Supplementary Materials for

Hydrothermal growth of MnO_2/RGO/$Ni(OH)_2$ on nickel foam with superior supercapacitor performance

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Experimental details

Synthesis of NF supported MnO_2/RGO/$Ni(OH)_2$ composite: Graphene oxide (GO) was synthesized by a modified Hummer's method [1, 2]. The synthesis of MnO_2/RGO/$Ni(OH)_2$ composite was carried out through a hydrothermal process, by immersing the cleaned Ni foam (NF, Alfa Aesar) in a mixed solution of GO and manganese nitrate hexahydrate ($Mn(NO_3)_2 \cdot 6H_2O$, 98.0 wt%, Sinopharm Chemical Reagent Company). Typically, GO (30 mg) and $Mn(NO_3)_2 \cdot 6H_2O$ (1 m mol) were added to deionized water (50 ml) and dispersed in an ultrasonication bath for 30 min. The NF (1 × 2 cm^2) substrate, with the bare area of 1 × 1 cm^2, was then immersed in this aqueous solution. The substrate and solution were then loaded into a Teflon-lined stainless steel autoclave (100 ml in volume) for hydrothermal reaction at 200 °C for 24 h. The final product was washed with water and ethanol in turn, and then dried in a vacuum oven at 80 °C for 12 h. The MnO_2/RGO/$Ni(OH)_2$/NF composite samples

were denoted as MRNN. MnO_2/$Ni(OH)_2$/NF (MNN) and RGO/$Ni(OH)_2$/NF (RNN) composites were also prepared under the identical conditions, except that there was no GO or $Mn(NO_3)_2 \cdot 6H_2O$ involved.

Characterization: Wide-angle (10°-80°, 40 kV/200 mA) powder X-ray diffraction (XRD) was conducted using an X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm). X-ray photoelectron spectroscopy (XPS) spectra were collected on an ESCALAB 250Xi (Thermo Fisher, U.S.A.) instrument. The morphology and elemental composition of the samples were investigated by field-emission scanning electron microscopy (FESEM, Hitachi S-4800), transmission electron microscopy (TEM, JEOL JEM-2011), and energy dispersive spectroscopy (EDS, Bruker, AXS, Quantax 400-30), respectively.

Electrochemical Measurements: The electrochemical measurements were performed using a standard three-electrode cell in 1 M KOH aqueous solution. All the composite samples with an approximate area of 1 × 1 cm^2 were directly used as working electrodes, while platinum foil (2 × 3 cm^2) and a saturated calomel electrode (SCE) served as the counter and reference electrodes, respectively. Cyclic voltammograms (CV) and galvanostatic charge/discharge measurements were carried out using an electrochemical workstation (CHI660e, Shanghai). The loading of MnO_2/RGO/$Ni(OH)_2$ (weight of active material per unit area of electrode) was determined according to the method reported in a previous work [1]. Typically, after the electrochemical measurements, MnO_2/RGO/$Ni(OH)_2$/NF electrode was treated in de-ionized water and ethanol in a sonication bath for 30 min, respectively. And then it

was subsequently ultra-sonically treated in hydrochloric acid (10 wt%), and it is found that the MnO_2, RGO, and $Ni(OH)_2$ of the composites were well removed from the Ni foam when the irradiation time reached 5 min. Thus, the loading amount of MnO_2/RGO/$Ni(OH)_2$ (weight of active material) was determined by the weight difference (Δm) of the above electrode before testing (m1) and after ultrasonic treatment for 5 min (m2) as follows:

$$\Delta m = m1 - m2 \tag{1}$$

And the specific capacitance C_s can be calculated from the following equation:

$$C_s = \frac{C}{S} = \frac{I * \Delta t}{\Delta V * S} \tag{2}$$

where I (A) is the charge-discharge current; Δt (s) is the discharge time; ΔV (V) is the potential window; and S (cm^2) is the geometric surface area of the MRNN composite electrode.

Supplementary Figures

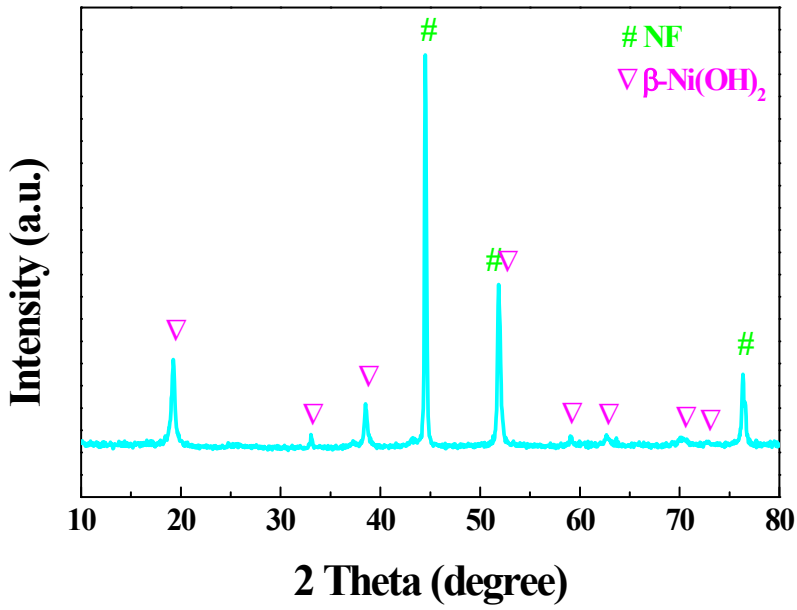

Fig. S1 XRD pattern of RGO/$Ni(OH)_2$/NF (RNN) composite

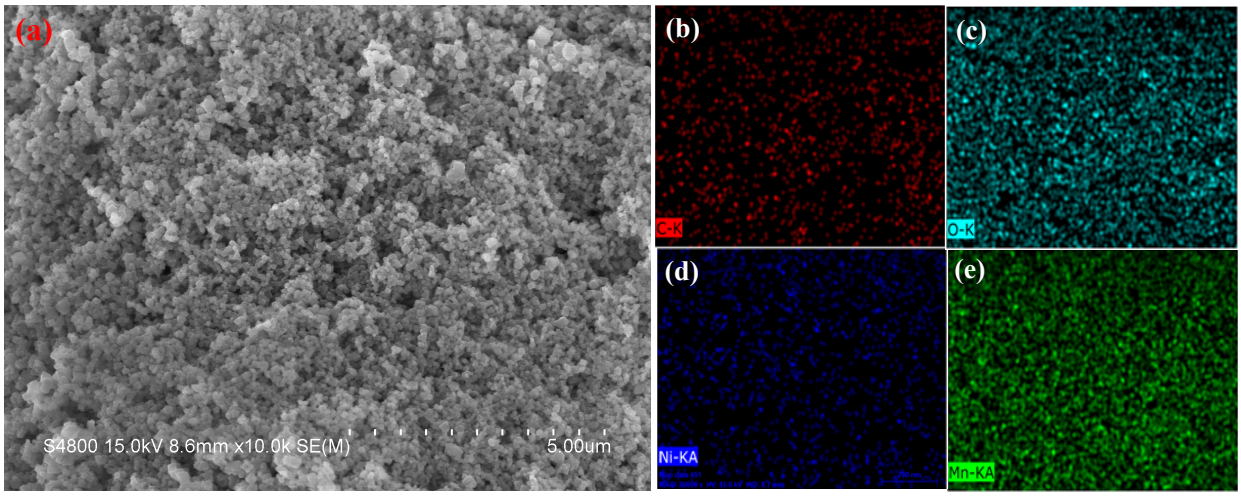

Fig. S2 (a) Top-view FESEM image of MnO_2/RGO/$Ni(OH)_2$/NF. (b-e) Corresponding EDS mapping of the MRNN composite: (b) C element, (c) O element, (d) Ni element, and (e) Mn element.

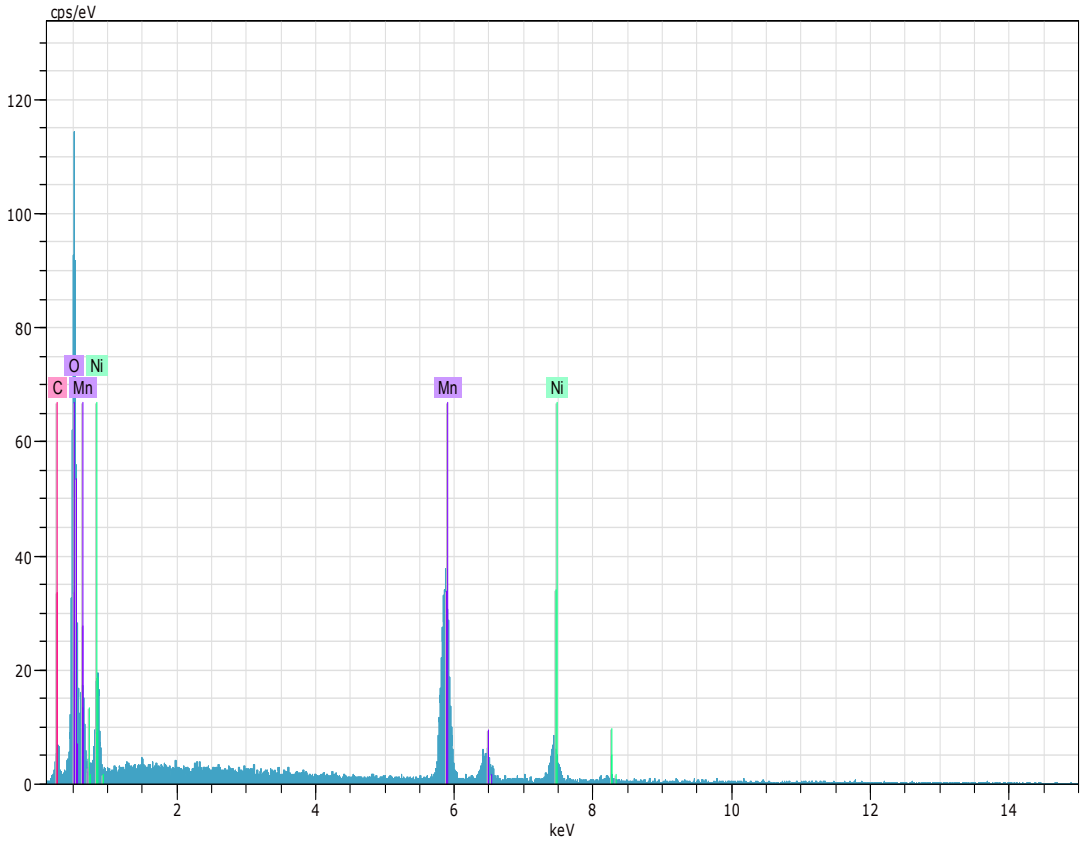

Fig. S3 EDS spectrum of MRNN composite.

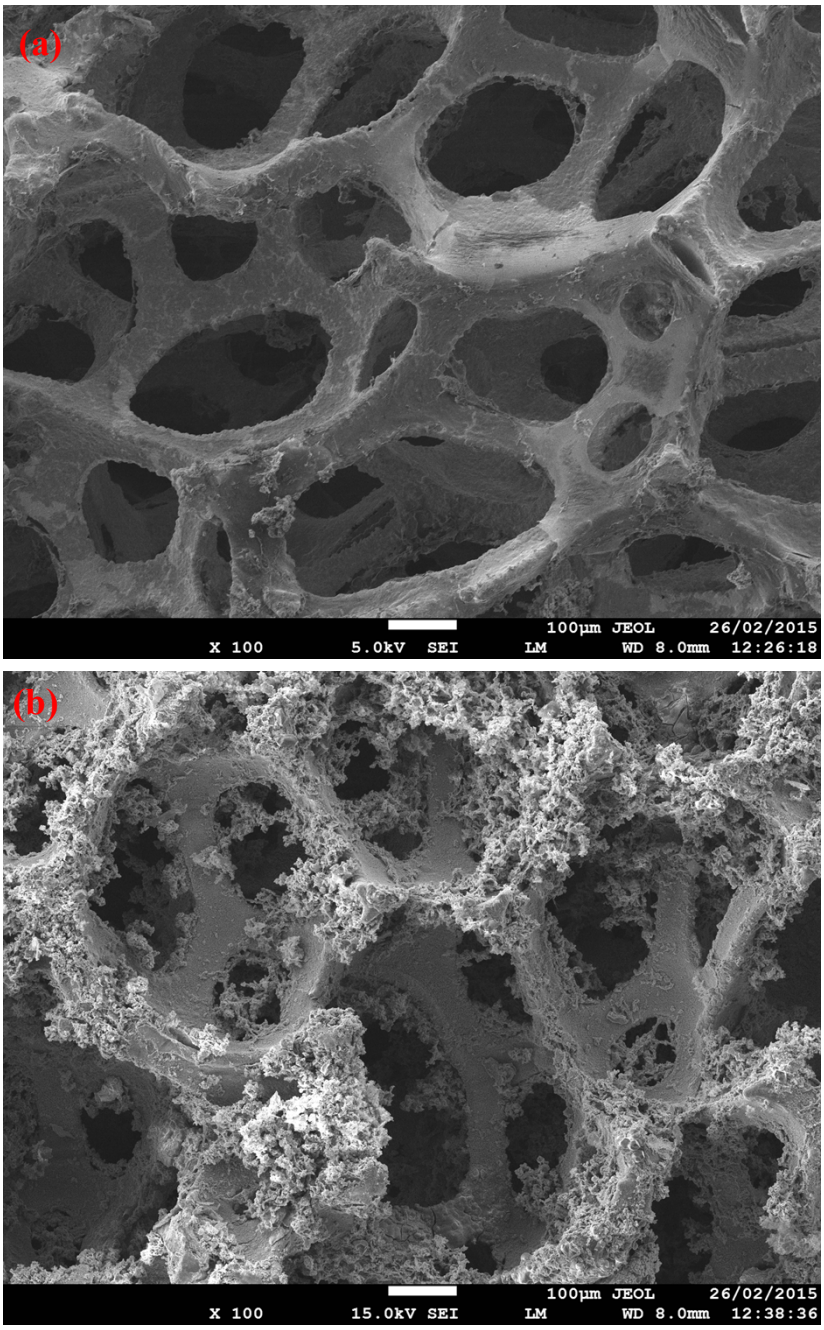

Fig. S4 Low magnification FESEM images of (a) RGO/$Ni(OH)_2$/NF, and (b) MnO_2/RGO/$Ni(OH)_2$/NF.

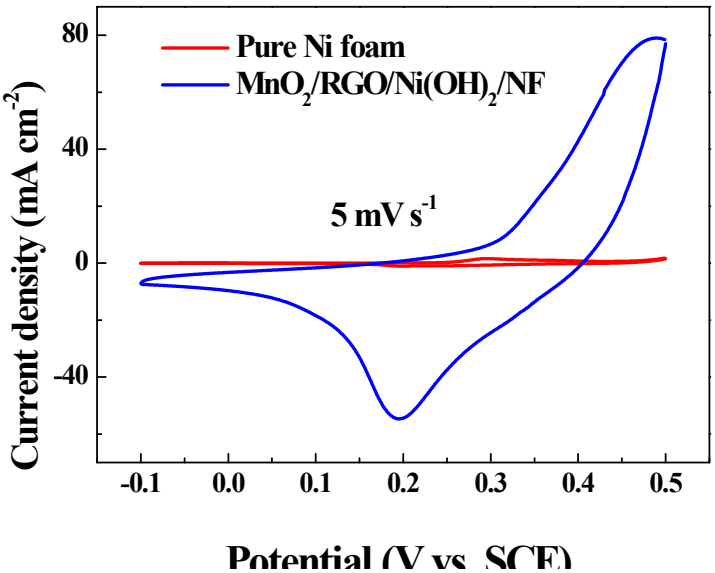

Fig. S5 Cyclic voltammetry (CV) curves of MnO_2/RGO/$Ni(OH)_2$/NF composite and pure nickel foam at a scan rate of 5 mV s^{-1}.

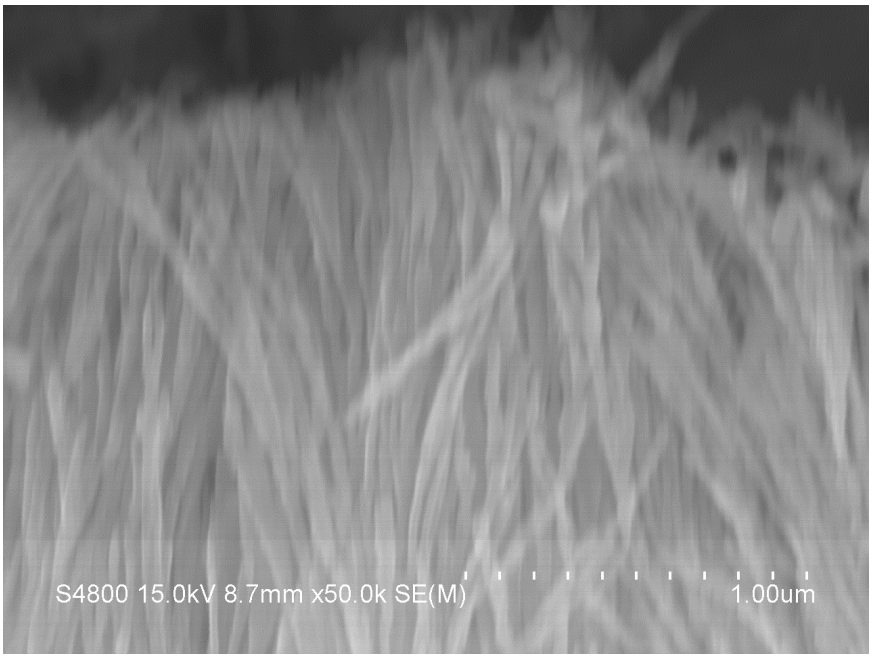

Fig. S6 FESEM image of MnO_2/RGO/$Ni(OH)_2$/NF after charged and discharged for 5000 cycles.

References

[1] S.D. Min, C.J. Zhao, G.R. Chen, X.Z. Qian, Electrochim. Acta 115 (2014) 155-164.
[2] W.S. Hummers, R.E. Offeman, J. Am. Chem. Soc. 80 (1958) 1339-1339.