Supporting Information for

Carbon Embedded α-MnO_2@Graphene Nanosheet Composite: A Bifunctional Catalyst for High Performance Lithium Oxygen Batteries

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Material Preparation

Graphene oxide (GO) was prepared by the modified Hummers' method. Typically, a mixture of expanded graphite (0.5 g), $NaNO_3$ (0.5 g), $KMnO_4$ (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.

Graphene was synthesized from the thermal reduction of GO, including a preliminary hydrothermal treatment and a subsequent calcinations at 1500℃ under N_2 atmosphere.

α-MnO_2@GN composite was prepared from the redox reaction of graphene and $KMnO_4$ by mass ratio of 1:20 under a water bath of 90 ℃ for 0.5 h.

Material characterization

The crystallographic information was investigated by powder X-ray diffraction (XRD, Philips X'pert Pro Super X-ray diffractometer using Cu Kα radiation with λ=1.5418 Å) at a 2θ range of 10-800. The mass content of rGO in the composite was determined by a Diamond TG/DTA analyzer (Perkin Elmer) under a N_2/O_2 atmosphere at a heating rate of 5 ℃ min^{-1}. The detailed morphologies of the as prepared samples were characterized by field emission scanning electron microscopy (FESEM, HITACHI S-4800), transition electron microscopy (Tecnai, F30). XPS measurements were carried out by using an Omicron photoelectron spectrometer (Al Kα with 1486.6 eV operating at 15 kV, 30 W and 600μm spot size) and an Omicron Sphera II hemispherical electron energy analyzer. The base pressrer of the systems was 1.0×10^{-9} mbar.

Electrochemical testing

The oxygen electrode was prepared by casting the α-MnO_2@GN composite and Kynar2801 (a copolymer based on PVDF) (by mass ratio of 9:1) onto a nickel foam current collector. The mass loading of the O_2 catalyst in the electrode is about 0.8-1 mg and the area of the nickel foam is about 0.785 cm^2. A Swagelok type designed electrochemical cell composed of electrolyte (1M $LiClO_4$ in DMSO), a glass fiber membrane, a metallic lithium anode and the prepared cathode was used to test the electrochemical performance. All parts of the cell were dried in a 80 ℃ vacuum drying oven overnight before they were assembled into the Swagelok type cell in a Argon-filled glove box. Electrochemical performance of the cell was tested under 1 atm O_2 atmosphere at room temperature using a Neware battery test system (Neware Co., Ltd, Shenzhen, China).

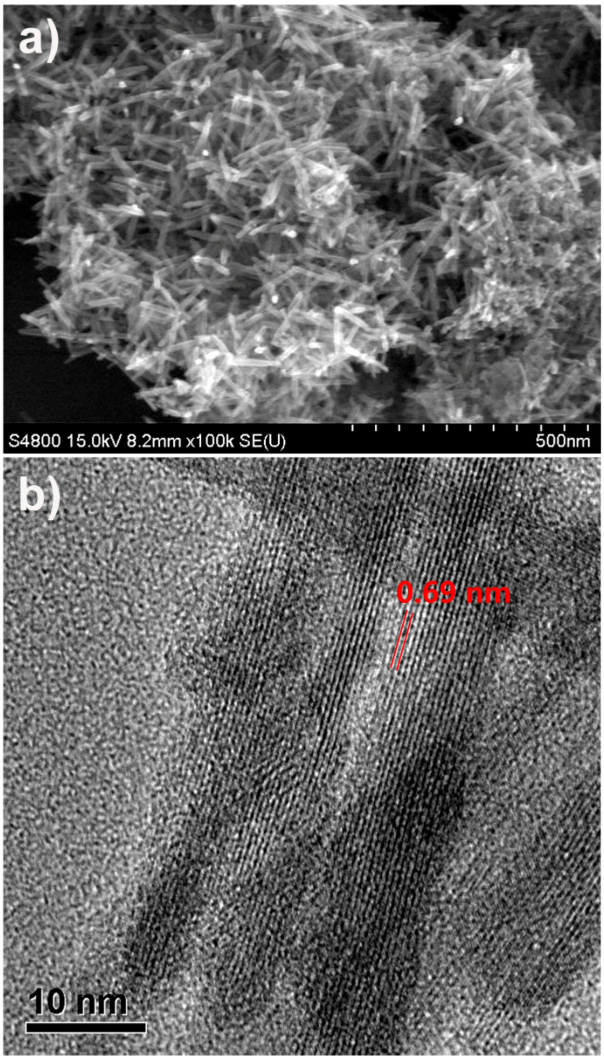

Figure S1. a) An SEM image of the α-MnO_2 nanorods. b) A HRTEM image of the α-MnO_2 nanorod.

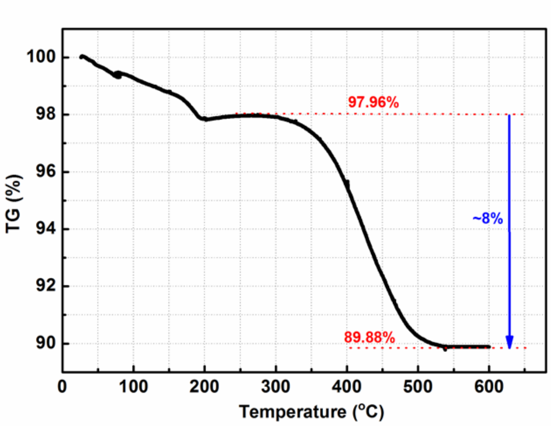

Figure S2. TG curve of the α-MnO_2@GN composite. The weight percentage of the graphene in the α-MnO_2@GN composite is ~ 8%.

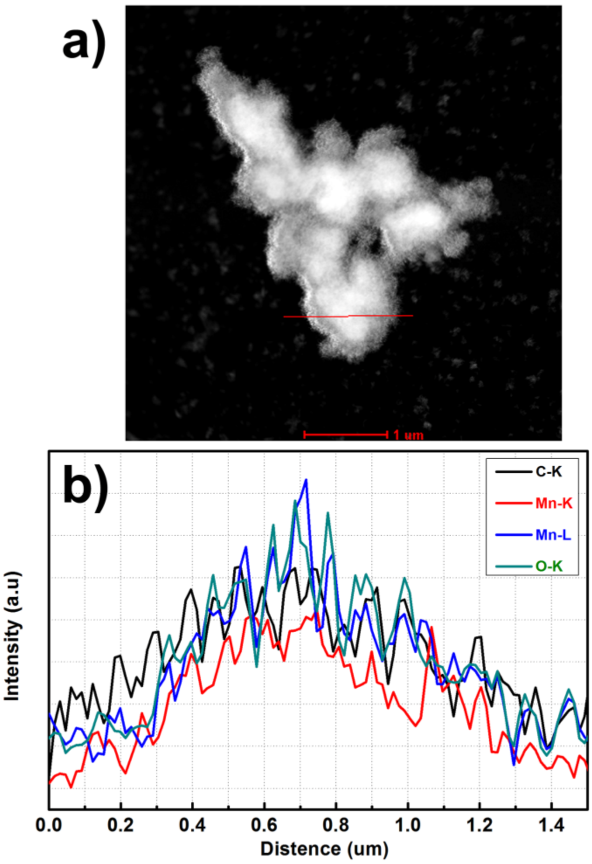

Figure S3 (a) HAADF image of the α-MnO_2@GN composite and (b) the corresponding EDS linear scanning result.

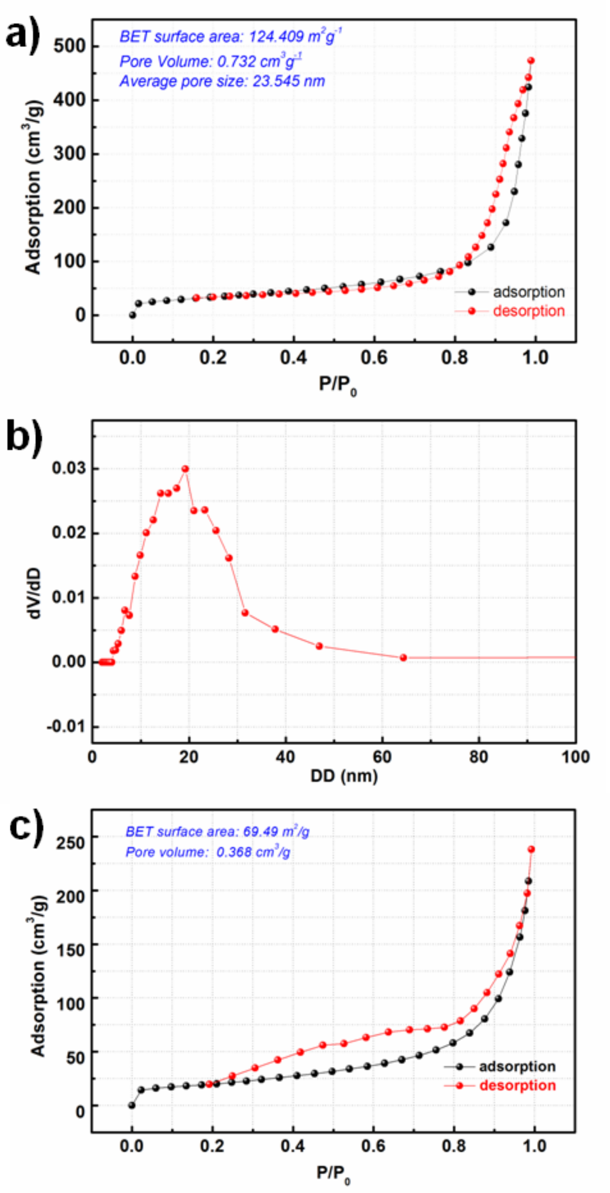

Figure S4. N_2 adsorption-desorption isotherm of a) the α-MnO_2@GN composite, c) α-MnO_2 nanorods. b) The BJH the pore size distribution of the α-MnO_2@GN composite.

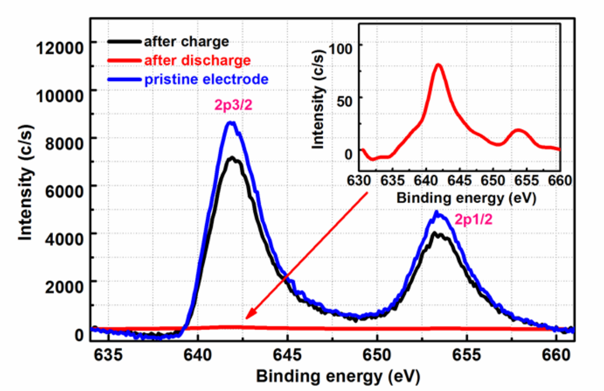

Figure S5. Mn2p XPS spectrums of the pristine discharged and charged α-MnO_2@GN composite electrodes. Inset is the magnified image of the discharged electrode.