

## Electronic Supplementary Information

# Quantitative investigation on hydrogenation to the performance of MnO<sub>2</sub>/H-TiO<sub>2</sub> composite electrodes for supercapacitor

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## Experimental Section

**Synthesis of TiO<sub>2</sub> NWs.** TiO<sub>2</sub> NWs were firstly grown on the CMF substrate by a seed-assisted hydrothermal method. In brief, the cleaned CMF substrate was immersed into 0.2 M titanium (IV) chloride aqueous solution for 20 min, and then was heated on a hotplate in air at 350 °C for 20 min to form TiO<sub>2</sub> nanoparticles on the surface of CMFs (TiO<sub>2</sub> seeded CMFs). Concentrated hydrochloric acid of 40 mL, which was diluted with deionized (DI) water up to 6 M, was mixed with titanium n-butoxide of 0.6 mL, and then was stirred to clarification to form a precursor solution. Together with the seeded CMFs, the precursor solution was transferred to a 40 mL Teflon-lined stainless steel autoclave. Afterward the sealed autoclave was heated in an electric oven at 150 °C for 5 h. When it cooled down to room temperature, the samples were collected and rinsed with DI water several times, followed by annealing at 550 °C in air for 1 h. As expected, the white TiO<sub>2</sub> NWs were uniformly coated on the surface of CMFs.

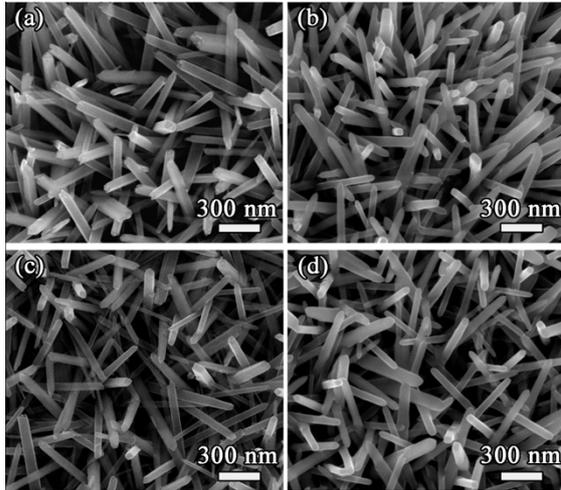


Figure S1. The typical SEM images of (a) TiO<sub>2</sub>/CMF NWs and (b-d) H-TiO<sub>2</sub>/CMF NWs at 400 °C, 600 °C, and 800 °C, respectively.

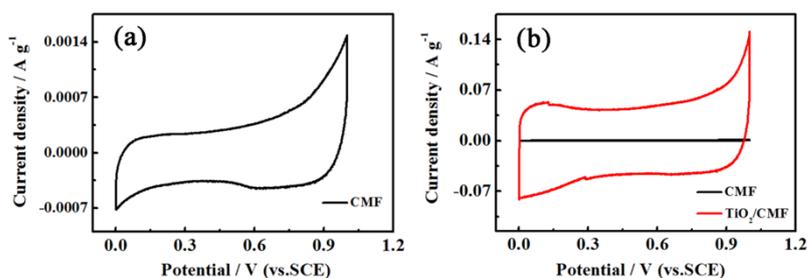


Figure S2. (a) The CV curve of CMF substrate for freestanding electrode at the scan rate of  $10 \text{ mV s}^{-1}$ . (b) The CV curves of CMF electrode and  $\text{TiO}_2/\text{CMF}$  NW electrode at the scan rate of  $10 \text{ mV s}^{-1}$ .

To further clarify the role of CMFs, we studied the electrochemical performance of CMF substrate for freestanding electrode, as shown in Figure S2 (a) and (b). From them, the capacitive current density of CMF electrode is so small that it can be negligible just compared with that of  $\text{TiO}_2/\text{CMF}$  electrode. According to the Eq. (2) in the main paper, the specific capacitance of the CMF electrode is only  $0.08 \text{ F g}^{-1}$ , which is much smaller (about 2%) than that of the  $\text{TiO}_2/\text{CMF}$  electrode. Moreover, due to the dense NWs growing on the surface of CMFs, any area of CMFs in the composite electrode can hardly contact with the solution for storing charge. So the CMF substrate can hardly contribute the capacitance for the whole  $\text{MnO}_2/\text{TiO}_2/\text{CMF}$  NW composite electrode. Therefore the CMF substrate with excellent electrical conductivity only acts as the current collector in the composite electrode.

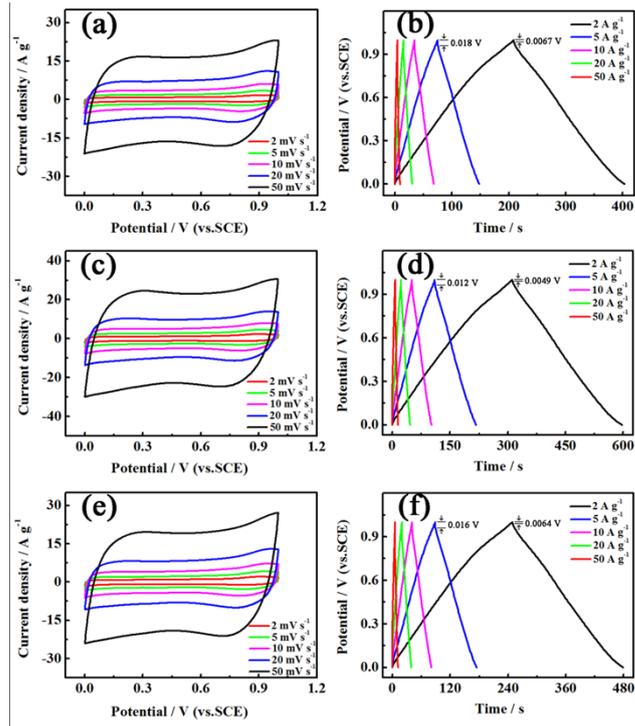


Figure S3. The CV curves of MnO<sub>2</sub>/H-TiO<sub>2</sub>/CMF NW composite electrodes at (a) 400 °C, (c) 600 °C, and (e) 800 °C, respectively. The GCD curves of MnO<sub>2</sub>/H-TiO<sub>2</sub>/CMF NW composite electrodes at (b) 400 °C, (d) 600 °C, and (f) 800 °C, respectively.

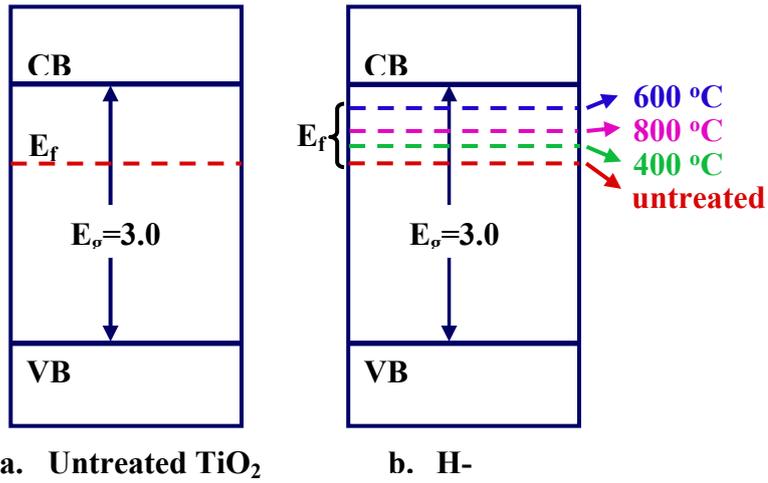


Figure S4. The energy band structure of (a)  $\text{TiO}_2$  and (b) H- $\text{TiO}_2$  at 400 °C, 600 °C, and 800 °C, respectively. ( $E_f$ : Fermi level,  $E_g$ : band gap, CB: conduction band and VB: valence band.)