# Synthesis of Oxidized Graphene Anchored Porous Manganese Sulfide Nanocrystal via the Nanoscale Kirkendall Effect for supercapacitor

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## 1. Experimental Section

### 1.1 Preparation of GO

Graphene oxide (GO) was obtained by further oxidization treatment to the samples, which were prepared through Hummers' method from graphite powder (500 mesh).[1] Typically, graphite (2.0 g) and $NaNO_3$ (1.0 g) were mixed with 46 mL concentrated $H_2SO_4$ (98% pure) and kept the mixture in an ice bath with continuously stirring. Then 6.0 g $KMnO_4$ was added into the suspension and the suspension was maintained at 35 °C for 2 h under stirring. The obtained suspension was diluted with 92 mL water, and heated to 98 °C for 15 min. After that, the suspension was further diluted with 130 mL water and treated by 3wt. % $H_2O_2$ until the solution turned light yellow. After centrifuging, washing and drying the graphite oxide was collected, and then the GO sample was obtained by ultrasonic exfoliation of the graphite oxide. To get the GO with more surface functional groups, the GO sample was treated by further oxidization as follow. The as-prepared GO sample (10mg) and 50 mg $KMnO_4$ were dissolved in 10 mL distilled water with the aid of ultrasonication, then the suspension was kept at room temperature for 2 h under stirring. 1 mL HCl and 1 mL $H_2O_2$ were added dropwise to remove the manganese oxides residues. The GO was obtained after water-washing and vacuum freeze-drying.

**1.2 Preparation of MnS/GO nanocomposites**

MnS/GO nanocomposites were prepared via a facile hydrothermal reaction. To investigate the effect of $NH_3$ and sulfur-sources on the morphology and electrochemical properties of MnS/GO, two samples were prepared for comparison. **(A)** 50 mg of GO and 50 mL distilled water were mixed thoroughly, then 50 mg $MnCl_2 \cdot 4H_2O$ was added and stirring for 20 min. Next, under vigorous ultrasonic stirring, 0.15 g thiourea was added slowly. After 20 min of stirring, the mixture was put into a 100mL Teflon-lined autoclave to be heated 120 °C for 12 h. The sample, denoted as MnS/GO was obtained by washing and drying in vacuum at 60 °C for 24 h. **(B)** The another sample was obtained by a similar process just added 3 mL 2 M $NH_3 \cdot H_2O$ before adding the thiourea, which was denoted as MnS/GO-$NH_3$.

**1.3 Physicochemical characterizations**

The morphology and microstructure of the obtained samples were investigated using filed emission scanning electron microscopy (FESEM, KYKY-2800B) and transmission electron microscopy (TEM, HT7700). The crystal structures of the electrode materials were characterized using a typical X-ray diffraction (XRD) patterns (Bruker AXS D8 diffractometer with Cu K Rradiation) and high-resolution transmission electron microscopy (HRTEM, JEM 2010 model, JEOL Ltd. Corp., Japan). Fourier transform infrared (FTIR) measurements of the samples were performed on Nicolet 380 FT-IR using KBr method.

**1.4 Fabrication of electrode and electrochemical measurements**

The working electrode was prepared by mixing the as-prepared active materials,

acetylene black and polytetrafluoroethylene (PTFE) with a weight ratio of 70:15:15. After ultrasonic dispersing for 20min, the slurry was coated onto a nickel foam current collector and dried in vacuum at 80 °C for 12 h. Finally, the working electrode was obtained by pressing the active material coated nickel foam at 10 MPa for 1 min. The electrochemical tests including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS, 0.1 Hz-100 KHz) were performed on CHI 660A workstation, galvanostatic charge-discharge (GC) tests on Land CT 2001A. All the measurements were carried out in 2.0 M KOH electrolyte with a conventional three-electrode system where Hg/HgO electrode and Pt foil ($1 \times 1$ cm$^2$) were used as reference electrode and counter electrode, respectively.

Asymmetric supercapacitors were assembled to evaluate the practical applications of GO anchored MnS electrode materials. The KB 600 active carbon treated by $HNO_3$ and the as-prepared active materials were used as negative and positive materials, respectively. The obtained asymmetric supercapacitors were referred as MnS/GO(2.07mg)-AC(2.65mg), MnS/GO-NH$_3$ (3.26mg)-AC (3.38mg), respectively. The electrolyte used in the tests was 2M KOH solution.

The specific capacitances (**Figure 2c** and **4c**) calculated by their CV curves via **Equation S1**, where $C$ (F g$^{-1}$), ($V$-$V_0$), $I(V)$ , $m$ (g) , and $v$ (v s$^{-1}$) are the specific capacitance, potential window, current density, mass of active material, and potential scan rate, respectively.

$$C = \frac{\int_{V_0}^{V} I(V)dV}{mv(V - V_0)} \qquad (S1)$$

The specific capacitance (**Figure 3c**) calculated by the charge-discharge curves via
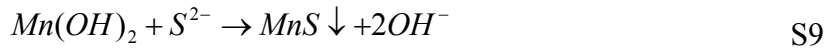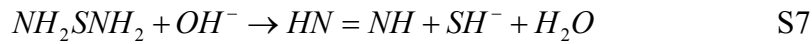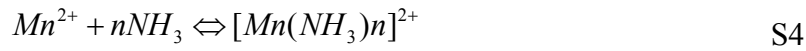
the equation given by **Equation S2**:

$$C_s = \frac{I \cdot \Delta t}{\Delta V \cdot m}$$
(S2)

where $C_s$ (F g$^{-1}$), $I$ (A), $\Delta t$ (s), $\Delta V$ (V) and m (g) represent the specific capacitance, discharge current, discharge time, potential range of discharge and the mass of active material, respectively.

The Coulombic efficiency (**Figure S4b**) calculated via the equation given by **Equation S3**, where C$_{sc}$ and C$_{sd}$ were the specific capacitance of charge and discharge process, respectively.

$$CE = \frac{C_{sd}}{C_{sc}} \times 100\%$$
(S3)

## 2. Supplementary Equations

$$Mn^{2+} + nNH_3 \Leftrightarrow [Mn(NH_3)n]^{2+}$$
S4

$$NH_3 + H_2O \Leftrightarrow NH^{4+} + OH^{-}$$
S5

$$Mn^{2+} + 2OH^{-} \Leftrightarrow Mn(OH)_2 \downarrow$$
S6

$$NH_2SNH_2 + OH^{-} \rightarrow HN = NH + SH^{-} + H_2O$$
S7

$$SH^{-} + OH^{-} \rightarrow S^{2-} + H_2O$$
S8

$$Mn(OH)_2 + S^{2-} \rightarrow MnS \downarrow + 2OH^{-}$$
S9
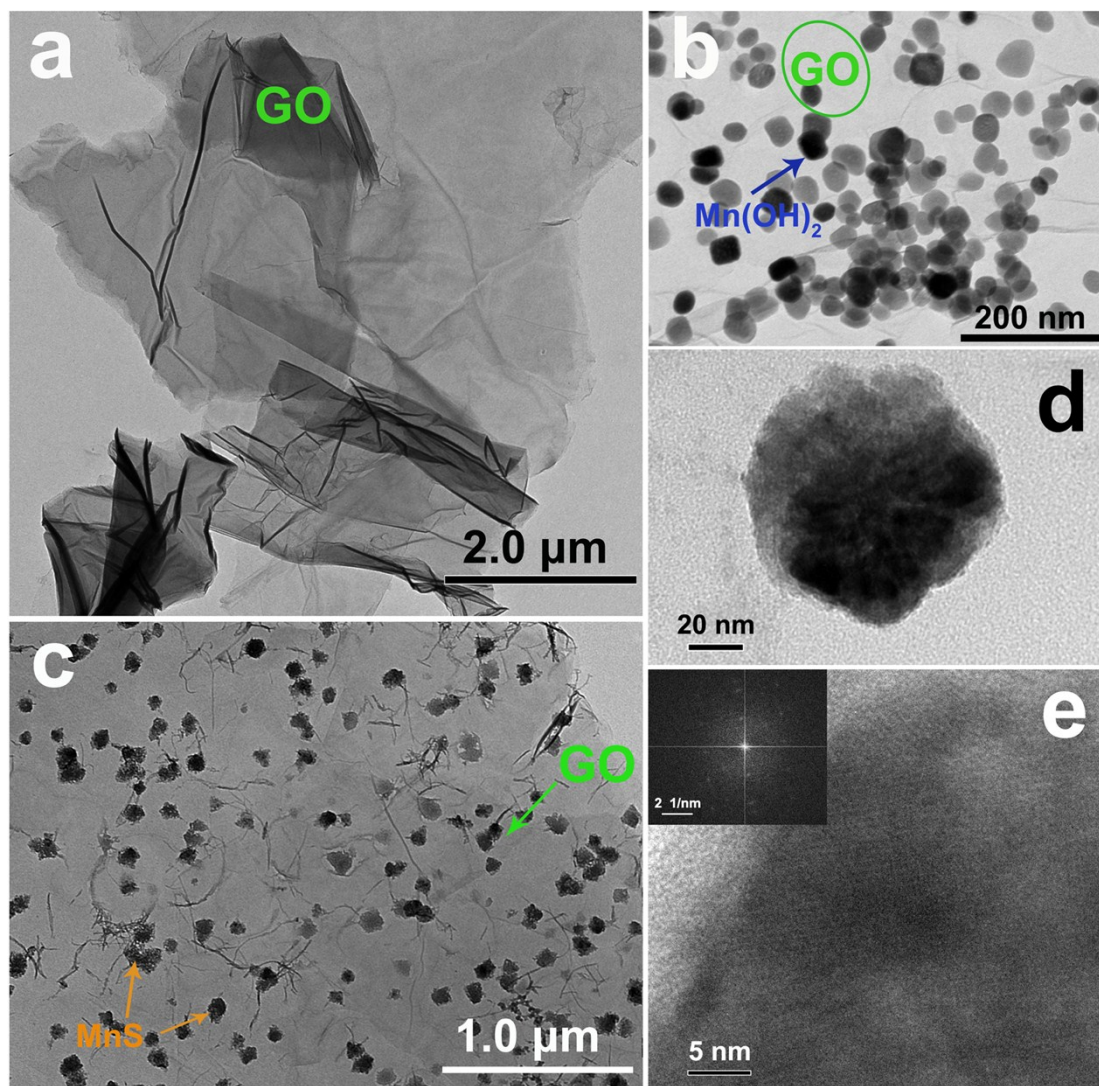
## 3. Supplementary Figures



**Figure. S1**. TEM images of (a) pure GO sheets, (b) Mn(OH)$_2$/GO and (c) MnS/GO; (d) high magnified TEM image and (e) HRTEM image of MnS/GO.
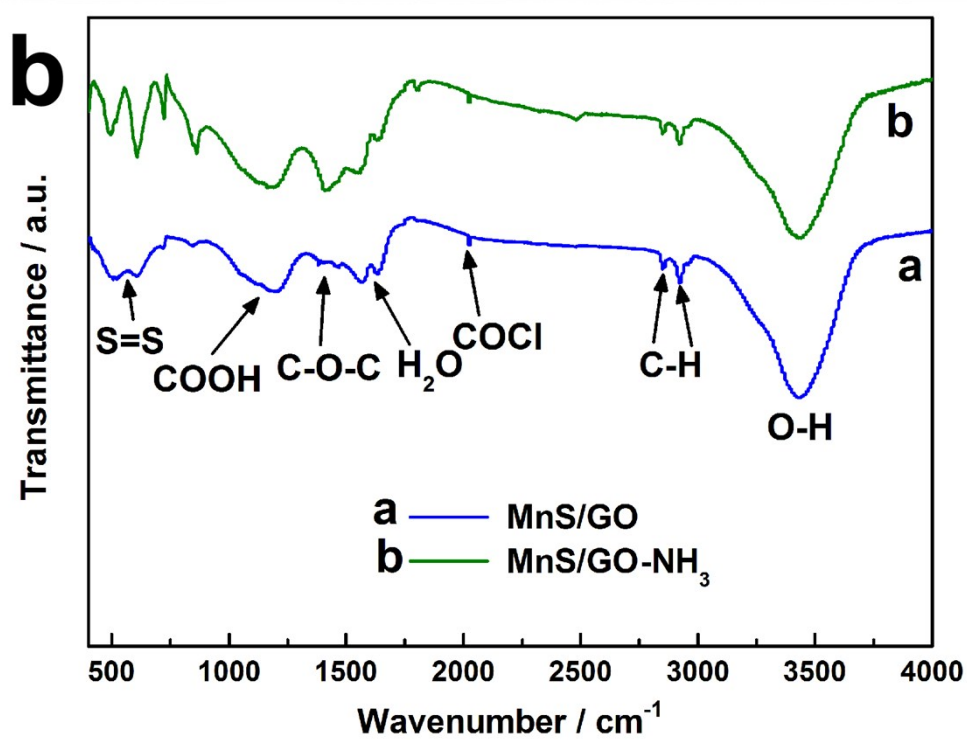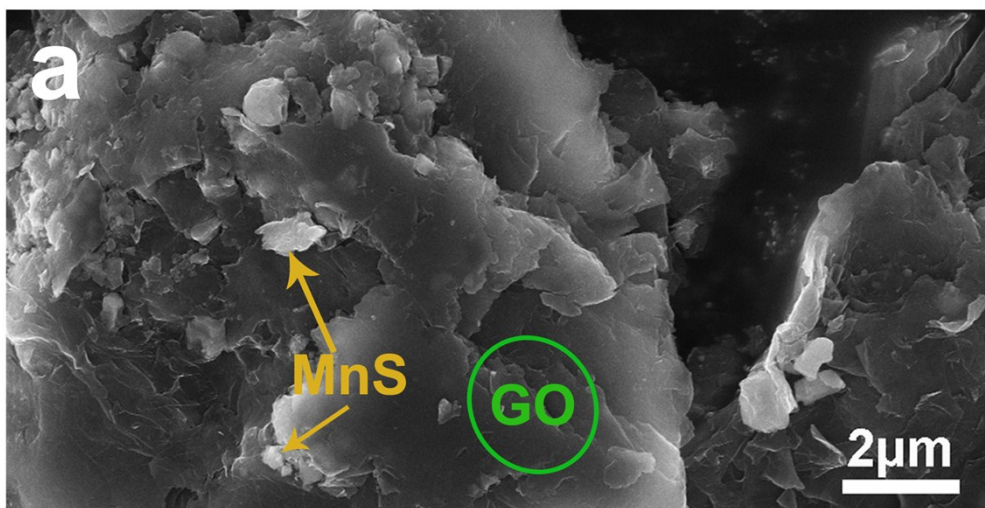
**Figure S2**. (a) FESEM image of MnS/GO sample and (b) Fourier transform infrared spectroscopy
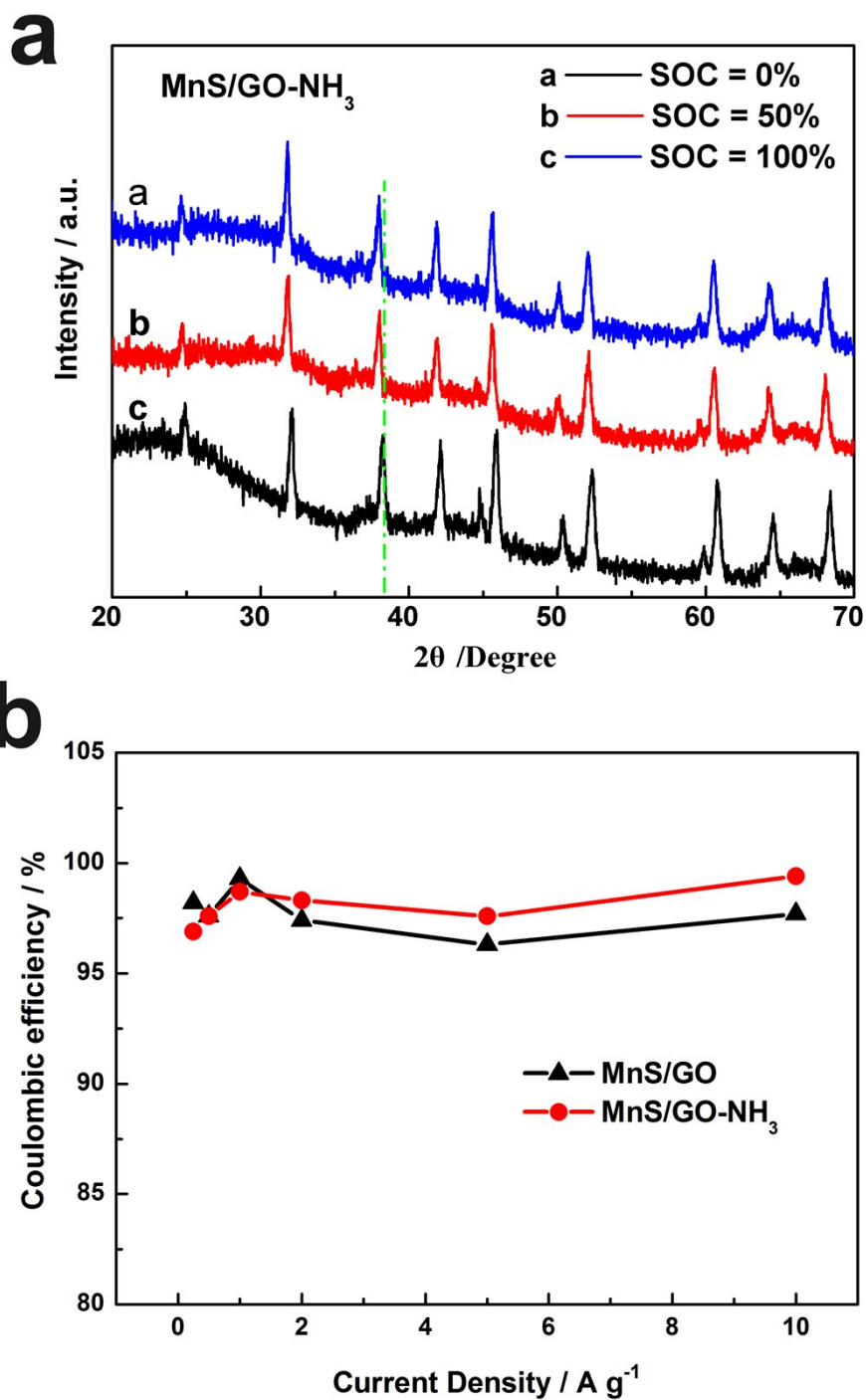
(FTIR) of the samples

**Figure. S3**. (a) XRD patterns of MnS/GO-NH$_3$ electrode materials at different SOC (b)

Coulombic efficiency of MnS/GO-NH$_3$ and MnS/GO electrode at various current densities.
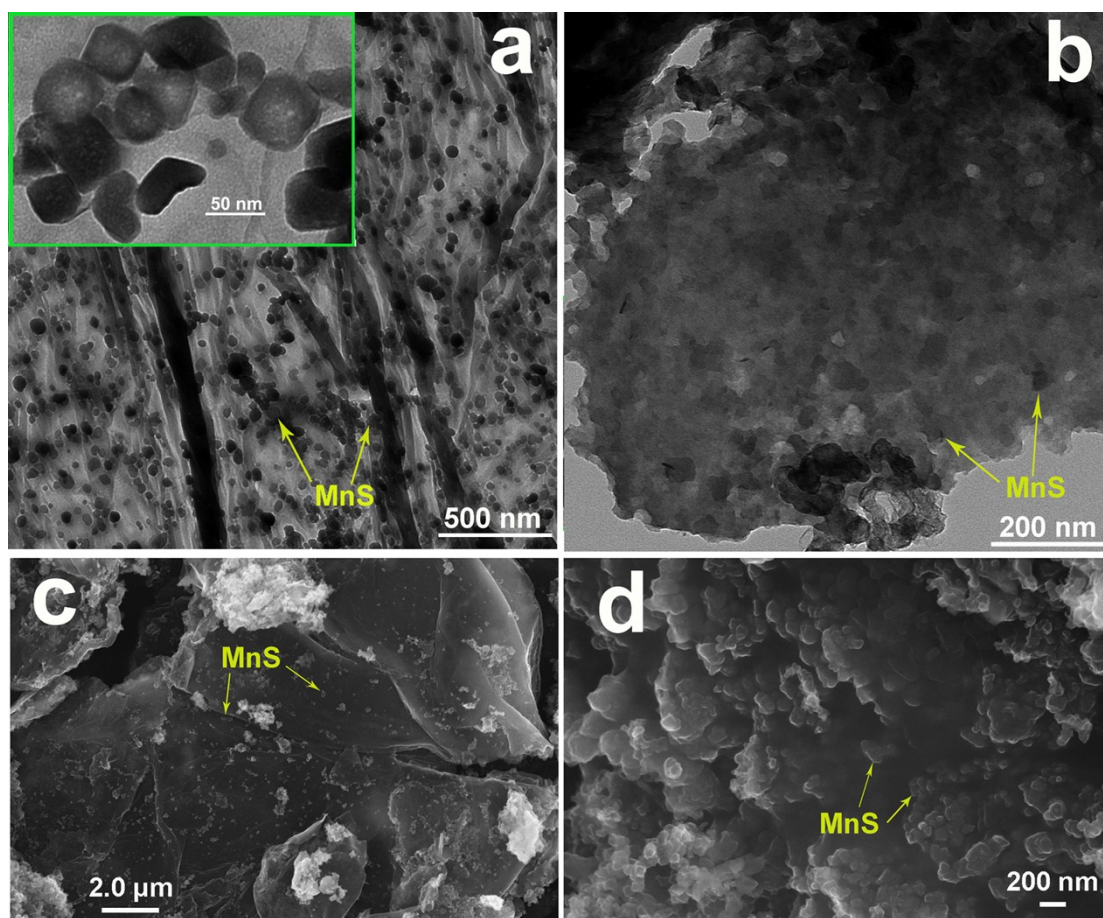
**Figure S4**. TEM images (a, b) and SEM images (c, d) of the MnS/GO-NH$_3$ (a, c) and MnS/GO (b,

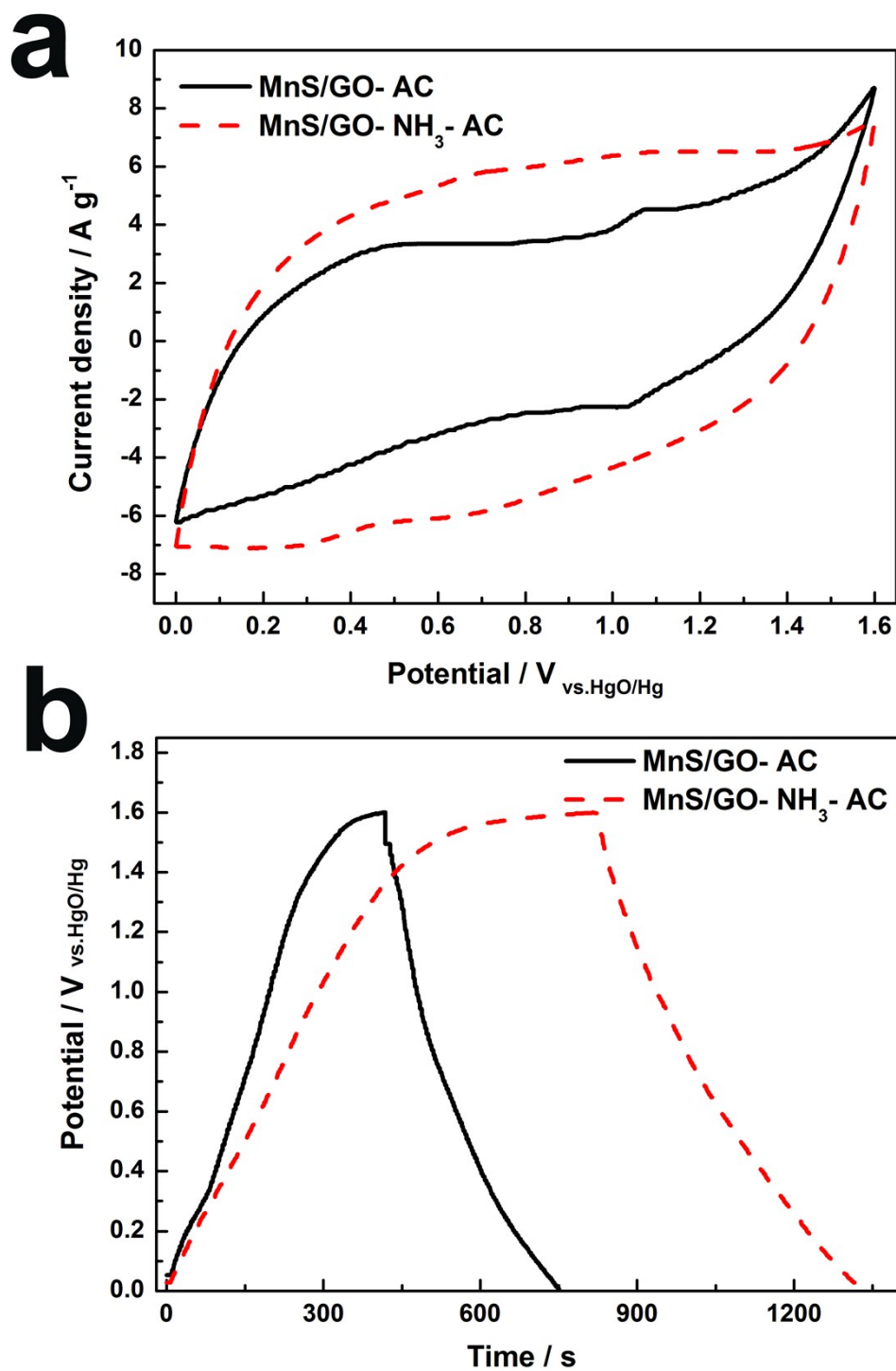d) electrode materials after 1000 charge-discharge cycling.

**Figure. S5**. (a) CV curves of MnS/GO-AC and MnS/GO-NH$_3$-AC at 100 mV s$^{-1}$, (b) charge-

discharge curves of MnS/GO-AC and MnS/GO-NH$_3$-AC at 1.1 mA

## Reference

1. W. S. Hummers, R. E. Offeman, Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, 80,

1339-1339.