Electronic Supplementary Information (ESI)

Direct growth of flower-like manganese oxide on reduced graphene oxide towards efficient oxygen reduction reaction

Jintao Zhang, Chunxian Guo, Lianying Zhang, and Chang Ming Li*

Experimental details

Low-temperature growth of flower-like manganese oxide clusters on reduced graphene oxide sheets

Graphene oxide was prepared by a modificed hummer's method, and subsequetly was reduced to RGO sheets with the assistance of microwave. 200 mL of manganous chloride ($MnCl_2$) solution (20 mM) was mixed with ethylenediaminetatraacetic acid disodium salt (EDTA) solution. 80 mg of as-prepared RGO sheets was dispersed in the above solution under sonication. After sonicating for 1 h, 200 mL of sodium hydroxide (250 mM) was added to the system. Then, 200 mL of potassium persulfate ($K_2S_2O_8$) was added to initiate the redox reaction. After standing at 30 ^{o}C for overnight, the solid product was collected by filtration, washed with DI water and finally with ethanol, followed by vacuum drying at 80 ^{o}C. The obtained sample was denoted as RGO-MnO_2. In order to synthesize the pristine MnO_2 clusters, no carbon material was added in the preparation process.

Characterization

Samples were characterized using powder X-ray diffraction (XRD) on a Shimadzu diffractometer with Cu KR radiation at a step size of 0.06° per second. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI-5300 ESCA spectrometer (PerkinElmer) with an energy analyzer working in the pass energy mode at 35.75 eV. An Al Kα line was used as the excitation source. Field-emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Japan) and high-resolution transmission electron microscopy (HRTEM, JEOL-2100F, 200 kV) were used to characterize sample morphologies. Rotating disk electrode (RDE) with glassy carbon substrate was used to evaluate the catalytic activities of the samples. 5 mg/mL of the catalyst suspension in ethnol was prepared by uisng ultrasonication. Typically, 6 µl of catalyst ink was introduced on to a glassy carbon electrode with dimeater of 5 mm by using a microsyringe. For the electrochemical measurements, a computer controlled work-station (CHI660, CH instrument) was used to measure the electrochemical properties of the samples at ambient temperature (about 22 °C). The electrochemical cell had a three-electrode configuration with a bright Pt plate as the counter electrode and an Ag/AgCl electrode as the reference electrode. 0.1 M oxygen-saturated KOH solution was employed as the electrolyte.

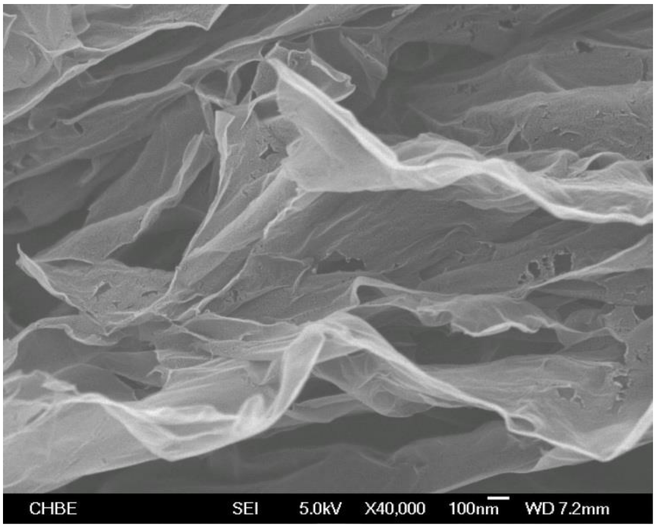

Fig. S1 SEM image of RGO sheets.

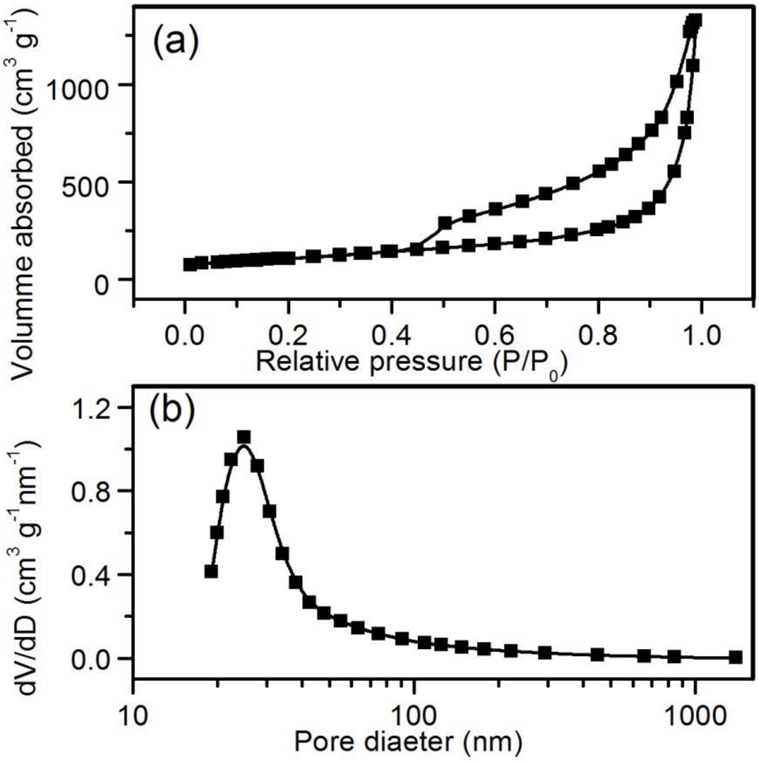

Fig. S2 N_2 adsorption–desorption isotherm of RGO (a) and the corresponding pore size distribution (b).

Fig. S2 shows the N_2 adsorption–desorption isotherms and the BJH pore size distribution (PSD) curves of samples RGO. A Type IV isotherm is seen in Fig. S2a, indicating the presence of mesopores The BJH pore size distribution curve in Fig. S2b indeed shows a narrow distribution centred at ~25 nm. The mesopores would be attributed to the interstitial space between the interlayers of RGO sheets. With the assistance of microwave heating, GO sheets were reduced by the removal of oxygenate groups in the form of gas (e.g. CO, CO_2). The release of these gases would facilitate to the exfoliation of graphene sheets, leading to a high BET surface area of ~381 m^2 g^{-1}.

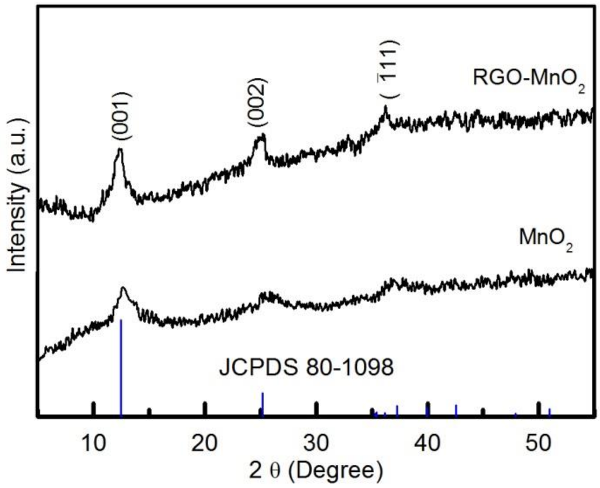

Fig. S3 XRD patterns of RGO-MnO_2 and MnO_2 clusters.

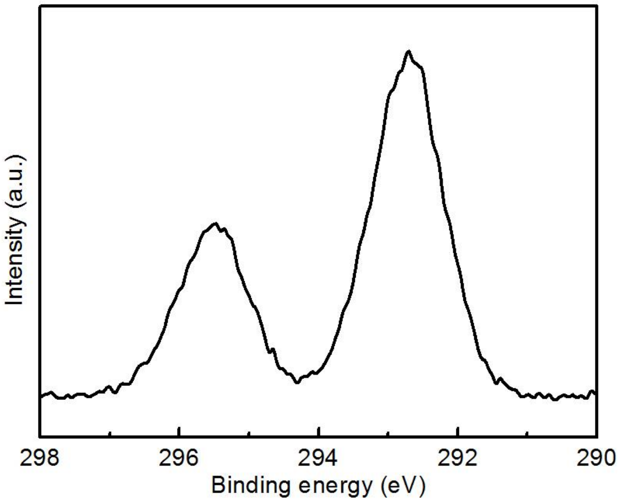

Fig. S4 The core level XPS signal of K 2p for RGO-MnO_2.

For birnessite-type MnO_2, edge-shared MnO_6 octahedra are separated from each other by the intercalation of guest cations, usually hydrated alkaline cations (such as K^+, Na^+), generating a two dimensional (2D) lamellar structure. The core level XPS signal of K 2p exhibits two typical peaks centered at 292.7 eV and 295.5 eV, respectively, suggesting the formation of K-birnessite.

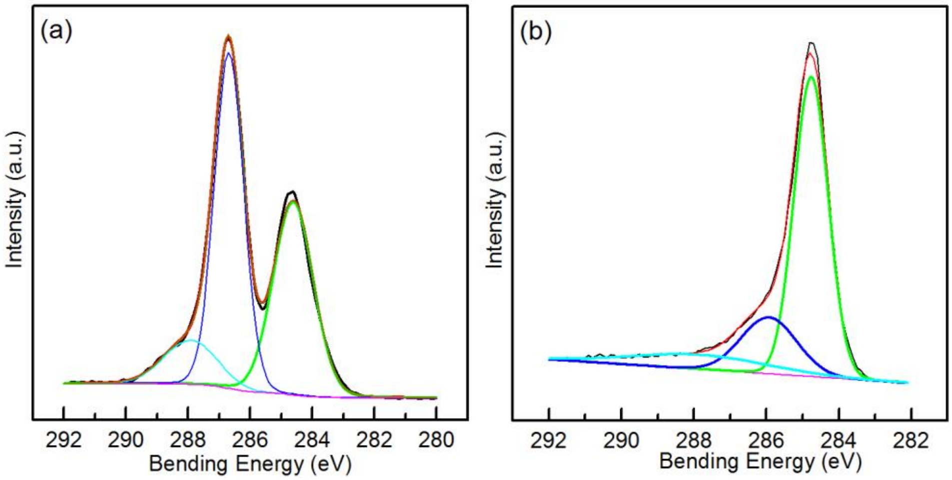

Fig. S5 The core level XPS signal of GO (a) and RGO (b).

The core-level XPS signal of C 1s (Fig. S5a) for GO exhibited a main peak centered at about 284.6 eV originated from the graphitic sp^2 carbon atoms. The peaks located at 285.8 eV and 288.5 eV were due to carbon atoms connecting with oxygenate groups, such as C–O and O–C=O. After reduction with the microwave-assisted method, the ratio of C/O in RGO sheets is about 14.1. The presence of peaks ascribed to oxygenate groups evidences the presence of residual oxygenate groups on RGO sheets.

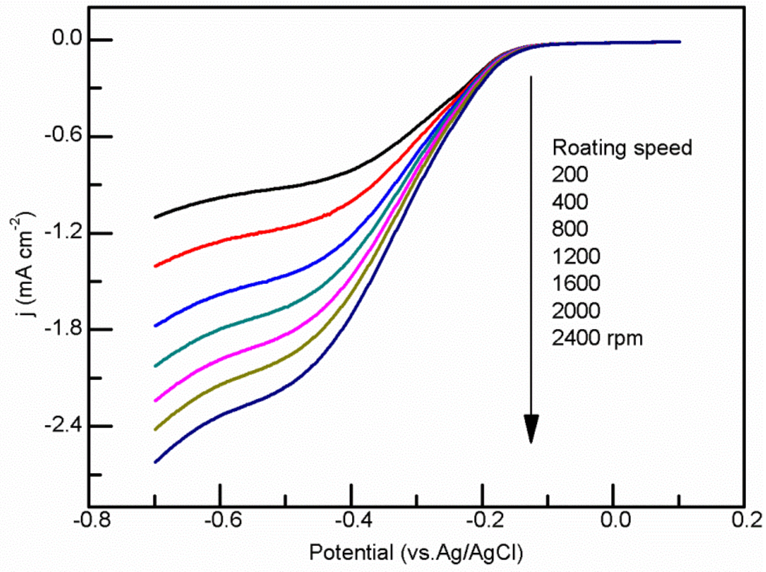

Fig. S6 LSV curves for oxygen reduction reaction at RGO electrode in oxygen-saturated 0.1 M KOH with different rotating speeds.

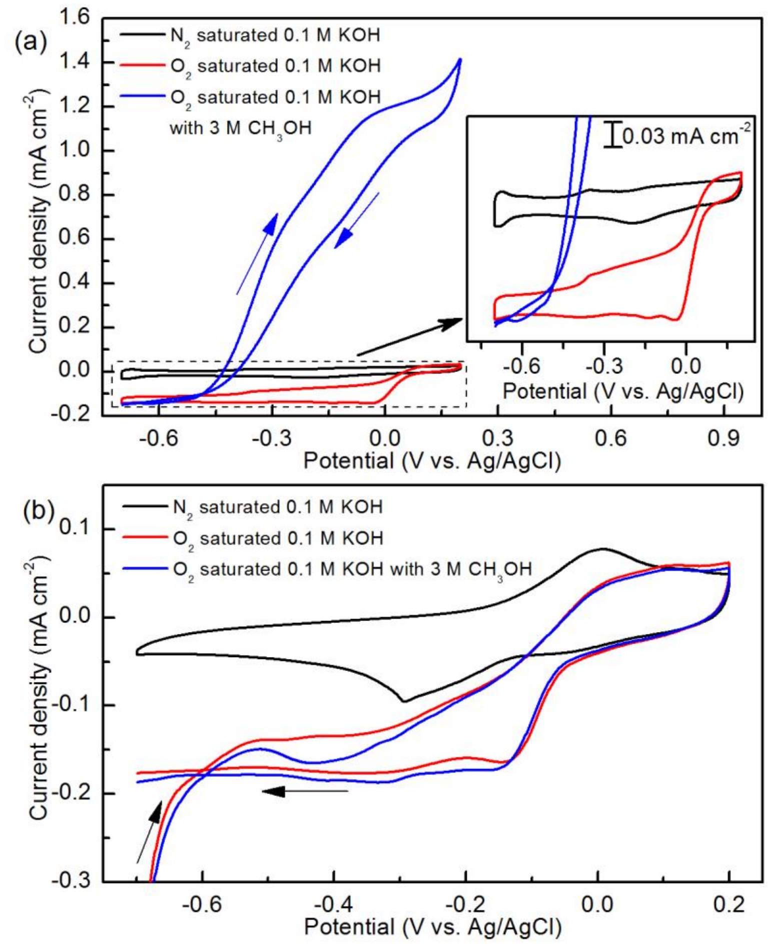

Fig. S7 Cyclic voltammograms of Pt catalyst (a) and RGO-MnO_2 (b) in N_2 saturated 0.1 M KOH and O_2 saturated 0.1 M KOH with and without 3 M CH_3OH, respectively..

As shown in Fig. S7a, significant methanol oxidation current is observed at Pt catalyst in the presence of 3 M methanol and oxygen reduction is suppressed seriously. The reduction current is only observed at the potential of less than -0.45 V (the enlarge figure in Fig. S8a). In contrast, no oxidation current for methanol oxidation is observed at RGO-MnO_2 (Fig. S7b). The results demonstrate that RGO-MnO_2 has high selectivity to ORR and is effective to address the methanol crossover effect.