Supporting Information

A Flexible and Binder-free Reduced Graphene oxide /$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ Composite Electrode for High-performance Sodium Ion Batteries

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S1 Experimental

In a typical procedure, 200mL deionized water containing 2wt% agarose powder ($(C_{12}H_{18}O_9)_n$) was heated to 130 ℃ in oil bath pan to dissolve. For preparing $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ materials, stoichiometric mixtures of $CH_3COONa*2H_2O$, $Mn(CH_3COO)_2*4H_2O$ and $Ni(CH_3COO)_2*4H_2O$ were dissolved in deionized water. Then this aqueous solution was added to agarose aqueous solution slowly under stirring and kept at 130℃ for 10 minutes to form uniform solution. Finally, the mixed solution was cooled down to ambient temperature. When the temperature was below about 35℃, the gel was formed and then dried under 60℃ for 24h. The dried gel was calcined at 800℃ for 8h in air and then cooled to ambient temperature to obtain $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ materials. Reduced graphene oxide (RGO) was produced by the reduction of graphene oxide synthesized by a modified Hummer's method and the details can be found in literature. [1]

Reduced graphene oxide/ $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ composite electrode(GNNM) was prepared via two simple steps. Firstly, 30wt% RGO and 70wt% $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ materials were ultrasonic dispersed in ethanol solution for 1h, then vacuum filtrated to obtain GNNM electrode. The composite electrode was dried at 120℃ for 24h in the vacuum before worked in GNNM electrode- Na cell. The loading of active material ($Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$) was 5-6 mg/cm^2. For preparing GNNM-binder composite electrode, GNNM electrode was dipped into

N-methyl-2-pyrrolidone (NMP) solutions containing 0.03g/ml PVDF for 24h, and then was taken out and dried under 80℃ for 12h to remove NMP. For this GNNM-binder composite electrode, the loading of active material was 5.4 mg/cm^2, and the loading of PVDF was 0.52 mg/cm^2.

The cathodes for $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$-Na cell were prepared by slurrying 70wt% $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ powder, 15wt% super P, and 15wt% PVDF in N-methyl-2-pyrrolidone (NMP), and then casting the mixture onto an aluminum foil. After vacuum drying at 80^{o}C for about 2h, the electrode disks (12 mm) were punched and weighed. The cathode active material loading was 5-6 mg/cm^2. For $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$-Na cell, GNNM electrode-Na cell and GNNM-binder electrode-Na cell, the cathodes were incorporated into coin cells (CR2016) with sodium metal foil and 1.0 M $NaClO_4$/EC+PC (1:1, v/v) electrolyte in an argon filled glove box.

The structural properties of the as-prepared materials were determined by X-ray diffraction (XRD, D/max-2200/PC, Rigaku Co., Ltd.) with filtered Cu Kα radiation. The morphologies of the as-prepared materials were analyzed by scanning electron microscopy (SEM, Sirion 200, FEI COMPANY) and an atomic force microscope (AFM, Nanonavi E-Sweep, SII). X-ray photoelectron spectroscopy (XPS, KRATOS AXIS Ultra-DLD, Kratos Analytical) was obtained with a monochromatic Al Kαradiation source. The galvanostatic charge-discharge tests were conducted using a battery test system (Land CT2001A model, Wuhan Jinnuo Electronics Co., Ltd.). Electrochemical impedance spectroscopy (EIS) was performed using a solartron equipment (SI 1287+ SI 1260, Solartron Analytical Ltd.) within a frequency range of 0.1 Hz-100K Hz at open circuit potential (2.5V). The amplitude of the alternating voltage was 5mV. All electrochemical experiments were carried out at 25℃.

S2 TG results of the GNNM electrode

From the thermogravimetric (TG) analysis, RGO is oxidized with increasing temperature. When the temperature reaches about 450 ℃, only $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ materials is left and accounts for 69.8%. The results are consist with our designs.

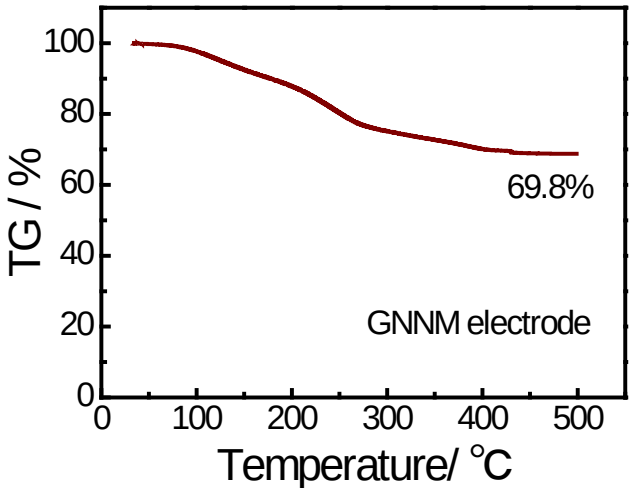

Figure S2. TG curve of GNNM electrode

S3 SEM images of the prepared GNNM electrode

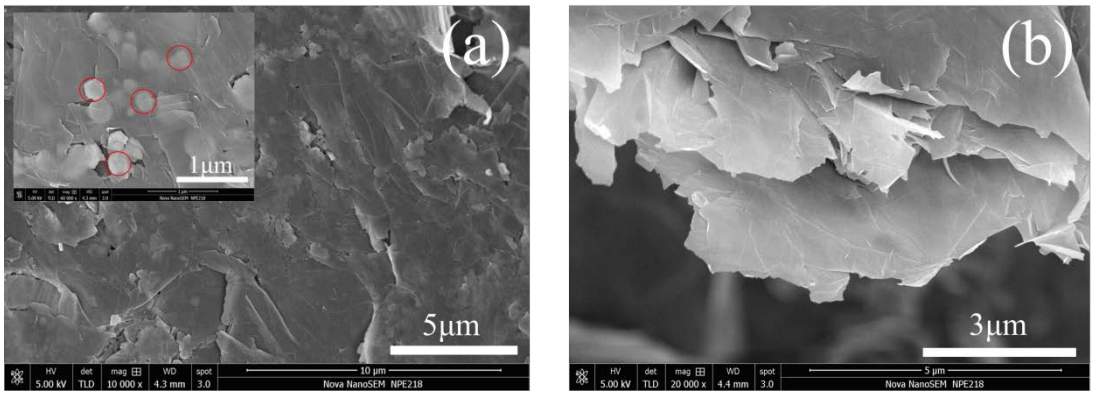

Figure S3. (a) SEM images of the prepared GNNM electrode. The details are shown in the inset image; (b) SEM image for the side view of GNNM electrode.

S4 Stability of the GNNM electrode

After stored in the 1.0 M $NaClO_4$/EC+PC (1:1, v/v) electrolyte one month, it is clear seen that the GNNM electrode is very stable with no charge.

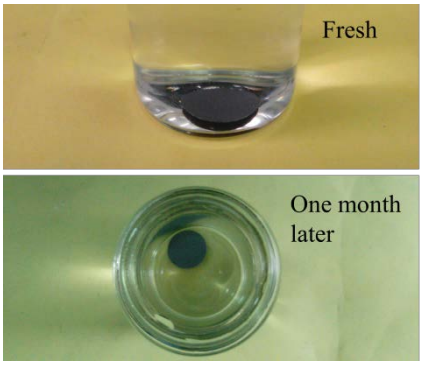

Figure S4. Photos of GNNM electrode for fresh and stored in the 1.0 M $NaClO_4$/EC+PC (1:1, v/v) electrolyte one month.

S5 Electrochemical properties of the GNNM-binder electrode

The figure S5 shows the charge/discharge curves and EIS results of GNNM electrode and GNNM-binder electrode. Compared with GNNM electrode, the addition of PVDF in the GNNM-binder electrode results in a little capacity drop and decreases the electron conductivity. In their EIS spectrums, the Na-ion conductivity is also changed by the addition of PVDF. These maybe due to that the PVDF in the RGO network of GNNM electrode would limit the fast transfer of Na ion and thus change the ion conductivity.

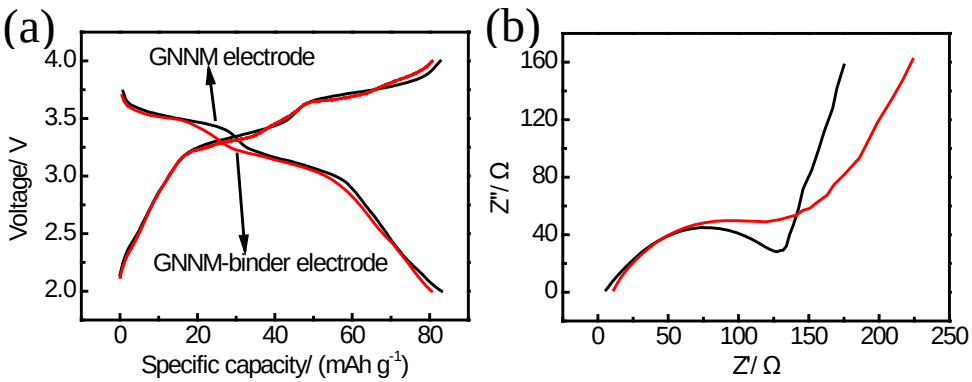

Figure S5. (a) The first galvanostatic charge–discharge profiles of GNNM electrode and GNNM-binder electrode; (b) The Nyquist plots of GNNM electrode and GNNM-binder electrode charged/discharged after 3 cycles.

References:

1. A. P.Yu, I.Roes, A.Davies, Z. W.Chen, *Applied Physics Letters*, 2010, **96**, 253105.