Supplementary Information

Electrochemical growth of octahedral Fe$_3$O$_4$ with high activity and stability toward oxygen reduction reaction

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Experiment section

Materials

Commercial 20% Pt/C catalyst was purchased from Alfa Aesar. Nafion® 117 solution was purchased from Aldrich. All other chemicals were of analytical grade and from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used throughout the experiments.

Characterization

X-ray photoelectron spectroscopy (XPS) was performed at room temperature with monochromatic Al Kα radiation (1486.6 eV) using a Quantum 2000 system (PHI, USA). X-ray diffraction (XRD) pattern was measured on an X'pert Pro diffractometer (Philips, USA), using Cu Kα radiation. Field emission scanning electron microscopy (FE-SEM) images and energy dispersive spectroscopy (EDS) were observed on a JSM-7500F field emission scanning electron microanalyzer (JEOL, Japan). [57]Fe Mössbauer spectra of the as-prepared materials were recorded using a Topologic 500A spectrometer and a proportional counter at room temperature. The source was [57]Co in rhodium. The Mössbauer spectra was fitted by two overlapping six-line sub-spectra. One of the sub-spectra with larger magnetic splitting was assumed to have a static magnetic field, the other one with smaller magnetic splitting was assumed to have a distribution in its magnetic field. Accordingly,[57]Fe Mössbauer spectral parameters such as the isomer shift (*IS*), the electric quadrupole splitting (*QS*), the effective or average magnetic field (*H*), the full linewidth at halfmaximum (FWHM) and the relative spectral area (*A*) of different components on the

1

absorption patterns were calculated. The *IS* values were quoted relative to α-Fe at room temperature. The magnetization of the sample was measured with a vibrating sample magnetometer (VersaLab , Quantum Design, USA) at room temperature. Indium tin oxide (ITO)-coated glass was used to deposit Fe_3O_4 for surface characterization. SEM imaging, XPS analysis and hysteresis loop of as-deposited Fe_3O_4 were carried out on the ITO substrate itself. For XRD measurement and Mössbauer spectra, the material is scrapped off from the ITO substrate and redispersed in 95% ethanol and drop dried on the Si substrate. As for TEM measurement, the as-deposited Fe_3O_4 sample was removed carefully from the ITO electrode using ultrasonication in isopropanol and coating the TEM grids with a few microliters of the solution. Fe_3O_4 loading on the glassy carbon disk electrode in electrochemical measurements was determined by Thermo 6300 Inductively Coupled Plasma-atomic (ICP) emission spectrometry. The ICP samples were prepared by immersing as-synthesized Fe_3O_4 glassy carbon disk electrode in 0.1 M HCl.
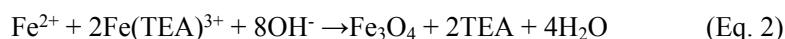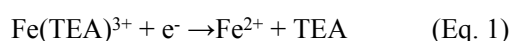
Electrochemical measurements

The electrochemical measurements were carried out in a conventional three electrode cell using CHI 660C electrochemical workstation. Prior to the deposition of the Fe_3O_4 crystals onto the electrode surface for electrocatalytic assessment, the glassy carbon (GC) disk working electrode (5.0 mm diameter) was polished with alumina slurries (1.0, 0.3 and 0.5 μm) and cleaned by sonication in absolute alcohol and deionized water for 10 min successively. After the Fe_3O_4 crystals were deposited onto the electrode surface, then the electrode was dried by a gentle nitrogen flow for 2 min. A Pt coil and double junction Ag/AgCl (3 M KNO_3) acted as the counter and reference electrode, respectively. All potentials in this study refer to that of RHE. The potential difference between Ag/AgCl and RHE is 0.962±0.002 V, based on the calibration measurement in H_2 saturated 0.1M KOH with two polished Pt wires as the working and counter electrodes, respectively and the Ag/AgCl as the reference electrode. CVs were run at a scan rate of 1mV s^{-1}, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions.
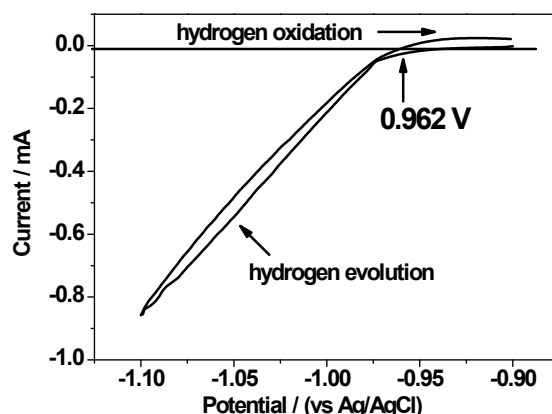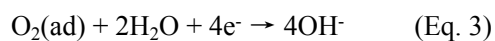
So in 0.1 M KOH, E (RHE) = E (Ag/AgCl) + 0.962 V.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out in a N_2 and O_2-saturated 0.1 mol L^{-1} KOH solutions, with a scan rate of 50 mV s^{-1} and 5 mV s^{-1}, respectively. Electrolyte was saturated with oxygen by bubbling O_2 prior to the start of each experiment. A flow of O_2 was maintained over the electrolyte during the recording of CVs and LSVs in order to ensure its continued O_2 saturation. The working electrode was cycled at least 5 times before data were recorded at a scan rate of 5 mV s^{-1}. In control experiments, CV and LSV measurements were also performed in N_2 by switching to N_2 flow through the electrochemical cell. Chronoamperometry and methanol-tolerant tests were conducted at 0.56 V in 0.1 M KOH saturated with O_2. All electrochemical experiments were carried out at room temperature. The accelerated durability test was performed by cycling between 0.2 and -1.0 V for 10 000 cycles in O_2-saturated 0.1 mol L^{-1} KOH solution, with scan rate of 100 mV s^{-1}. The kinetics of the ORR were studied by the RDE method with a CHI660C electrochemical workstation and Pine modulated speed rotator (USA). For comparison, 5 mg of Pt/C and 16 μL of 5 wt % Nafion solution were dispersed in 1 ml of 3:1 v/v water/isopropanol mixed solvent by at least 30 min sonication to form a homogeneous ink. Then 2.4 μL of the catalyst ink (containing 12 μg of Pt/C) was loaded onto a glassy carbon electrode. The Fe_3O_4 loading was 0.6 mg cm^{-2} by ICP test and the Pt/C (20%) catalysts loading was controlled at 60 μg cm^{-2}, respectively.

Equations

$$Fe(TEA)^{3+} + e^- \rightarrow Fe^{2+} + TEA \qquad \text{(Eq. 1)}$$

$$Fe^{2+} + 2Fe(TEA)^{3+} + 8OH^- \rightarrow Fe_3O_4 + 2TEA + 4H_2O \qquad \text{(Eq. 2)}$$

3

$O_2(ad) + 2H_2O + 4e^- \rightarrow 4OH^-$ (Eq. 3)

The kinetic parameters can be analyzed with the Koutecky–Levich equations (eq. 4 and 5):

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{B\omega^{1/2}} \qquad \text{(Eq. 4)}$$

$$B = 0.62nFC_0D_0^{2/3}v^{-1/6} \qquad \text{(Eq. 5)}$$

Where J is the measured current density, J_K and J_L are the kinetic- and diffusion limiting current density, respectively, ω is the electrode rotation rate, n is the overall number of electron transferred, F is the Faraday constant, C_O is the bulk concentration of O_2 dissolved in the electrolyte, D_O is the diffusion coefficient for O_2, v is the kinematic viscosity of the electrolyte, and k is the electron transfer rate constant.[1] According to Eq. 4 and eq. 5, the number of electrons transferred can be obtained from the slope and intercept of the Koutecky–Levich plots, respectively.
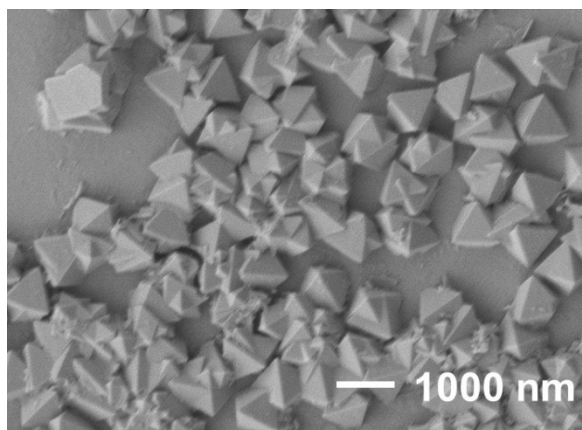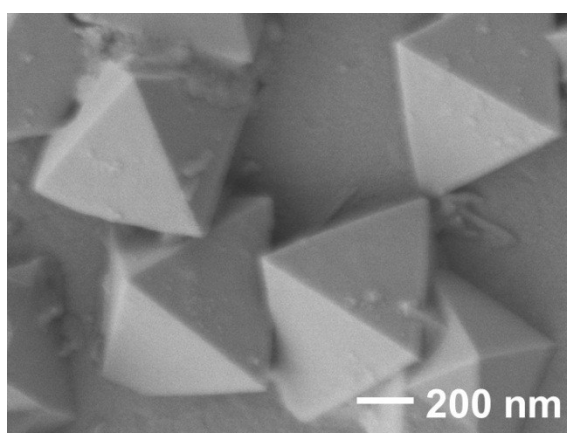
Figures and Tables
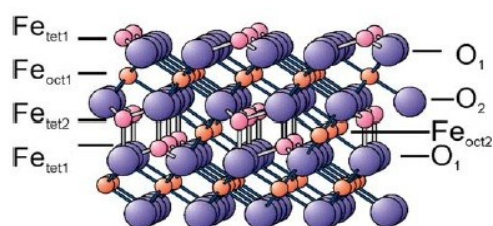
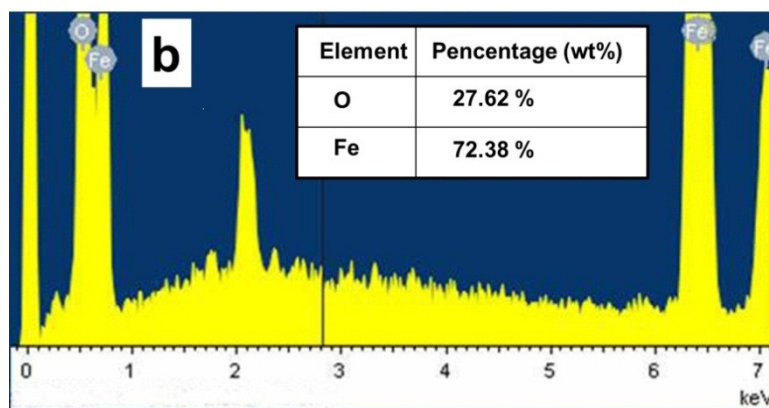**Fig. S1**   Side and top view of Fe_3O_4.[2]
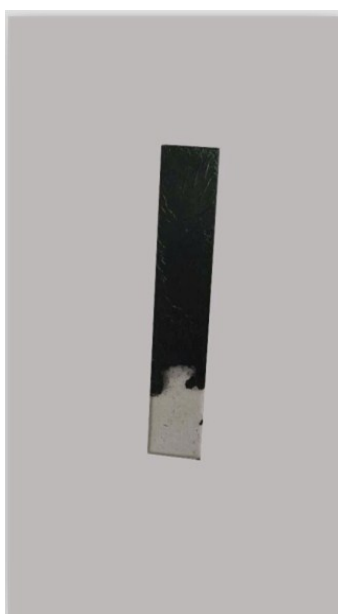
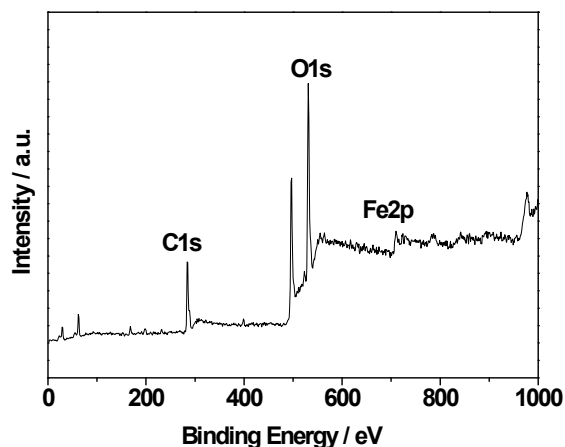**Fig. S2** Photograph of the as-deposited product on ITO coated glass.

Fig. S3 SEM image of the as-deposited product at lower magnification.

Fig. S4 SEM image of the as-deposited product at higher magnification.

Fig. S5 EDS image of the as-deposited product.

Fig. S6 XPS spectra of full spectrum of as-synthesized product on ITO.

Tab. S1 Physical parameters of different Fe_3O_4, Pt and PtPd catalysts

in 0.1 M saturated KOH with O_2 at 1600rpm[a]

Materials	Loading/mgcm^{-2}	$J_{0.9V}$ /mAcm^{-2}	J_{0V} /mAcm^{-2}	Onset /V[b]	Ref.[c]
octahedral Fe_3O_4	0.6	0.20	4.53	0.90	This work
Pt/C	0.06	0.23	5.02	0.92	This work
Fe_3O_4/N-C-900	0.15	$0.10 \sim 0.20$	~ 4.75	0.85	Ref.5b
Fe_3O_4/N-GAS	0.14	~ 0.10	~ 4.22	0.81	Ref.5a
PtPd/N-CNT	0.20	~ 0.40	~ 6.80	1.09	Ref.13

[a] All the potential values from references were converted to *vs*. RHE for comparison.

[b] In order to minimize the effect of residual currents on the potential value, the onset potential in this research has been defined as a potential required for generating an ORR current density of 0.1 mAcm^{-2} in the LSV measurement.

[c] Ref. 5a , Ref. 5b and Ref. 13 are the cited references in the main text.
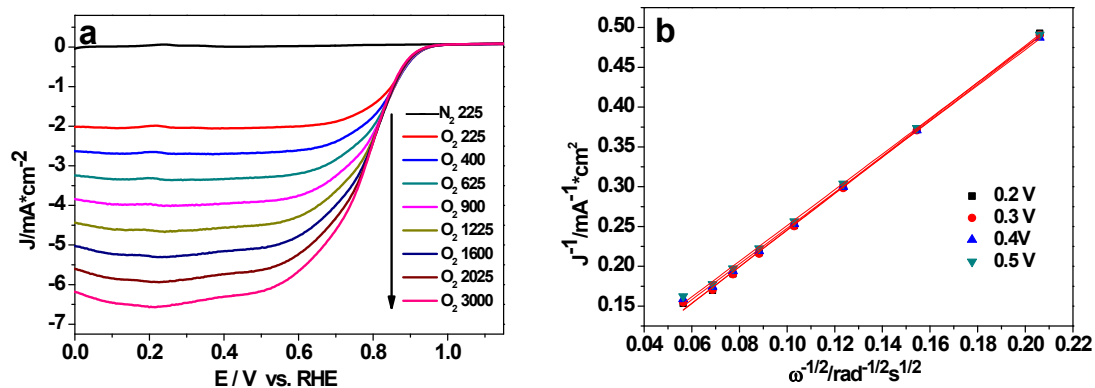
Fig. S7 (a) LSV curves under different rotating speeds and (b) the calculated K–L plots of Pt/C.
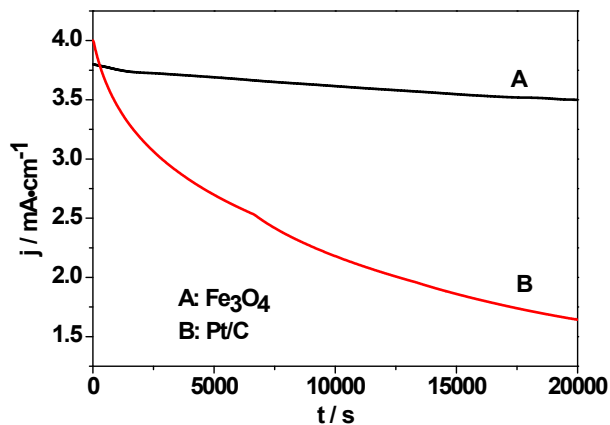
Fig. S8   j-t curves of Fe_3O_4 and Pt/C at 0.56 V in 0.1 M KOH saturated with O_2.

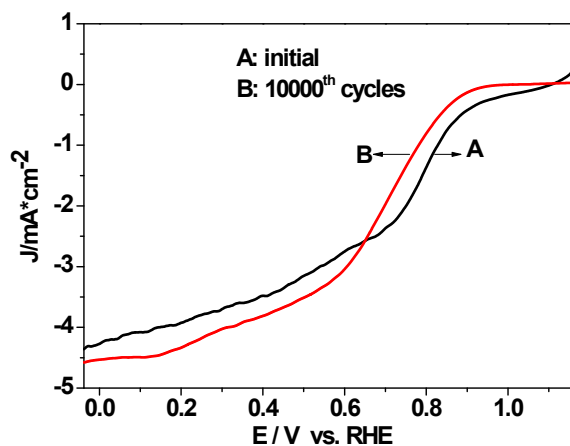**Fig. S9** ORR polarization curves of as-deposited Fe_3O_4 catalyst before and after 10 000 cycles in 0.1 M KOH saturated with O_2 at a rotating rate of 1600 rpm (scan rate: 5 mV s^{-1}).
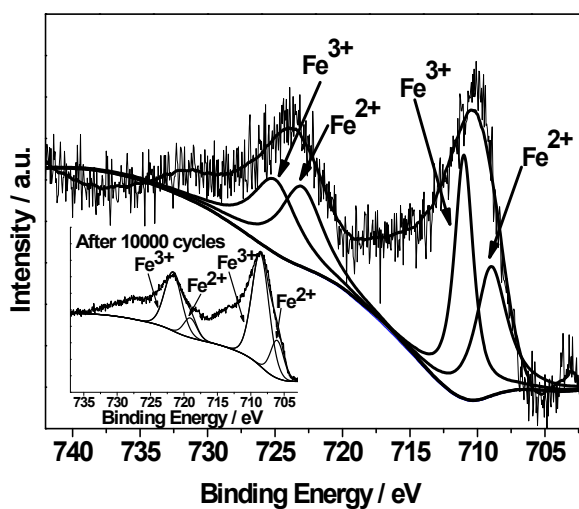

Fig.S10 Fe2p XPS spectra of as-deposited Fe_3O_4 catalyst
before and after 10,000 cycles stability test.

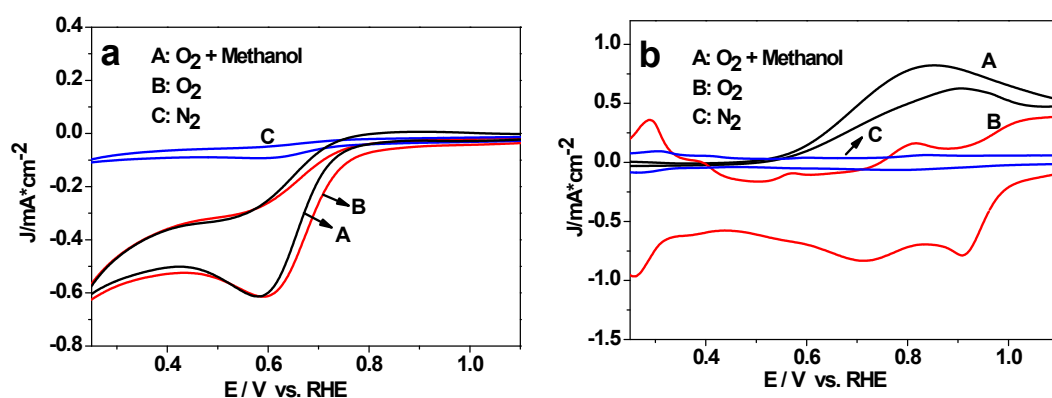**Fig. S11 (a)** CV curves of as-deposited Fe_3O_4 catalyst and (b) Pt/C catalyst in O_2-saturated 0.1M KOH solution with and without 10vol% methanol at a scan rate of 10 mVs^{-1}.

References

[1] Y. Lu, Y. Wang and W. Chen, *J. Power Sources*, 2011, **196**, 3033.

[2] C. Lemire, R. Meyer, V. E. Henrich, Sh. Shaikhutdinov and H. J. Freund, *Surface Science*, 2004, **572**, 103.