Supporting information for

MnO₂ Nanoflakes Anchored on Reduced Graphene Oxide Nanosheets as A High Performance Anode Material for Lithium-Ion Batteries

The synthesis of graphene oxide (GO)

Graphene oxide (GO) was prepared by the modified Hummers' method. Typically, a mixture of expanded graphite (0.5 g), NaNO₃ (0.5 g), KMnO₄ (3g) was added into H_2SO_4 (98%, 60 mL) and the solution was kept in magnetic stirring for 12 h at room temperature. The obtained sticky green solution was slowly poured into ~ 400 mL deionized water with continuous stirring. Then, 30% H_2O_2 was added into the above solution drop by drop until the color of the solution turned from crimson to orange. The solution was cool down and was then centrifuged and washed with water for three times. The final brown homogeneous gel was GO.



Figure S1. a) The rate performance of the pure rGO. b) Voltage profiles of the rGO at current density vary from 0.1 A/g to 5A/g in the potential range of 0.02 V and 3.0 V (vs. Li/Li^+).



Figure S2. Cyclic voltammetry curves of MnO₂/rGO composite and MnO₂/rGO mixture at a scan rate of 0.02 mV/s in the potential range of 0.01 and 3.0 V (vs. Li/Li⁺).



Figure S3. Voltage profiles of the MnO₂/rGO composite electrode at current densities vary from 0.1 A/g to 5 A/g in the voltage window between 0.01 and 3.0 V. Capaicty is calculated based on the mass of the composite.

XPS results reveal that MnO₂ is the charged product of the MnO₂/rGO composite electrode while MnO is the charged product of MnO₂/rGO mixture electrode. This can also be confirmed by a chemical chromogenic reaction according to the different properties of Mn (2+ oxidation state, MnO) and Mn (4+ oxidation state, MnO₂). In detail, MnO is soluble in H₂SO₄ and will present in the solution in the form of Mn²⁺ while MnO_2 is not soluble and will be in the form of precipitation. Then, Mn^{2+} in the solution can be oxidated to MnO_4^- by $(NH_4)_2S_2O_8$ in the presence of AgNO₃ and the solution color will change from colorless to purple. However, the above chromogenic reaction will not occur for the MnO2 precipitation because MnO2 can not be oxidated by $(NH_4)_2S_2O_8$ in the same consistion. Here, the active materials were scraped-up from the charged MnO₂/rGO composite and MnO₂/rGO mixture electrodes and then dissolved into concentrated sulphuric acid. Subsequently, the obtained solutions were diluted with water and then centrifuged after they were cooled down. Finally, suitable amount of AgNO₃ and (NH₄)₂S₂O₈ were added into the solutions. The detailed phenomenon is displayed in Figure S4 and the result is that Mn²⁺ (MnO) was indeed

detected in the charged MnO_2/rGO mixture electrode while MnO_2 was regenerated in the charged MnO_2/rGO composite electrode, which is consistent with the XPS results.



Figure S4. The procedure and detailed phenomenon of the chromogenic reaction for the identification of MnO and MnO₂.



Figure S5. The rate performance of pure MnO_2 electrode.