

## Supporting Information

### High-performance Supercapacitor Electrodes based on hierarchical **Ti@MnO<sub>2</sub> Nanowire Arrays**

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## Experimental details

### *Materials Synthesis:*

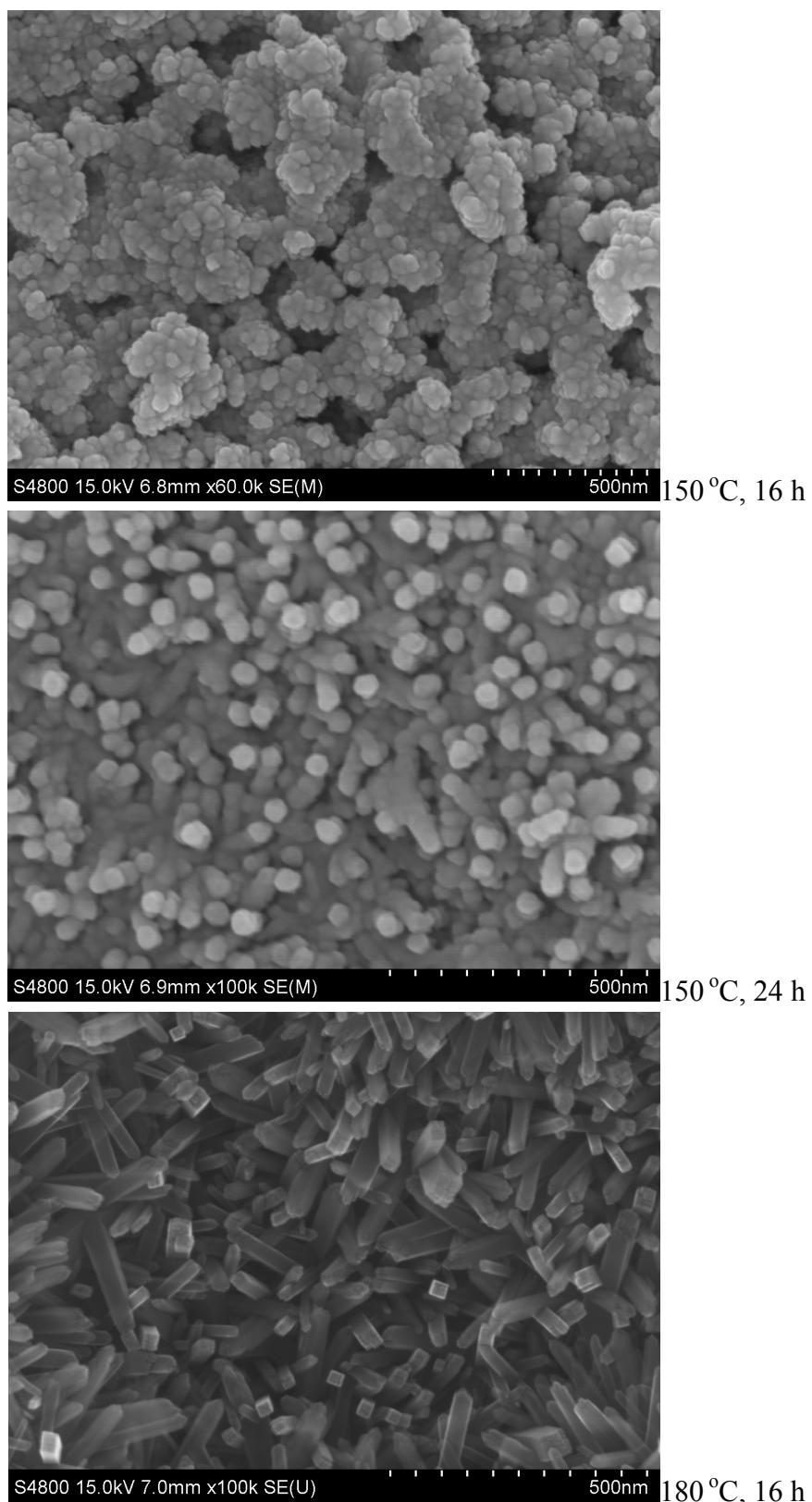
For the fabrication of Ti NAs, Ti foil ( $2\text{cm} \times 2\text{cm}$ ) was washed with ethanol followed by distilled water, then immersed in 18 wt% HCl at  $85^\circ\text{C}$  for 10 min to get rid of the surface oxide layer. The pre-etched Ti foil was immersed into 5 mL of 3 wt% HCl at  $180^\circ\text{C}$  for 16 h in a Teflon vessel to obtain Ti NAs. After cooling down to room temperature, the obtained Ti NAs on Ti foil was washed with deionized water and dried for further use. To synthesize Ti@MnO<sub>2</sub> NAs, the as-prepared Ti NAs were directly used as substrate for the electrodeposition. Briefly, the MnO<sub>2</sub> nanoflakes were electrodeposited by a cyclic voltammetric technique in the potential range between 0.1 and 0.8 V vs. Ag/AgCl at a scan rate of 50 mV/s for 20 cycles in 0.01 M Na<sub>2</sub>SO<sub>4</sub> and Mn(Ac)<sub>2</sub>·4H<sub>2</sub>O solution. After deposition, the obtained Ti@MnO<sub>2</sub> NAs were washed with deionized water and dried at  $80^\circ\text{C}$  in vacuum. For comparison, MnO<sub>2</sub> thin film was directly electrodeposited on Ti foil by the same method. The loading of MnO<sub>2</sub> on the Ti foil and Ti NAs is in the range between 0.2 and 0.3 mg, which was measured by electronic microbalance with a resolution of 0.01 mg.

### *Materials Characterization:*

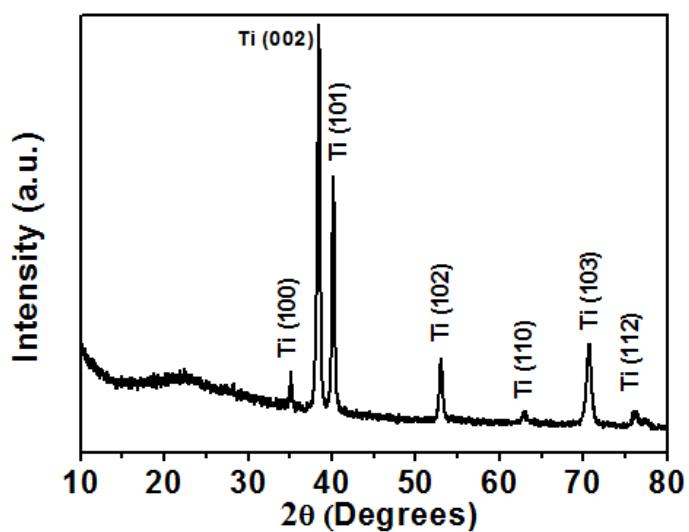
The as-prepared samples were characterized by powder X-ray diffraction (XRD, Bruker D8 advance), field emission scanning electron microscopy (FESEM, Hitachi S-4800 microscope) and transmission electron microscopy (TEM, Tecnai X-TWIN) equipped with an Energy Dispersive Spectroscopy (EDS). A focused ion beam (FIB, DA300) was used for the cross-section TEM specimen preparation.

### *Electrochemical Measurements:*

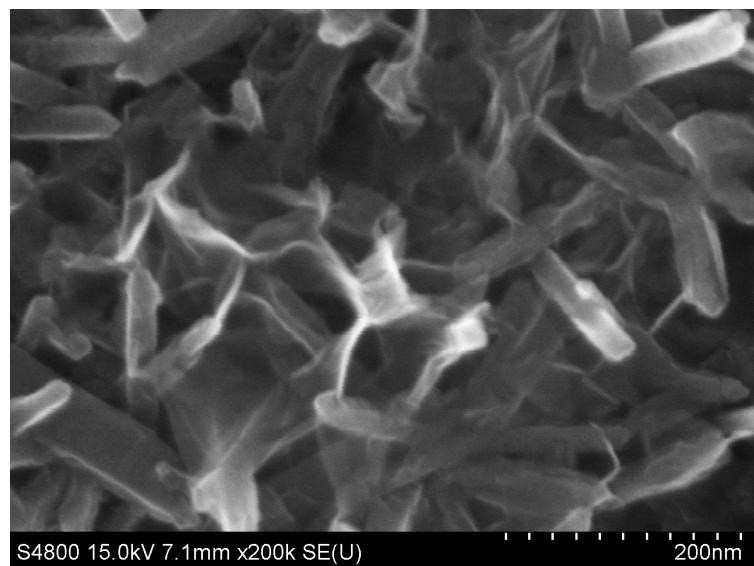
Electrochemical measurements were conducted using CHI 660D electrochemical workstation with a three-electrode cell at room temperature using 1 M Na<sub>2</sub>SO<sub>4</sub> as electrolyte. The as-fabricated samples were directly used as working electrodes; Pt foil and Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. Cyclic voltammetry (CV) measurements were carried out between 0 and 0.9 V at different scan rates of 10, 25, 50, 100 and 200 mV/s, respectively. Galvanostatic charge-discharge (GCD) measurements were conducted at various current densities of 1, 5, 10, 20 A/g, respectively. Electrochemical impedance spectroscopy (EIS) was performed by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 KHz at open circuit potential.



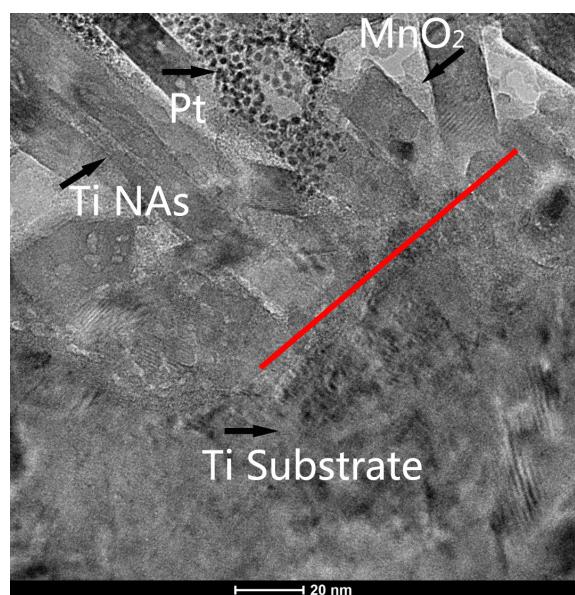
**Fig. S1** FESEM images of the Ti nanowires synthesized at different hydrothermal conditions.



**Fig. S2** XRD Pattern of the  $\text{Ti}@\text{MnO}_2$  NAs.



**Fig. S3** Enlarged SEM image of the  $\text{Ti}@\text{MnO}_2$  NAs.



**Fig. S4** High-magnification TEM image of Ti@MnO<sub>2</sub>/Ti substrate at the interface.