Electronic Supplementary Information (ESI)

Sponge-like $NiCo_2O_4/MnO_2$ ultrathin nanoflakes for supercapacitor with high-rate performance and ultra-long cycle life

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Experimental

1. Synthesis of sponge-like $NiCo_2O_4/MnO_2$ ultrathin nanoflakes

All chemicals used in the experiment were analytical grade. Graphite papers acted as current collector were first cut into a size of 10 mm × 40 mm, then pretreated with acetone and deionized water, each for 5 min sonicleaning, to ensure its surface was well cleaned. Then the graphite paper with a part left as working electrode for electrodeposition was put in a homogeneous solution containing 7 ml 0.05 M $Co(NO_3)_2$, 7 ml 0.05 M $Ni(NO_3)_2$, 7 ml 0.05 M $Mn(NO_3)_2$ and 1 ml dimethylsulfoxide. The electrodeposition was performed in a glass cell consisting of the clean graphite paper working electrode, a graphite counter electrode and Ag/AgCl reference electrode at room temperature. The electrodeposition potential was set at -1.0 V (vs. Ag/AgCl) with an Autolab electrochemical workstation (PGSTAT302N). After electrodeposition, the graphite paper with product was carefully rinsed with deionized water and finally dried in air. Finally, the sample was put in a quartz tube and annealed at 250 °C for 2 h with a ramping rate of 1 °C min^{-1}. In average, after annealing, the loading mass is about 0.55, 0.86, 1.29 mg cm^{-2} for 20, 30, 40 min of electrodeposition, respectively.

2. Characterization

As-prepared products were characterized with a D/Max-2550 PC X-ray diffractometer (XRD; Rigaku, Cu-Kα radiation), a scanning electron microscope (SEM; S-4800), a transmission electron microscope (TEM; JEM-2010F) equipped with an energy dispersive X-ray spectrometer (EDS), and an X-ray photoelectron spectroscopy (XPS; ESCALab250). The mass of the electrode

materials was weighed on an XS analytical balance (Mettler Toledo; δ= 0.01 mg).

3. Electrochemical characterization

Electrochemical measurements were performed on an Autolab Electrochemical Workstation (PGSTAT302N) using a three-electrode mode in 1 M KOH as the electrolyte at room temperature. The graphite paper supported multi-component composite acted directly as the working electrode. A Pt plate and Ag/AgCl were used as the counter electrode and the reference electrode, respectively. All potentials were referred to the reference electrode. The specific capacitance [F g^{-1}] and current density [A g^{-1}] were calculated based on the mass of materials.

The specific capacitance of the electrode is calculated from the CV curves according to the following equation:

$$C = \frac{Q}{\Delta V \cdot m}$$

where C (F/g) is the specific capacitance, m (g) is the mass of the active material on the electrode, Q (C) is an average charge during charge and discharge process, and ΔV (V) is the potential window.

The galvanostatic charge-discharge (CD) capacitance is calculated from the discharge curves using the following equation.

$$C = \frac{I \cdot \Delta t}{\Delta V \cdot m}$$

where I (A), Δt (s), m (g), and ΔV (V) are the discharge current, discharge time consumed in the potential range of ΔV, mass of the active material, and the potential windows, respectively.

The energy density and power density are calculated using the following equations, respectively:

$$E = \frac{1}{2} C \cdot \Delta V^2$$

$$P = \frac{E}{\Delta t}$$

where E (Wh/kg) is the energy density, P (kW/kg) is the power density, C (F/g) is the capacitance, ΔV (V) is the cell potential and Δt (s) is the discharge time consumed in the potential range of ΔV.

Supplementary Figures

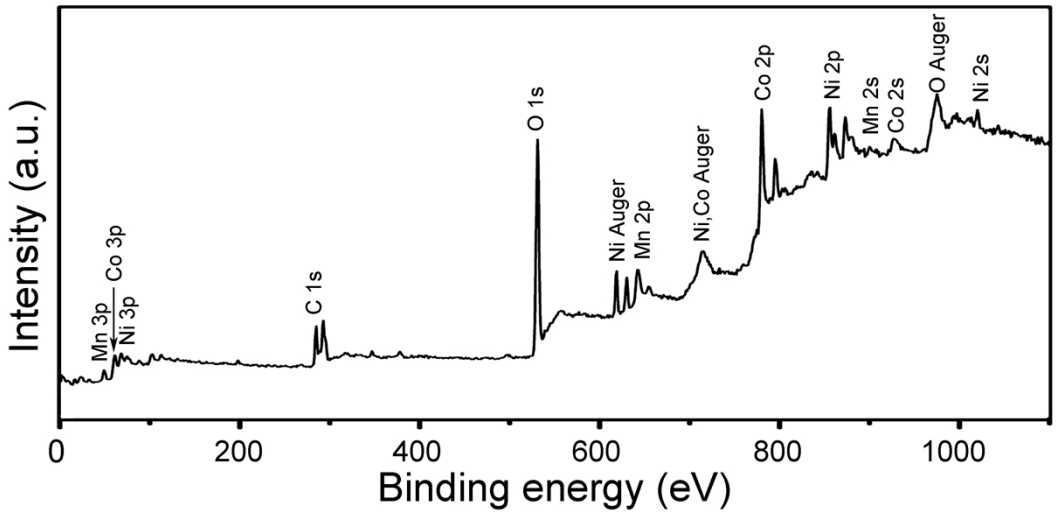

Fig. S1 XPS spectrum of sponge-like ultrathin nanoflakes.

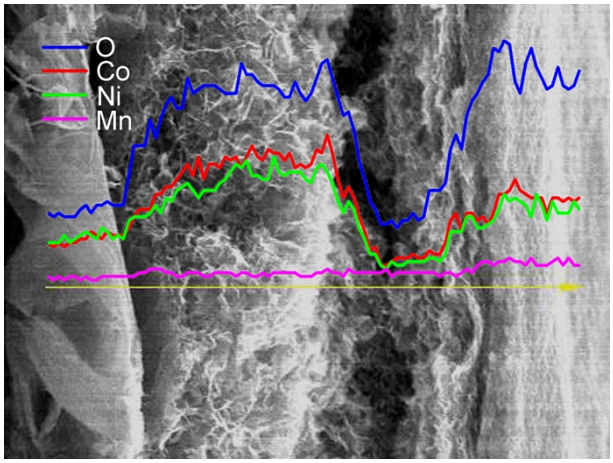

Fig. S2 Line-scanning of sponge-like ultrathin nanoflakes.

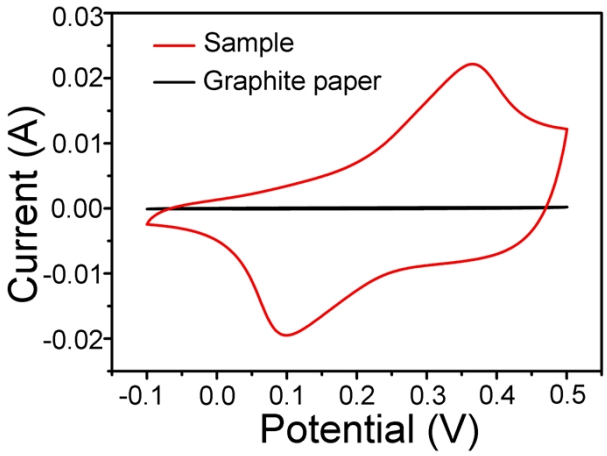

Fig. S3 CV curve of the graphite paper substrate compared with the ultrathin nanoflakes sample at

a scan rate of 20 mV s^{-1}.

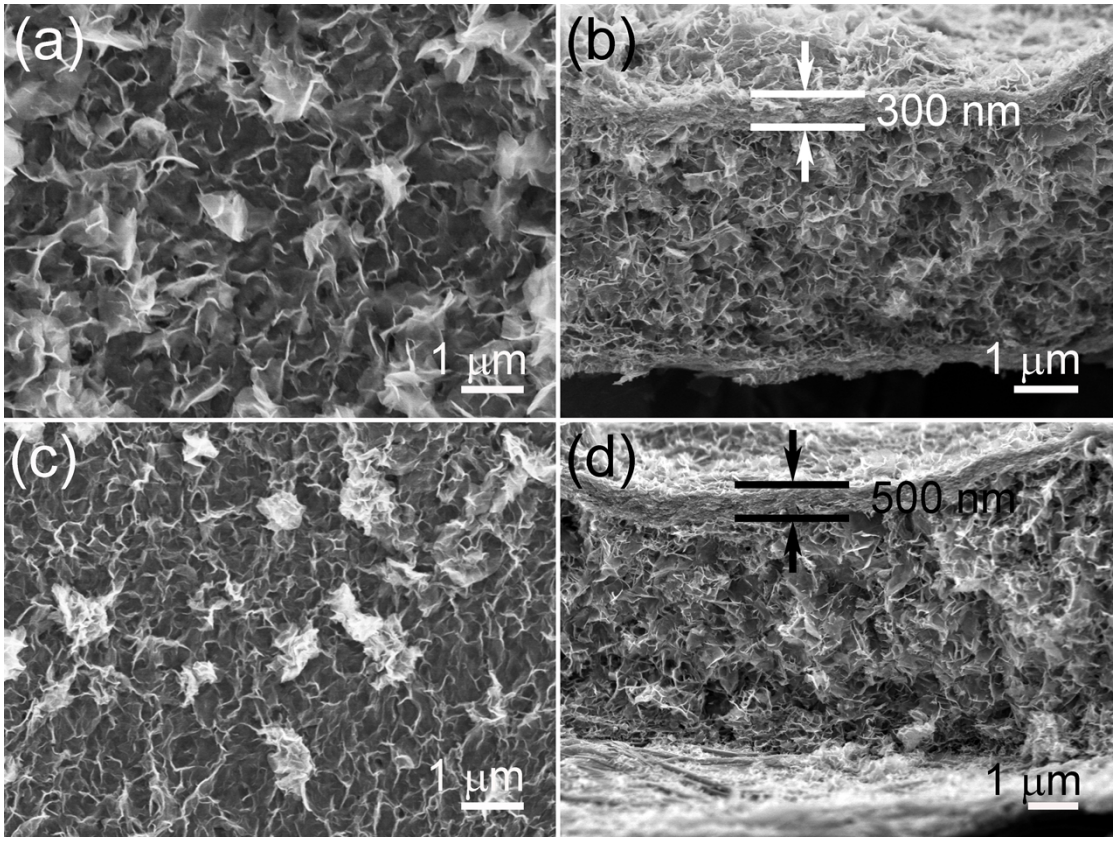

Fig. S4 (a,b) FESEM image of the top view and side view of as-synthesized electrode with 30 min of electrodeposition, respectively. (c,d) FESEM image of the top view and side view of as-synthesized electrode with 40 min electrodeposition, respectively.

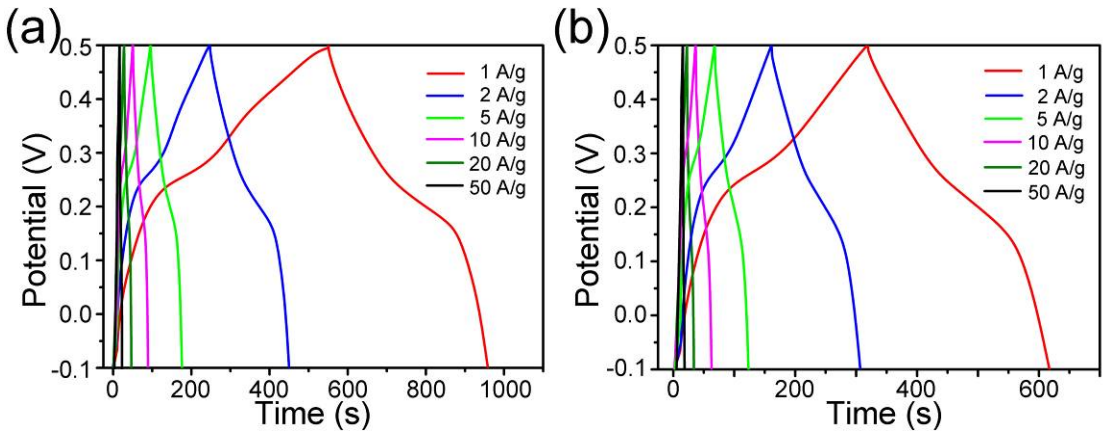

Fig. S5 Galvanostatic charge-discharge curves of the as-synthesized electrode with (a) 30 min and (b) 40 min electrochemical deposition at different current densities.

Table. S1 Specific capacitance values of the P2 and P3 samples.

Current (A g^{-1})	1	2	5	10	20	30	40	50
P2 (F g^{-1})	681	676	668	651	626	600	580	558
P3 (F g^{-1})	496	487	465	438	390	345	306	266

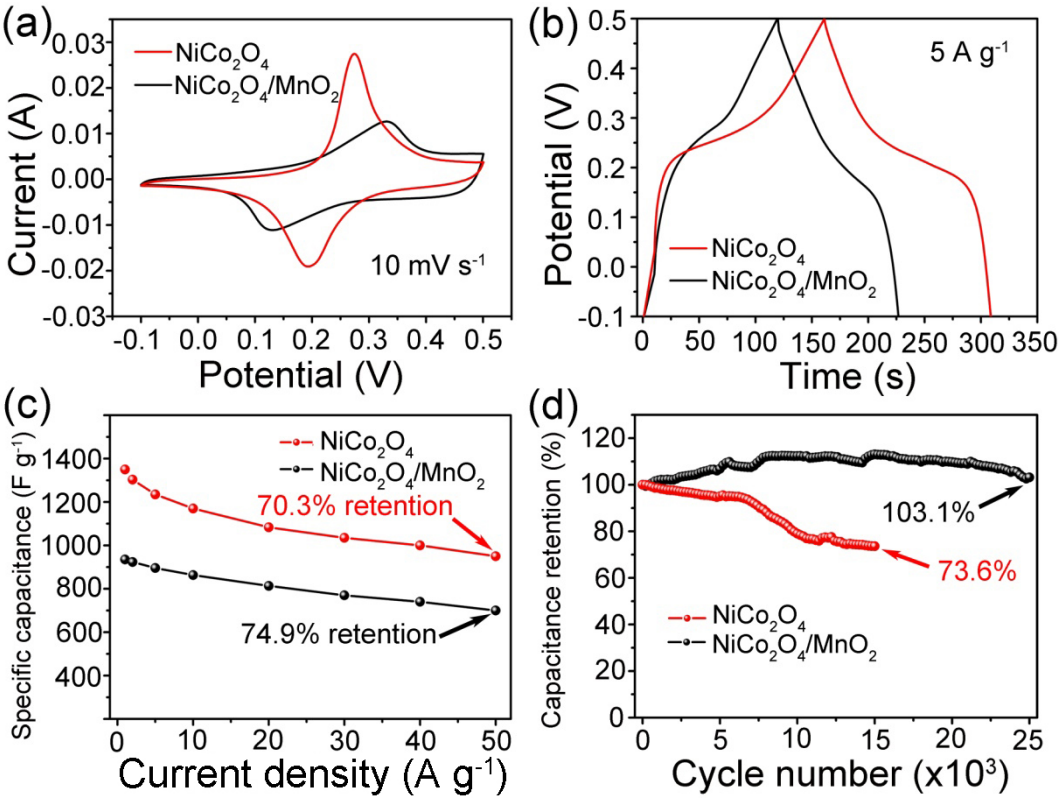

Fig. S6 (a) CV and (b) CD curves of $NiCo_2O_4/MnO_2$ and pure $NiCo_2O_4$. (c) Specific capacitance as a function of the current density of $NiCo_2O_4/MnO_2$ and pure $NiCo_2O_4$. (d) Cycling performance of $NiCo_2O_4/MnO_2$ and pure $NiCo_2O_4$ at a scan rate of 50 mV s^{-1}.