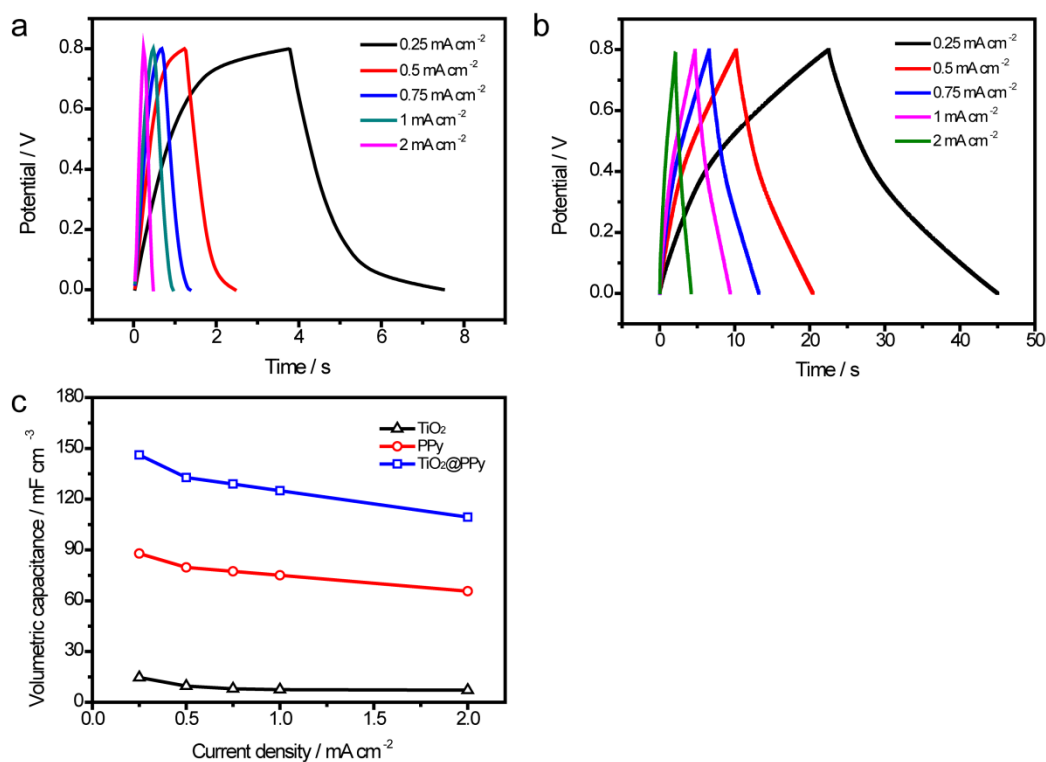


Figure S9. Galvanostatic charge/discharge curves of the TiO₂-SC device (a), and PPy-SC device (b) collected at different current densities. (c) Volumetric capacitance as a function of current density of the TiO₂-SC device, and PPy-SC device.

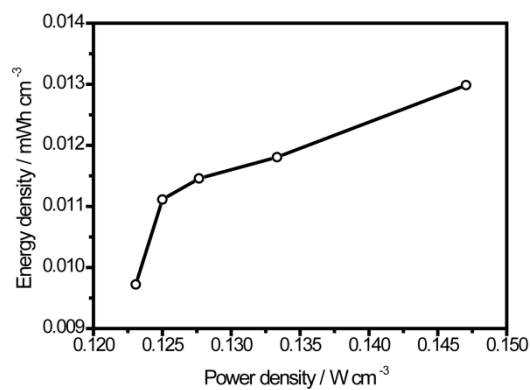


Figure S10. Ragone plots of TiO₂@PPy-SC device.

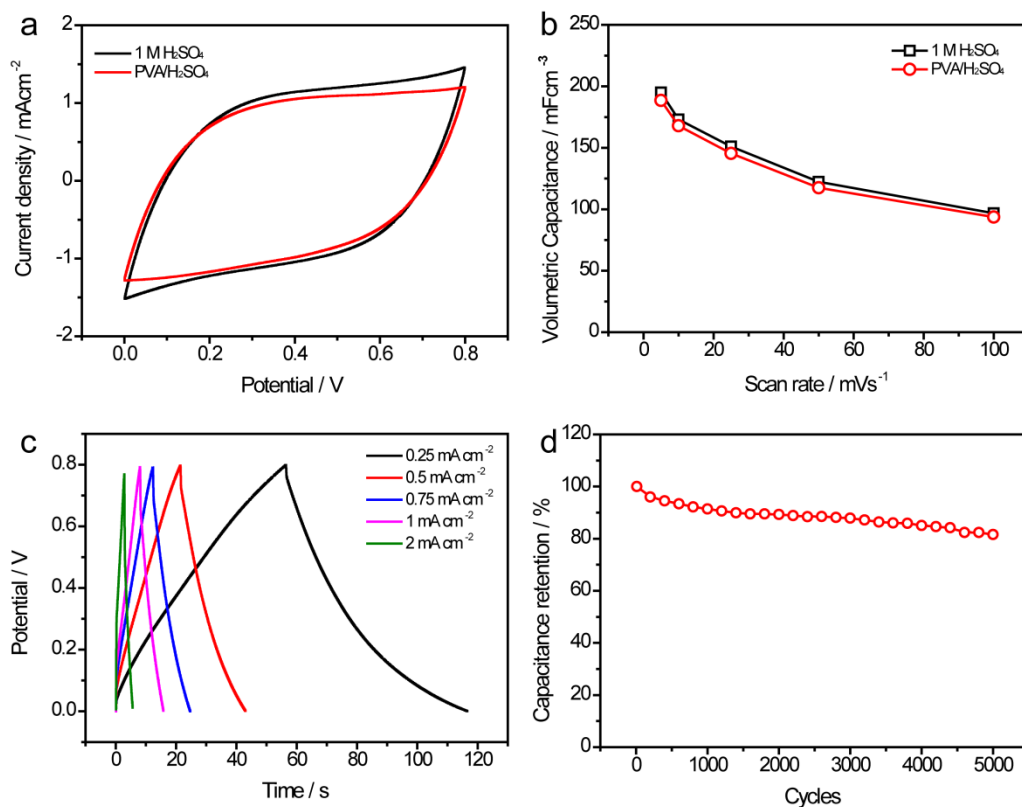


Figure S11. (a) CV curves collected for TiO₂@PPy-SC aqueous device and solid device at the scan rate of 100 mVs⁻¹. (b) Volumetric capacitance of TiO₂@PPy-SC aqueous device and solid device calculated from CV curves as a function of scan rate. (c) Galvanostatic charge/discharge curves of the TiO₂@PPy-SC aqueous device collected at different current densities. (d) Cycling performance of the TiO₂@PPy-SC aqueous device collected at 100 mVs⁻¹.