Supporting Information

TiO$_2$@C core-shell nanowires for high-performance and flexible solid-state supercapacitors

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Experimental Section

Preparation of TiO$_2$@C core-shell nanowires (NWs): H:TiO$_2$@C core-shell NWs were synthesized by a two-step hydrothermal method. TiO$_2$ NWs were firstly grown on carbon fabrics by a seed-assisted hydrothermal method reported elsewhere.[1]. The clean carbon fabrics (CFs) were immersed into 0.2 M titanium(IV) chloride aqueous solution for 10 min and heated on a hotplate in air at 350 °C for 10 min, forming TiO$_2$ nanoparticles on the CFs surface. 15 ml of concentrated hydrochloric acid (37 %) was diluted with 15 ml deionized (DI) water, and mixed with 0.45 ml titanium n-butoxide. This clear solution mixture together with the CFs coated with TiO$_2$ nanoparticles were transferred to a Teflon-lined stainless steel autoclave (40 ml volume). The sealed autoclave was heated in an electric oven at 150 °C for 5 hours,

and then allows it cool down slowly at room temperature. The obtained sample was annealed in air at 550 °C for 1 hour. Then, 25 ml of 0.1 M glucose aqueous solution and CFs coated with TiO_2 NWs were transferred to a Teflon-lined stainless steel autoclave (40 ml volume) at 180 °C for 3 hours. Finally, the sample was annealed in N_2 at 800 °C for 1 hour. A blank carbon fabric was coated under the same conditions (denoted as C@CFs), as a control sample.

Fabrication of solid-state SCs: The device was assembled by two pieces of TiO_2@C NWs electrodes with a separator (Whatman 8 μm filter paper) sandwiched in between and polyvinyl alcohol (PVA)–H_2SO_4 gel as a solid electrolyte. The PVA–H_2SO_4 gel electrolyte wasmade by mixing 3 g H_2SO_4 and 3 g PVA in 30 ml deionized water and thus heat up to 85 °C for 1 h under vigorous stirring. All the electrodes and the separator were immersed into the PVA/ H_2SO_4 solution for 5 min and then were solidified for 6 h at room temperature. Finally ,they were assembled one by one and kept at 45 °C for 12 h to further evaporate the excess water.

Material Characterization and electrochemical measurement: The morphologies, chemical compositions, and the microstructures of the products were characterized by field-emission scanning electron microscope (FE-SEM, JSM-6330F), transmission electron microscopy (TEM, JEM2010-HR, 200 KV), X-ray Photoelectron Spectroscopy (XPS, ESCALab250, Thermo VG) and Raman spectroscopy (Renishaw inVia). Electrochemical measurements were were conducted on an electrochemical workstation (CHI 660D). The electrochemical tests of the individual electrode were performed in a three-electrode cell, in which platinum (Pt) wire and saturated calomel electrode (SEC) electrodes were used as counter and reference electrodes, respectively.

Calculation

Areal capacitances of single electrode calculated from CV curves:

The areal capacitances of electrodes were calculated from the CVs according to the following equation:[2-3]

$$C_a = \frac{Q}{\Delta V \cdot S} \tag{1}$$

where C_a (mF/cm^2) is the areal capacitance, Q (C) is the average charge during the charging and discharging process, ΔV (V) is the potential window and S (cm^2) is the surface area of the working electrode.

Areal capacitances of the device calculated from discharge curves:

The areal capacitances of electrodes measured by galvanostatic charge/discharge method were calculated based on the following equation:[2-3]

$$C_a = \frac{I \times \Delta t}{\Delta V \times V_{sc}} \qquad (2)$$

Where C_a (mF/cm^2) is the areal capacitance, I is the constant discharging current, Δt is the discharging time, ΔV (V) is the potential window, and V_{sc} (cm^3) is the volume of the whole device including electrodes, electrolyte and separator.

[1] G. M. Wang, H. Y. Wang, Y. C. Ling, Y. C. Tang, X. Y. Yang, R. C. Fitzmorris, C. C. Wang, J. Z. Zhang and Y. Li, *Nano Lett*, 2011, **11**, 3026-3033.

[2] S. M. Dong, X. Chen, L. Gu, X. H. Zhou, L. F. Li, Z. H. Liu, P. X. Han, H. X. Xu, J. H. Yao, H. B. Wang, X. Y. Zhang, C. Q. Shang, G. L. Cui, L. Q. Chen, *Energy Environ. Sci.* **2011**, *4*, 3502.

[3] J. Yan, E. Khoo, A. Sumboja, P. S. Lee, *ACS Nano*, **2010**, *4*, 4247.
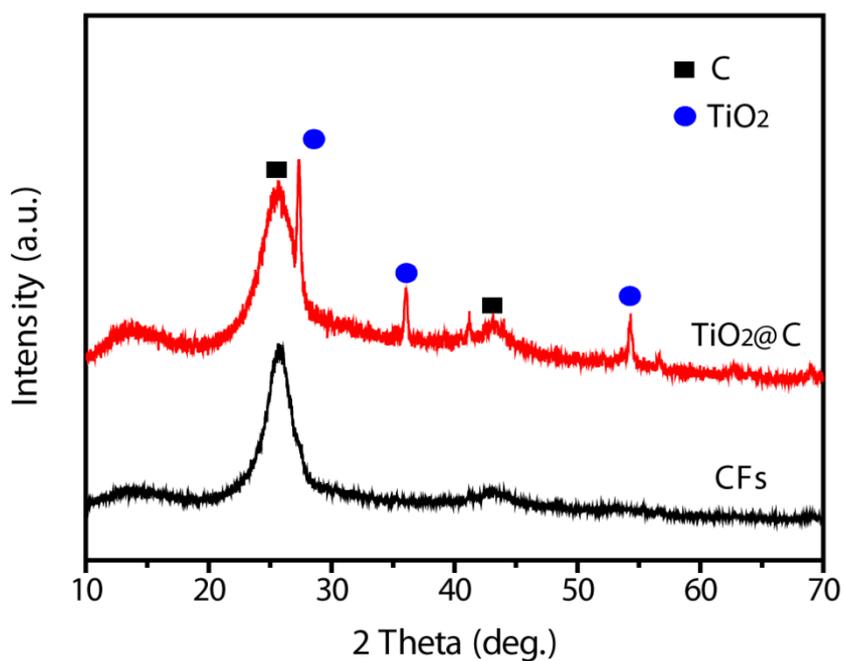
Figure S1. XRD patterns of the pristine CFs and TiO_2@C NWs on CFs.
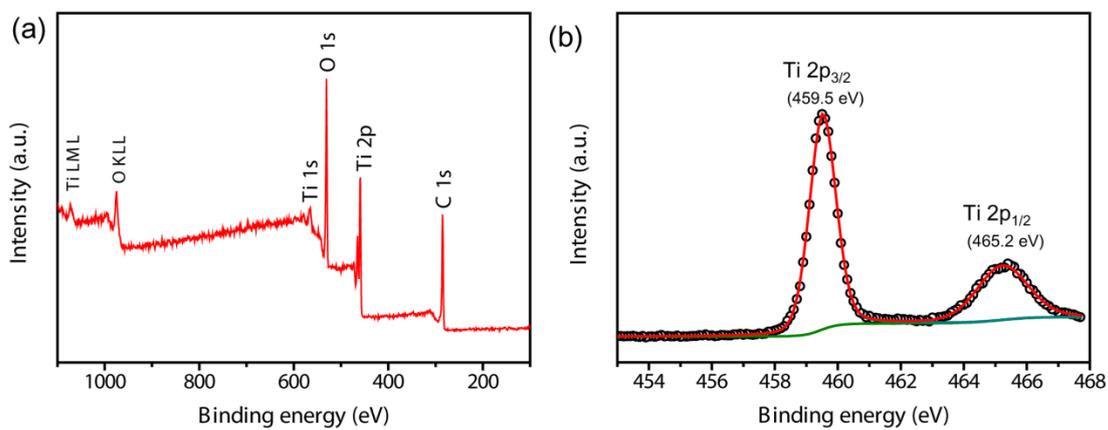
Figure S2. (a) XPS survey and (b) Ti 2p core level XPS spectra of as-prepared TiO_2@C NWs.
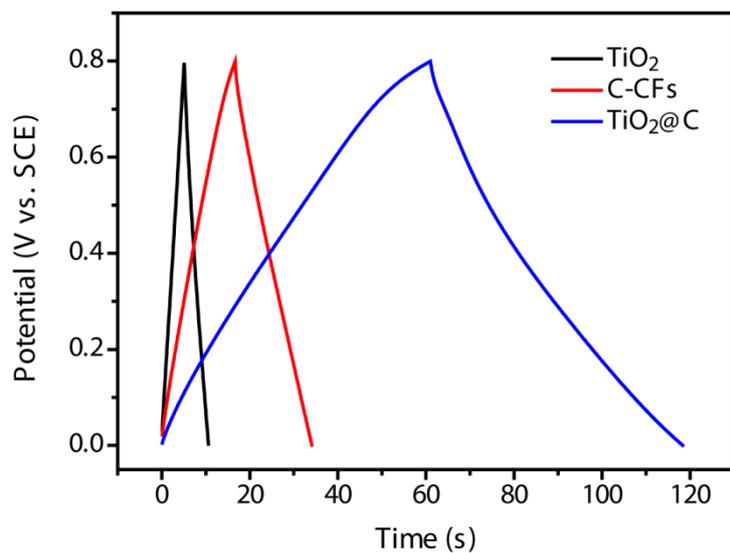
Figure S3. Galvanostatic charge/discharge curves for TiO_2, C-CFs and $TiO_2@C$ samples collected at a current density of 0.5m Acm^{-2}.
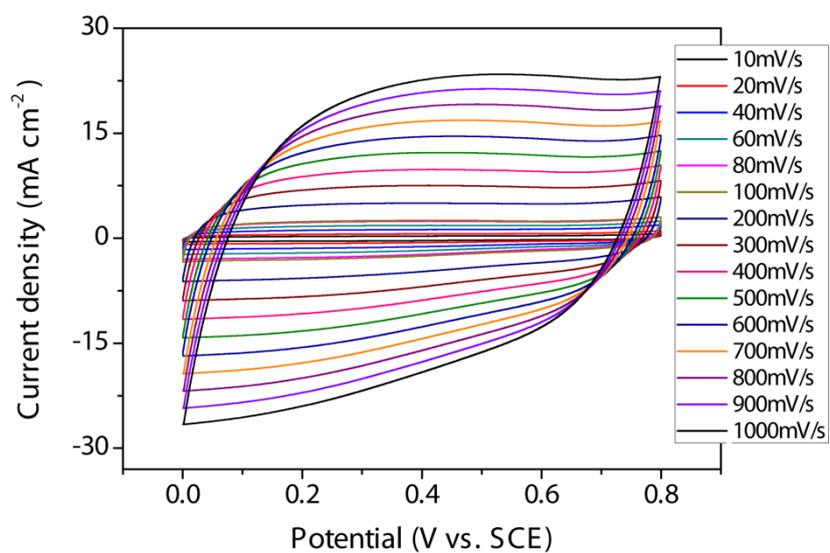
Figure S4. CV curves for $TiO_2@C$ samples collected at different scan rates in 1M H_2SO_4.
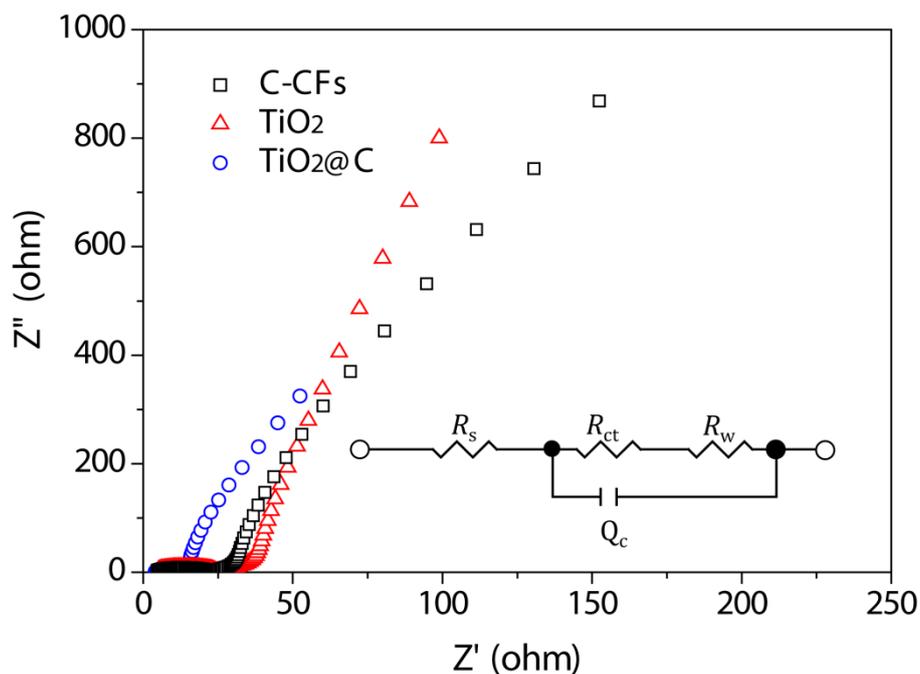
Figure S5. Nyquist plots collected for TiO_2 and $H\text{-}TiO_2$ electrodes in a frequency range between 100 kHz and 0.1 Hz at 0.1 V (vs. 1 M Ag/AgCl) (with a perturbation amplitude of 5 mV). Inset: the equivalent circuit of the $H\text{-}TiO_2$ electrode. Both the spectra display a depressed semicircle in the high frequency region and a straight line in the low-frequency region. The data can be fitted by an equivalent circuit consisting of the bulk solution resistance (R_s), the charge transfer resistance (R_{ct}), the resistance related to the ion diffusion (R_w), and the double-layer capacitance (Q_c).