

## Supporting Information

### Mesoporous Hybrid Material of Mn<sub>3</sub>O<sub>4</sub> Nanoparticles on Nitrogen-doped Graphene for Highly Efficient Oxygen Reduction Reaction

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## I. Experimental Section

### 1. Materials Synthesis

#### 1.1 Preparation of graphite oxide.

Graphite oxide was prepared from flake graphite by a modified Hummers' method.<sup>1</sup> In the first step, graphite flakes (5 g) were added into the mixture of H<sub>2</sub>SO<sub>4</sub> (15 mL, 98%), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2.5 g) and P<sub>2</sub>O<sub>5</sub> (2.5 g) at 80 °C. The reaction was carried out for 6 hours and after that it was cooled to room temperature. The product was washed and filtered with DI water until pH=7, and kept under ambient conditions overnight. In the second step, the reaction beaker with 115 mL of condensed H<sub>2</sub>SO<sub>4</sub> was placed in an ice bath. The pre-oxidized graphite and KMnO<sub>4</sub> (15 g) were added in sequence into the above beaker under stirring with keeping the temperature below 20 °C. The mixture was then kept at 35 °C for 3.5 hours and at 98 °C for 15 min, respectively, where DI water and 6.5 mL of H<sub>2</sub>O<sub>2</sub> (30%) were added. Subsequently, the resultant product was washed with 115 mL of HCl (1/10, v/v) and DI water, and dialyzed for 7 days.

A 5 mg/mL of graphene oxide (GO) was subjected ultrasonic treatment (950W, 1h) and centrifuged at 3000 rpm for 0.5 hour.

#### 1.2 Synthesis of Mn<sub>3</sub>O<sub>4</sub> nanoparticles on nitrogen-doped graphene (MNG).

The MNG hybrid was synthesized as follows. 2 mL 5 mg/mL of GO were added into 20 mL of ethanol, followed by addition of 2 mL of 0.2 M Mn(AC)<sub>2</sub> and 2 mL of NH<sub>4</sub>OH (28 %wt). The mixture was kept at 80 °C for 10 hours and loaded into a Teflon-lined stainless steel autoclave and heated at 150 °C for 3 hours. The sample was washed with water and ethanol, and freeze-dried.

## 2. Materials Characterization

Transmission electron microscopy (TEM) images were obtained on a Philips CM100 microscope at an acceleration voltage of 80 kV. X-ray diffraction (XRD) patterns were collected on a powder X-ray diffractometer at 40 kV and 15 mA using Co-K $\alpha$  radiation (Miniflex, Rigaku). The Raman spectra were conducted on iHR550 from HORIBA Scientific with 532 nm solid laser as the excitation source. Scanning electron microscopy (SEM) images were recorded on the FEI Quanta 450 at high vacuum with an accelerating voltage of 10 kV. Atomic Force Microscope (AFM) measurements were performed on NT-MDT Ntegra Solaris microscope. The X-ray photoelectron spectra (XPS) spectra were obtained using an Axis Ultra (Kratos Analytical, UK) XPS spectrometer equipped with an Al K $\alpha$  source (1486.6 eV). Nitrogen adsorption isotherms were collected on a Tristar II, Micromeritics adsorption analyzer at -196 °C. Prior to adsorption measurements, the samples were degassed at 200 °C for at least 10 h. Pore size distributions (PSD) were calculated using the adsorption branch of the isotherms by Barrett-Joyner-Halenda (BJH) method; the resulting PSD curves defined as  $dV/d(\log D)$ , where  $V$  is the volume adsorbed and  $D$  is the pore width, are presented in figures. The total pore volume was estimated from the volume adsorbed at a relative pressure ( $P/P_0$ ) of 0.994. The FTIR spectra were collected on the transmission module of Thermo Nicolet 6700 FTIR spectrometer at 2  $\text{cm}^{-1}$  resolution and 64 scans. Thermogravimetric analysis (TGA) was measured using a Setaram Labsys Thermogravimetric Analyzer in air atmosphere, over a temperature range from 25 to 800 °C with a heating rate of 10 °C/min.

## 3. Electrode Preparation and Electrochemical Tests

Electrochemical measurements were performed in a standard three-electrode glass cell on a 760 workstation (Pine Research Instruments, US) using rotation disk electrode and rotation ring-disk electrode (Princeton Applied Research, US) under ambient conditions. A Pt wire and an Ag/AgCl/KCl (3 M) were used as counter and reference electrodes, respectively.

2 mg of catalysts were ultrasonically dispersed in 1 mL of mixed solution of 2-propanol and Milli-Q water (1/3, v/v) with 30  $\mu\text{L}$  of 0.1% Nafion (15 wt% of Nafion in the catalyst), resulting in a catalyst concentration of 2  $\text{mg mL}^{-1}$ . 20  $\mu\text{L}$  of catalyst dispersion (25  $\mu\text{L}$  for rotation ring-disk electrode) was then transferred onto the rotating disk glassy carbon electrode via a controlled drop casting method, which yielded a loading of catalyst 0.2  $\text{mg cm}^{-2}$ . The resulting electrode was dried under ambient conditions. Nafion in the electrode mainly acted as the function of binders, which can enhance the immobilization of catalysts on rotation disk electrode. Also, Nafion itself has little ORR catalytic activity; therefore, we can evaluate the performance of catalysts accurately.

The overall electron transfer numbers per oxygen molecule involved in the typical ORR process can be calculated from the slopes of the Koutecky-Levich plots using the following equation<sup>2</sup>:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$
$$B = 0.2nFAC_0(D_0)^{2/3}\nu^{-1/6} \quad J_K = nFkC_0$$

in which  $J$  is the measured current density,  $J_K$  and  $J_L$  are the kinetic- and diffusion-limiting current densities,  $\omega$  is the electrode rotating speed in rpm, and  $B$  is the reciprocal of the slope,  $n$  is the number of electrons transferred per oxygen molecule,  $F$  is the Faraday constant ( $F = 96\,485\text{ C mol}^{-1}$ ),  $C_0$  is the concentration of  $O_2$ ,  $D_0$  is the diffusion coefficient of  $O_2$ ,  $\nu$  is the kinematic viscosity of the electrolyte, and  $k$  is the electron transfer rate constant. Since in this study the electrolyte was  $O_2$  saturated 0.1 M KOH,  $C_0$ ,  $D_0$  and  $\nu$  were used as  $1.2 \times 10^{-3}\text{ M}$ ,  $1.9 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$  and  $0.01\text{ cm}^2\text{ s}^{-1}$ , respectively. The constant 0.2 was adopted when the rotating speed is expressed in rpm.

Rotating ring-disk electrodes were prepared by the same method. The %  $HO_2^-$  and electron transfer number were determined by the following equations<sup>2</sup>:

$$\%HO_2^- = 200 \times \frac{I_R/N}{I_D + I_R/N} \quad n = 4 \times \frac{I_R/N}{I_D + I_R/N}$$

where  $I_R$  and  $I_D$  are the ring and disk currents, respectively, and  $N$  is the collection efficiency (0.4) of Pt ring.

### References:

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
2. (a) U. A. Paulus, T. J. Schmidt, H. A. Gasteiger and R. J. Behm, *J. Electroanal. Chem.*, 2001, **495**, 134; (b) Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat. Mater.*, 2011, **10**, 780.

### II. Supplementary Figures:

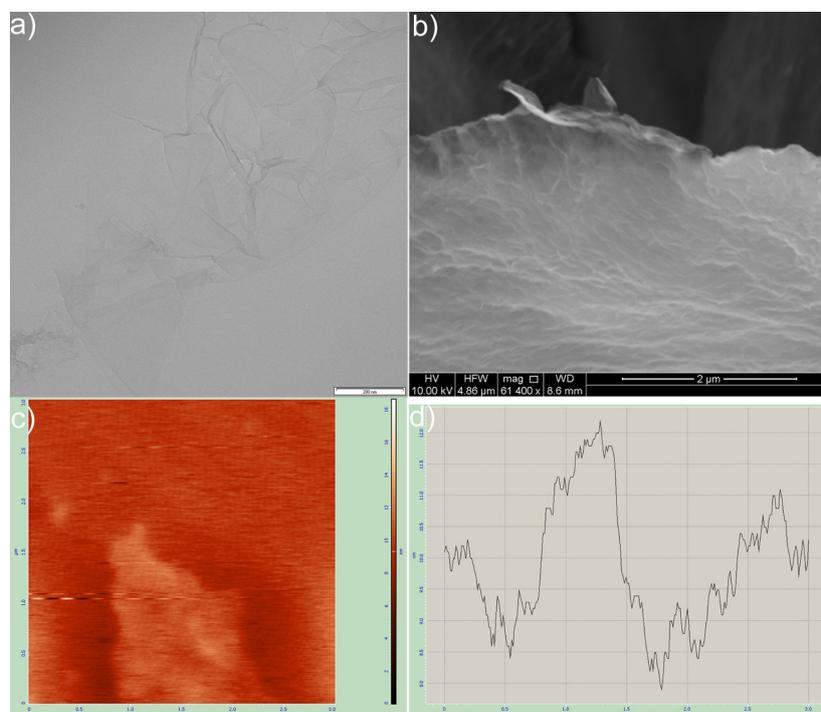


Fig. S1 (a) TEM image, (b) FESEM image, (c) AFM image and (d) height distribution curve from AFM image of graphene oxide sheets.

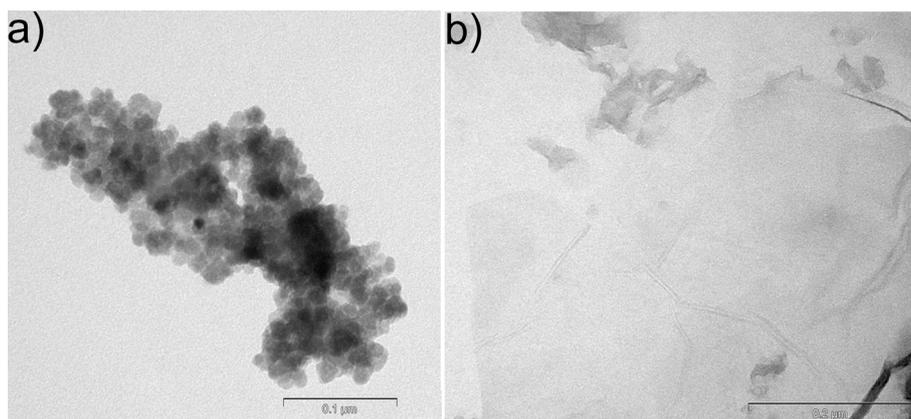


Fig. S2 TEM image of (a) MPs, (b) NG.

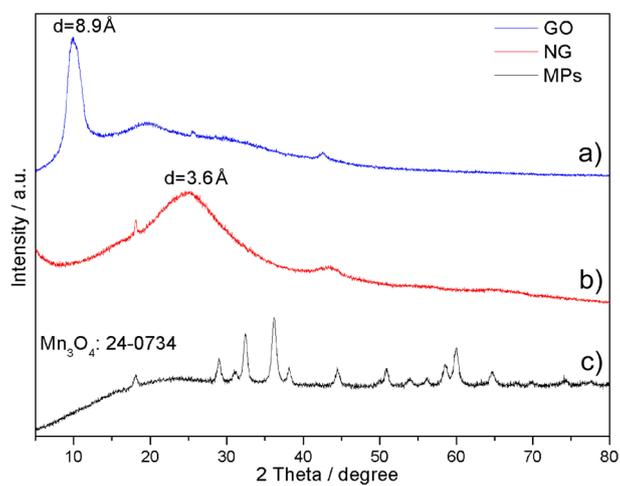


Fig. S3 XRD patterns of (a) GO, (b) NG and (c) MPs.

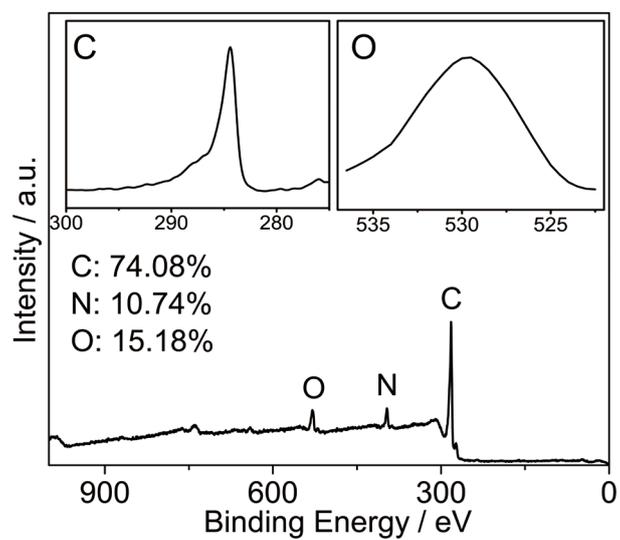


Fig. S4 XPS survey of NG. Insets show the C and O spectra.

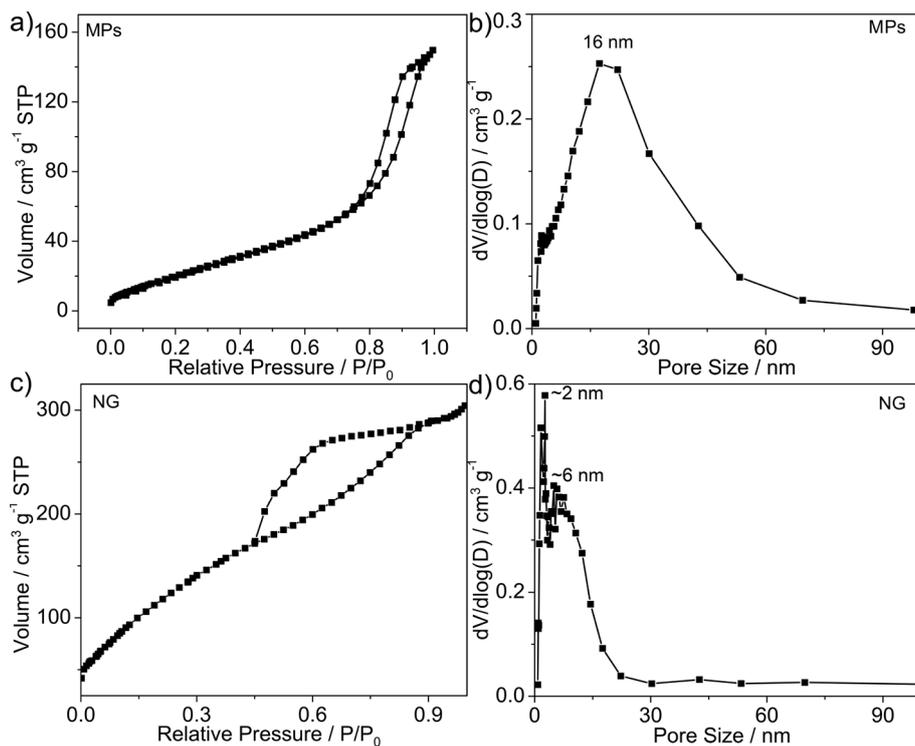


Fig. S5 Nitrogen adsorption and desorption isotherm and pore size distribution curves of (a, b) MPs and (c, d) NG.

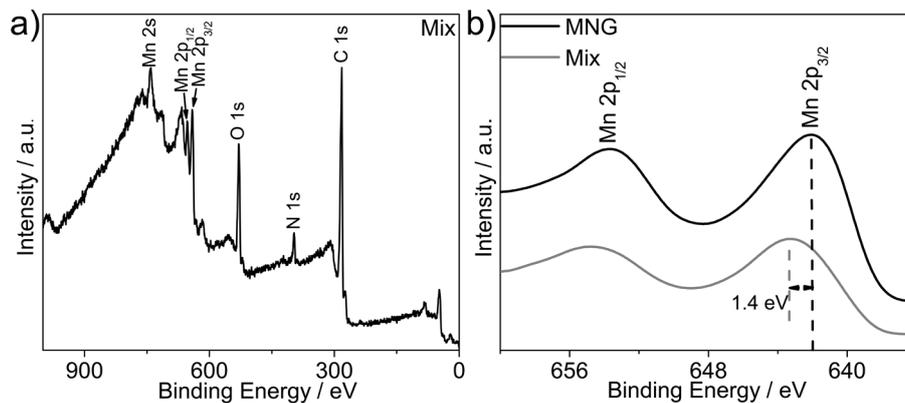


Fig. S6 (a) XPS survey spectrum of Mix; (b) XPS spectra of Mn 2p in MNG and Mix.

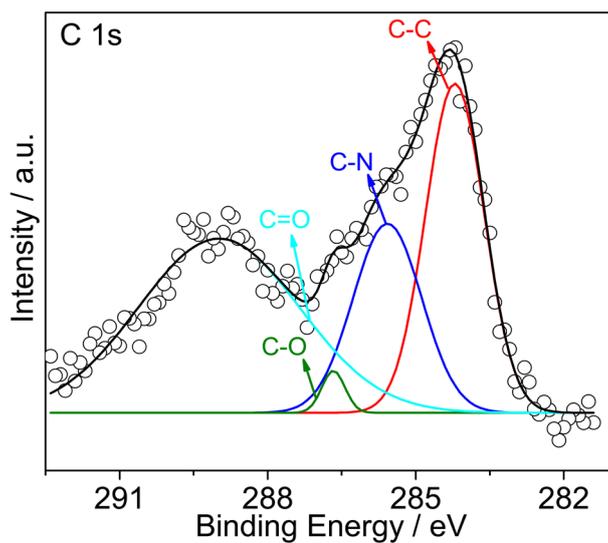


Fig. S7 XPS spectrum of C in as-synthesized MNG.

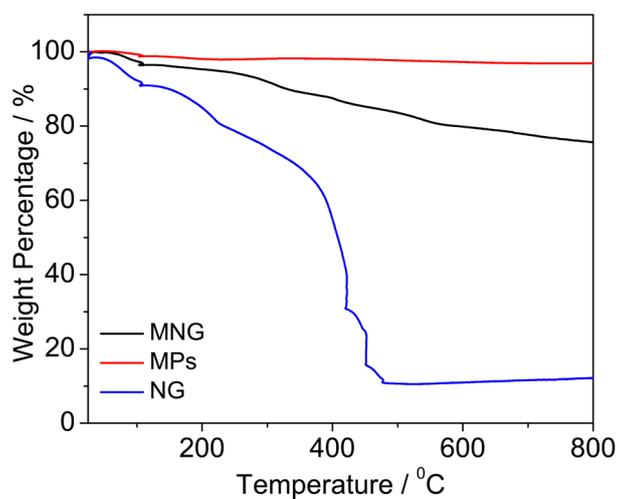


Fig. S8 TGA curves of MNG, MPs and NG in air.

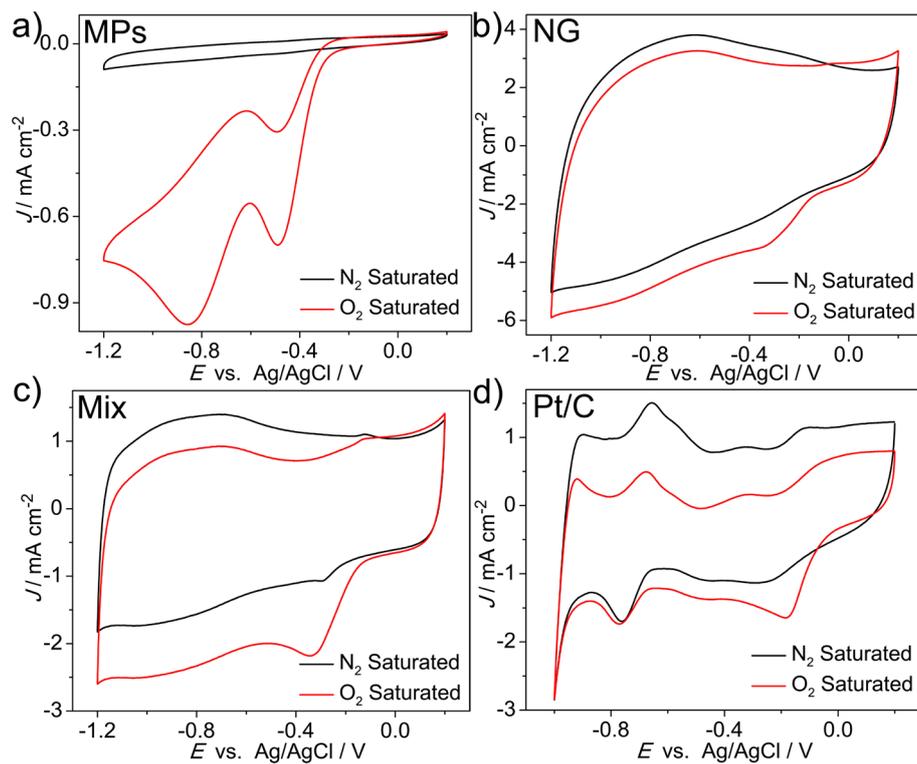


Fig. S9 CV curves of (a) MPs, (b) NG, (c) Mix (physical mixture of MPs and NG) and (d) Pt/C on rotating disk electrodes in  $\text{O}_2$  and  $\text{N}_2$  saturated  $0.1 \text{ M KOH}$  solutions. Catalyst loading was  $0.2 \text{ mg cm}^{-2}$  for all samples.

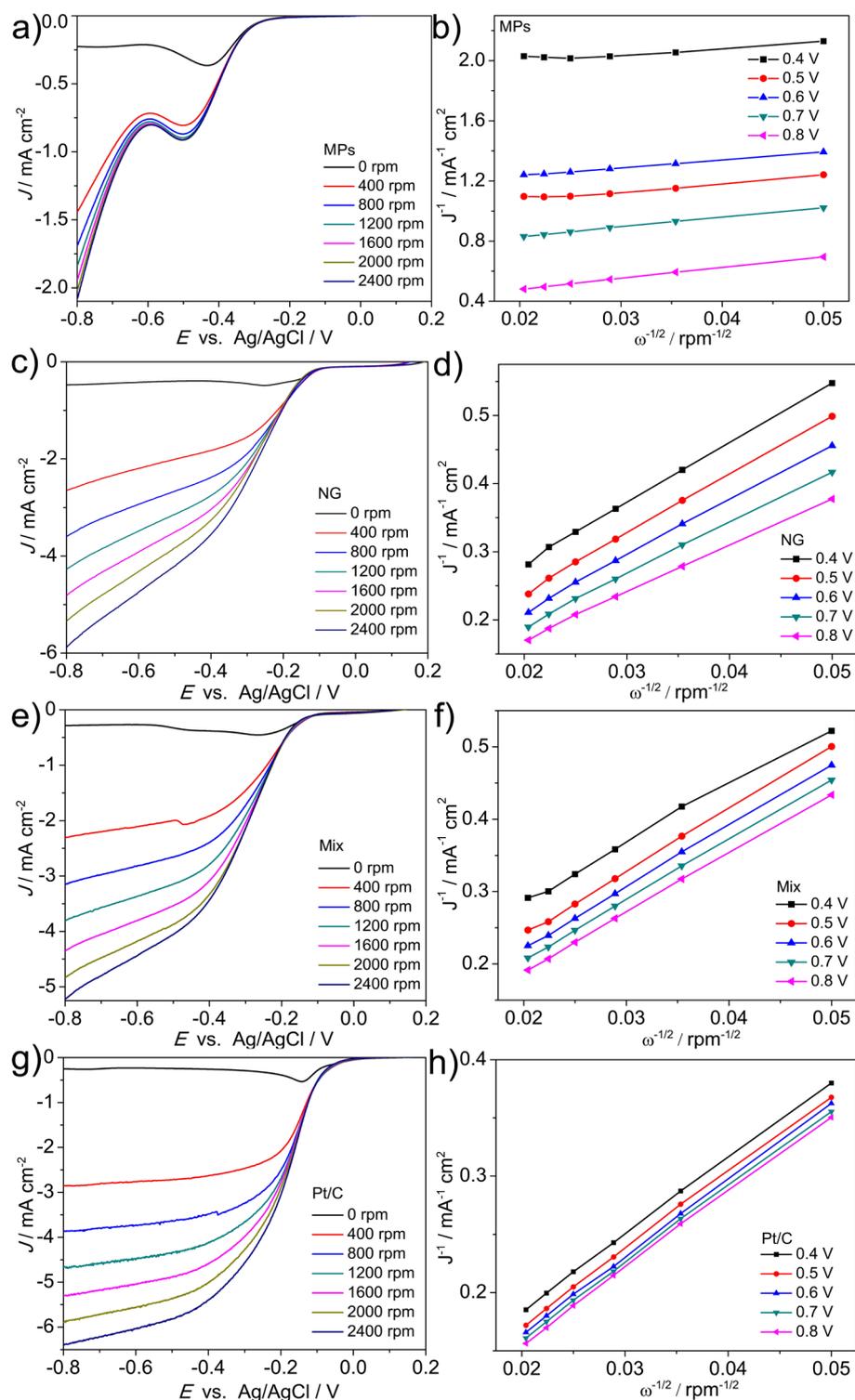


Fig. S10 (a, c, e and g) Detailed LSV curves of MPs, NG, Mix and Pt/C at different rotating speeds using rotating disk electrodes in O<sub>2</sub> saturated 0.1 M KOH solution with a sweep rate of 5 mV s<sup>-1</sup>. Catalyst loading was 0.2 mg cm<sup>-2</sup> for all samples; (b, d, f and h) the calculated Koutecky-Levich plots ( $J^{-1}$  versus  $\omega^{-0.5}$ ) for MPs, NG, Mix and Pt/C at different potentials.

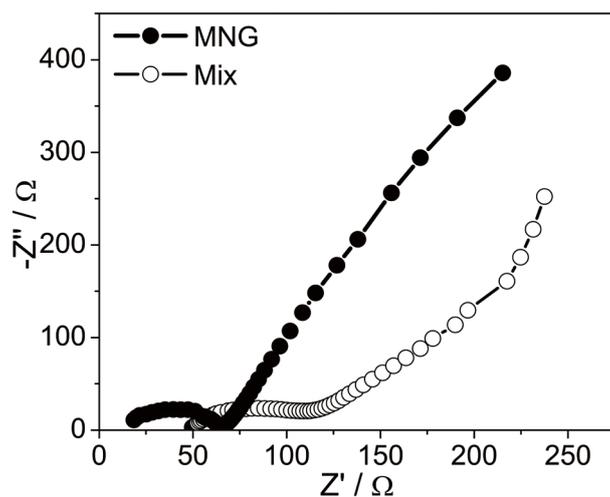


Fig. S11 Electrochemical impedance spectra of MNG and Mix in 0.1M KOH solution.

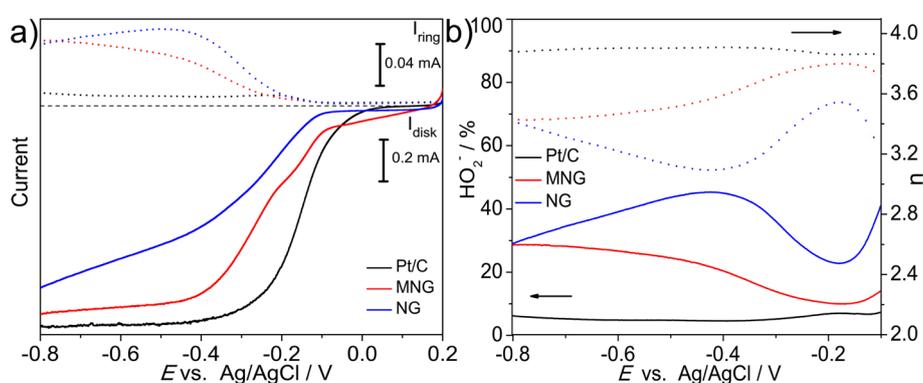


Fig.S12 (a) Rotating ring-disk electrode voltammograms (disk current as solid line, ring current as dotted line) of Pt/C, MNG and NG recorded at the rotating speed of 1600 rpm in  $O_2$ -saturated 0.1M KOH solution with a sweep rate of  $5 \text{ mV s}^{-1}$ ; (b) the  $HO_2^-$  percentages (solid line) and electron transfer numbers (dotted line) calculated for Pt/C, MNG and NG.

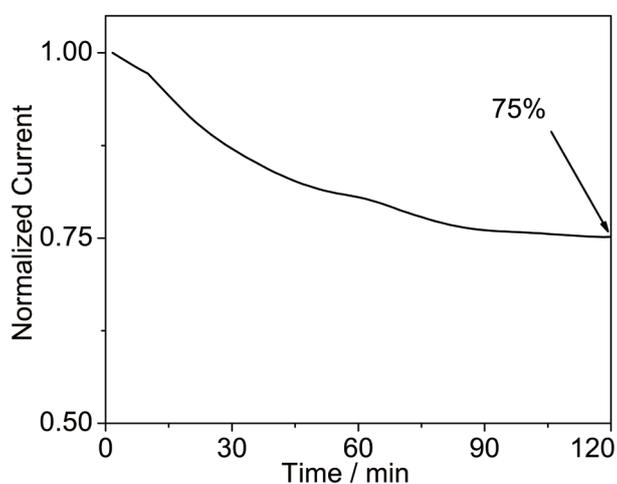


Fig. S13 Chronoamperometric response of Mix at  $-0.3 \text{ V}$  in  $O_2$ -saturated 0.1M KOH. Catalyst loading was  $0.2 \text{ mg cm}^{-2}$ .

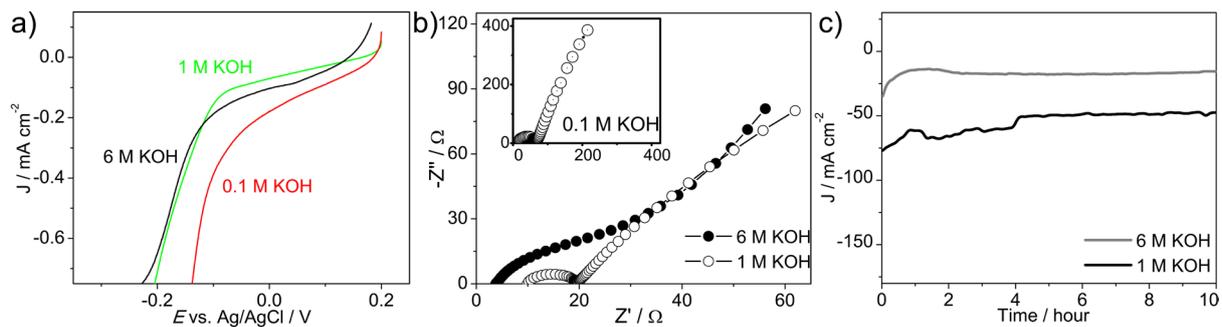


Fig.S14 (a) LSV curves at the rotating speed of 1600 rpm with a sweep rate of  $5 \text{ mV s}^{-1}$ , (b) Electrochemical impedance spectra, and (c) Chronoamperometric response (i-t) at  $-0.3 \text{ V}$  of MNG in  $\text{O}_2$ -saturated 0.1M, 1M and 6M KOH solutions. Catalyst loading was  $0.2 \text{ mg cm}^{-2}$  for all samples.