Supporting information

Reduction-induced Surface Amorphization Enhances Oxygen Evolution Activity in Co_3O_4

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Experimental Section

All starting materials were used as purchased from Sigma Aldrich. Cobalt acetate ($Co(Ac)_2 \cdot 4H_2O$) was used as cobalt source, sodium carbonate (Na_2CO_3) as the precipitant and ethylene glycol (EG) as the solvent.

A method reported in the literature was employed to synthesize Co_3O_4.[25] Typically, cobalt acetate and sodium carbonate were dissolved in EG and refluxed at 80 °C for one hour to harvest purple precipitates. Then these purple precipitates were then transformed to Co_3O_4 nanopowders by calcination at 450 °C in air for four hours. To reform the surface of these as-prepared Co_3O_4 nanopowders (Co_3O_4-AP), Co_3O_4-AP was reduced at 320 °C under 5 vol% H_2 + N_2 flow for one hour and then stored in air. This reformed sample is noted as Co_3O_4-R.

Thermogravimetry (TG) analysis was done by a Mettler Toledo TGA/DSC analyser under 5 vol% H_2 + N_2 flow at a flow rate of 10 mL/min. The heating rate is 2 °C/min. Crystallographic information was investigated by powder X-ray diffraction (XRD, Bruker D8). X-ray photoelectron spectroscopy (XPS) data was recorded on a Kratos Axis ULTRA X-ray Photoelectron Spectrometer. The incident radiation was Monochromatic Al Kα X-rays. The binding energy of various elements was corrected with the C 1s level of the carbon contamination at 284.8 eV. Transition electron microscopy (TEM) images were taken by FEI F20 transmission electron microscope. Samples for TEM were prepared by drop-drying ethanol suspension onto copper grid. Specific surface area was measured by BET method on ASAP2010 (Micromeritics).

Electrochemical measurements were performed in 0.1 M KOH electrolyte by a CHI 900C bi-potentiostat. Working electrode was prepared as follows: 3 mg of catalysts were dispersed in 3 mL of saturated chitosan aqueous solution assisted by 30 min ultrasound sonication to form a homogeneous ink; then 12 µL of the catalyst ink was cast onto the glassy carbon disk of a rotating ring-disk electrode (RRDE) with the loading ~0.1 mg/cm². The counter electrode is a Pt wire. Hg/HgO, KOH (0.1 M) was used as the reference electrode. The potential was converted to reversible hydrogen electrode (RHE) and corrected with iR compensation (R is the electrolyte resistance

measured by Electrochemical impedance spectroscopy (EIS)). Overpotential was computed using η = E(RHE) - 1.23 V. Linear sweep voltammogram (LSV) was recorded at a scanning rate of 10 mV/s under continuous rotation (1600 rpm), when a potential of 0.524 V was applied to the Pt ring. Tafel plot was obtained by recording the steady-state current at applied potentials descending in steps of 10 mV when the electrode was rotated at 1600 rpm. Cyclic voltammetry (CV) was recorded at a scanning rate of 30 mV/s. EIS was measured in a range of frequency from 100 kHz to 0.1 Hz with a 5mV ac amplitude.

Table S1. XPS spectra fitting parameters and assignments.				
		Co_3O_4-AP	Co_3O_4-R	Assignment
Co $2p_{3/2}$	P1	779.5 (1.5)[a]	779.5 (1.6)	Co (3+)
	P2	781 (1.7)	780.9 (1.7)	Co (2+) ms
	P3	782.5 (2.6)	782.4 (2.6)	Co (2+) ms
	S1	785.8 (3.1)	785.7 (3.1)	Co (2+) ss
	S2	789 (3.4)	789 (3.4)	Co (3+) ss
O 1s	I	529.7		oxide
			529.8	oxide
	II	531.3		O$^-$ compensating for deficiencies in the subsurface
			531	OH$^-$
	III	532.7		Weekly adsorbed species on the surface
			532	CO_3^{2-}
	IV		533.4	H_2O
C 1s	1	284.8	284.8	Carbon contamination C-C
	2	286.2	286.3	Carbon contamination C-O
	3	288		Carbon contamination C=O
			288.8	CO_3^{2-}
[a] Binding energy (full width at half maximum) ms: multiple splitting. ss: shake-up satellite				
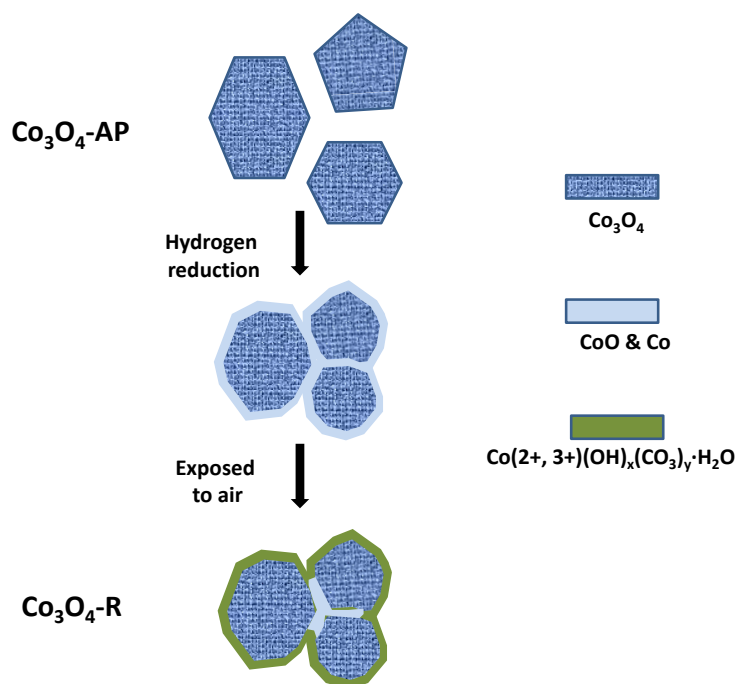
Scheme S1. Scheme of the surface reformation from Co_3O_4-AP to Co_3O_4-R.
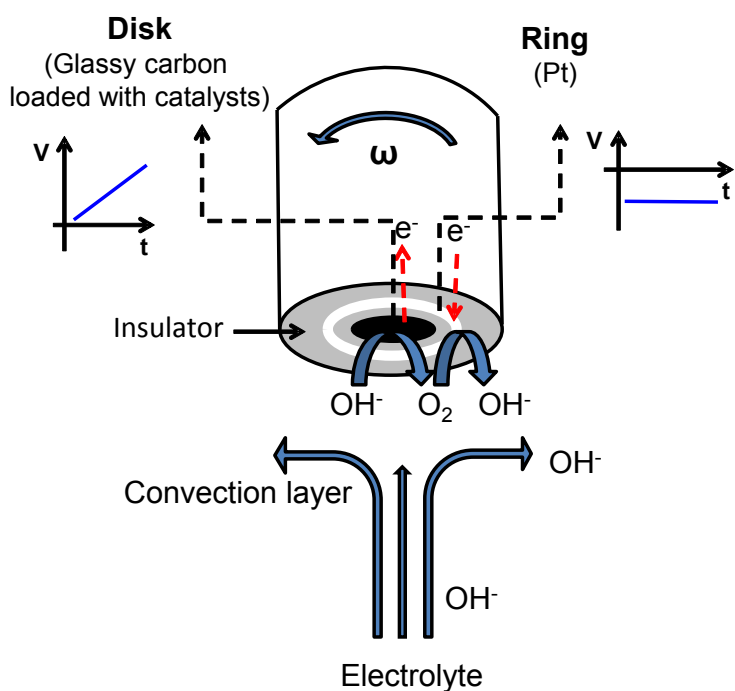
Scheme S2. The working principle of using ring electrode to detect the evolved oxygen species on disk electrode. A Pt ring electrode around the disk electrode was applied with a constant potential (0.524V) at which oxygen can be reduced. When OER occurs on the disk electrode, the evolved oxygen molecules are subsequently convected to the Pt ring electrode by flux and are reduced there. Therefore, the ring current is relevant to the quantity of oxygen evolved at the disk electrode and

can be used as a complementary factor to assess the OER activity without the interference of parallel parasitic Faradaic processes, such as the oxidation of cobalt.

Calculation of turn-over frequency (TOF)

TOF is expressed as the number of oxygen molecules produced per Co atom per second. TOF was calculated from the current density at overpotential (η) of 400 mV by assuming every Co atom was involved in OER catalysis (lower TOF limit).

$$TOF = (j/4F)/(m/M*3)$$

j: Current density at η = 400 mV (mA/cm^2);

F: Faraday constant (96485.3 C/mol);

m: Loading (0.0955 mg/cm^2);

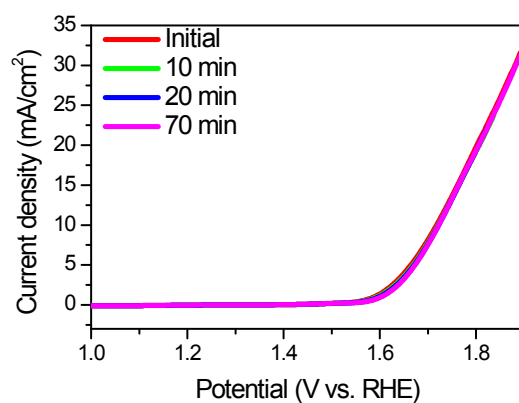M: Molar mass of Co_3O_4 (241g/mol).

Figure S1. Linear sweep voltammograms of Co_3O_4-R after anodic oxidation after anodic oxidation at overpotential of 400 mV for different durations.