

Electronic Supplementary Information

Reversible Phase Transformation of MnO₂ Nanosheets in Electrochemical Capacitor Investigated by In-situ Raman Spectroscopy

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Experimental Details:

Fabrication of MnO₂ Nanosheets Electrodes

The CC electrode was prepared by bonding a copper wire onto the edge of approximately 1 x 0.5 cm rectangle of CC. The bonding of Cu-wire was done by using silver paste, cured for 20 minutes at 80°C. The bonding pad was covered with epoxide in order to allow exposure of only the CC surface to the electrochemical deposition solutions. MnO₂ was electrochemically deposited onto this electrode in an electrolyte solution of 0.1 M H₂SO₄ + 0.1 M MnSO₄·5H₂O under galvanostatic condition of 0.5 mA/cm² for 2000 sec, and then rinsed with distilled water. The amount of MnO₂ deposited on the CC electrode was determined from the difference in weight of the electrode before and after electrodeposition, using a microbalance with a measurement accuracy of 10 μg (Sartorius BP 211D, Germany).

Measurement of the Characteristics of MnO₂ Nanosheets Electrodes

The microstructure and morphology of MnO₂ were investigated by means of field-emission scanning electron microscopy (HRSEM, JEOL-6700), X-ray diffraction spectroscopy (Bruker D8 Advance diffractometer), and Raman spectroscopy (LabRAM HR800). The chemical states of the elements were determined by electron spectroscopy (ESCA, Perkin-Elmer model PHI 1600). Electrochemical measurements were conducted using Solartron electrochemical test system (1470E) at ambient temperature. In order to

evaluate the electrochemical capacitance performance of MnO_2 nanosheets, cyclic voltammetry (CV) and galvanostatic charge/discharge method were used, as shown in Figure S1. All electrochemical measurements were carried out in 0.1M Na_2SO_4 aqueous solution as electrolyte, using a conventional three-electrode system consisting of the MnO_2 nanosheets electrode as the working electrode, square platinum sheet as the auxiliary electrode, and an Ag/AgCl reference electrode in 3 M KCl solution. All potentials reported in this article are with respect to that of Ag/AgCl (3 M KCl, 0.207 V vs. SHE) reference electrode.

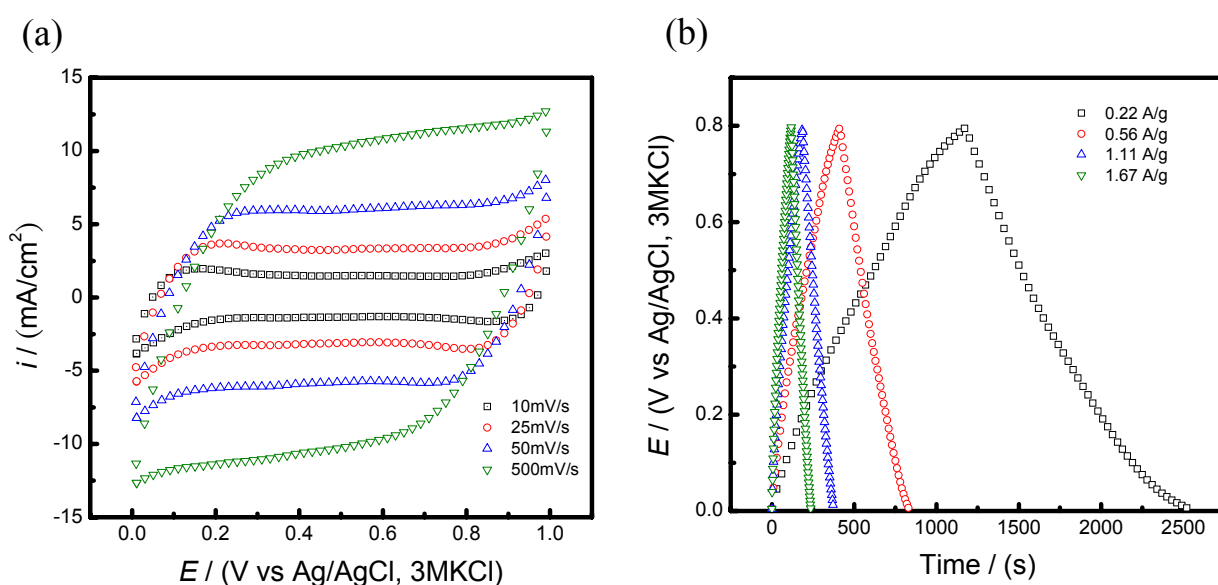


Figure S1. (a) Cyclic voltammograms of MnO_2 nanosheets hybrid electrodes at different scan rate from 10 to 100 mV/s; (b) Charge-discharge curves of MnO_2 nanosheets hybrid electrodes at different current density of 0.22 to 1.67 A/g.

X-ray Diffraction Pattern of As-grown MnO₂ Nanosheet

Figure S2 showed the X-ray diffraction pattern of MnO₂ nanosheet. It can be seen that the XRD patterns of neither of the hybrid electrodes with different deposition periods display any visible diffraction peaks corresponding to MnO₂, all of the strong diffraction peaks are associated with graphite. This indicates an amorphous nature of MnO₂ in these composites.

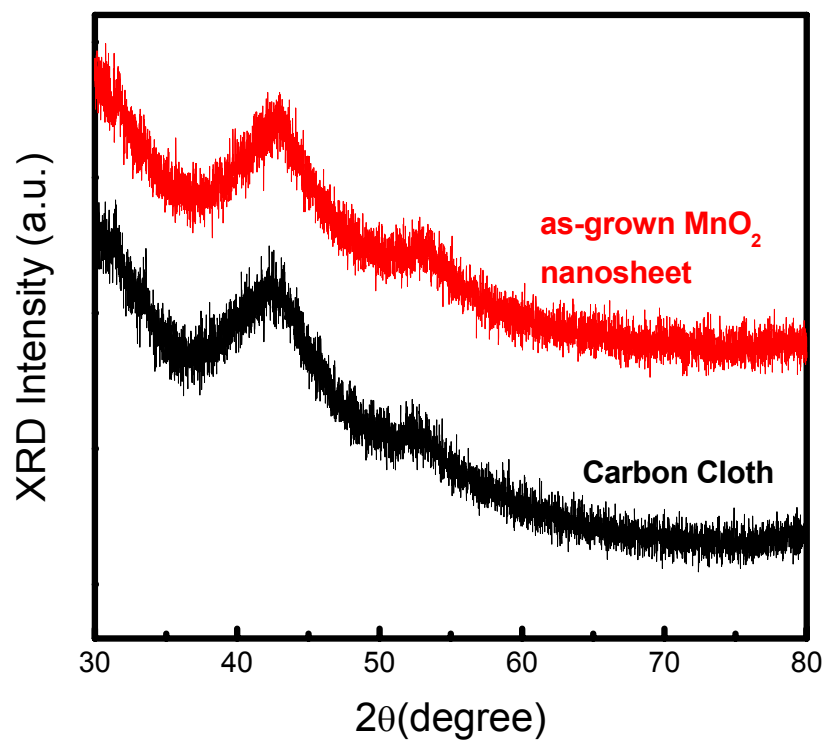


Figure S2. X-ray diffraction pattern of as-grown MnO₂ nanosheet.

In-situ Raman Spectra of MnO₂ Nanosheets

Figure S3 showed a series of Raman spectra of MnO₂ nanosheets electrode under a sequence of applied potential. Three major bands at 480-510, 570-580 and 625-650 cm⁻¹ can be identified, which exhibit reversible transformation in vibration bands during the potential sweep.

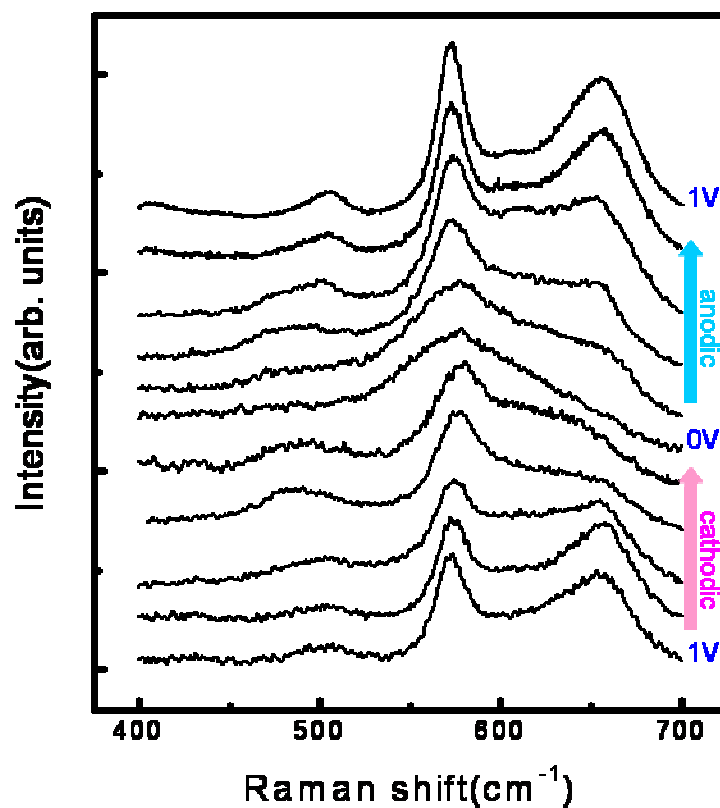


Figure S3. Eleven serial Raman spectra of MnO₂ nanosheets under various applied potentials.

Warburg Impedance

The Warburg impedance Z_W is associated with the cation diffusion in the electrode. Typically, Z_W is given as

$$Z_W = R_W \frac{\coth \sqrt{i\omega/\omega_0}}{\sqrt{i\omega/\omega_0}}$$

where R_W is the diffusion resistance (the Warburg resistance), ω is the angular frequency and ω_0 is the reciprocal of the diffusion time constant τ_d for finite diffusion. This relation between R_W and Z_W has been specified in the electronic supplementary information.