

Electronic Supplementary Information

Experimental Section

Materials

Cobalt (II) nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ammonium fluoride (NH_4F) and urea ($\text{CO}(\text{NH}_2)_2$), were purchased from Beijing Chemical Works. All reagents were used as received without further purification. Carbon cloth (CC) was bought from Hongshan District, Wuhan Instrument Surgical Instruments business. The water used in experiments was purified through a Millipore system.

Preparation of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}/\text{CC}$, $\text{Co}_3\text{O}_4/\text{CC}$ and AMO-CoO/CC

$\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ nanoarray was prepared as follows. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.582 g), NH_4F (0.296 g) and $\text{CO}(\text{NH}_2)_2$ (0.909 g) were dissolved in 50 ml distilled water to form a homogeneous transparent solution, which was then transferred to a 50 ml Teflon-lined stainless steel autoclave. A piece of CC (2 cm × 4 cm), which was carefully cleaned with water and ethanol in an ultrasound bath, was immersed in the above aqueous dispersion. The autoclave was sealed and kept at 120 °C for 6 h. The resulting material was taken out and washed with water, subsequently dried at 60 °C for 2 h. To obtain $\text{Co}_3\text{O}_4/\text{CC}$, the sample was calcined at 400 °C in air for 2 h. As for the preparation of AMO-CoO/CC, $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}/\text{CC}$ was dipped in 98 wt% H_2SO_4 for 5 seconds, followed by washing with alcohol.

Characterizations

Powder X-ray diffraction (XRD) data were obtained on a RigakuD/MAX 2550 diffractometer with Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). Scanning electron microscopy (SEM) measurements were conducted on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were made on a Hitachi H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements

Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in three-electrode electrochemical system, with AMO-CoO/CC as working electrode, graphite as counter electrode and Hg/HgO as reference electrode. All tests were carried out at room temperature.

Turnover frequency (TOF) calculation

The surface concentration of active sites associated with the redox Co species was first obtained via electrochemical method. Based on the electrochemical CV curves (Fig. 4a), the oxidation peak current of redox species demonstrates linear change on scan rates (Fig. 4b). The slope of the line can be calculated according to following formula:

$$\text{slope} = \frac{n^2 F^2 A \tau_0}{4RT}$$

n is the number of electrons transferred ($n=1$, as an one-electron process), F is Faraday's constant (96485 C/mol), A is the surface area of the electrode (cm^2), τ_0 is the surface concentration of active sites (mol cm^{-2}), and R and T are the ideal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and the absolute temperature (298 K), respectively. TOF values can be finally calculated based on the equation:

$$\text{TOF} = \frac{JA}{4FM}$$

J is the current density (A cm^{-2}) at certain overpotential, A is the area of the electrode (cm^2). "4" indicates the mole of electrons consumed for generating one mole O_2 from water, F is Faraday's constant (96485 C/mol) and m is the number of moles for active sites (mole).

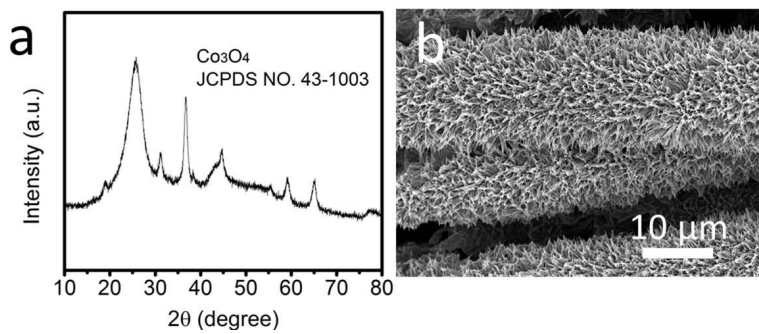


Fig. S1. (a, b) XRD pattern and SEM image of $\text{Co}_3\text{O}_4/\text{CC}$.

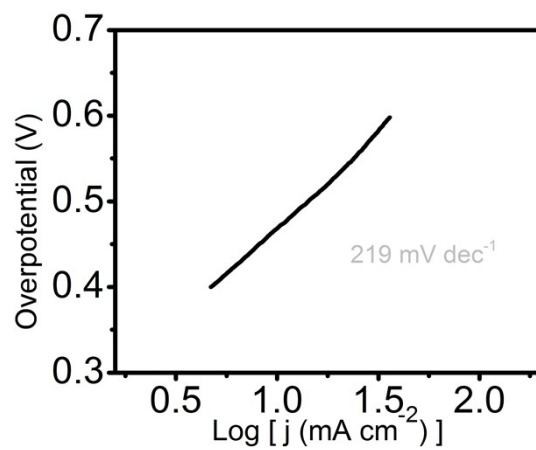


Fig. S2. Tafel plot of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}/\text{CC}$ in 1.0 M KOH.

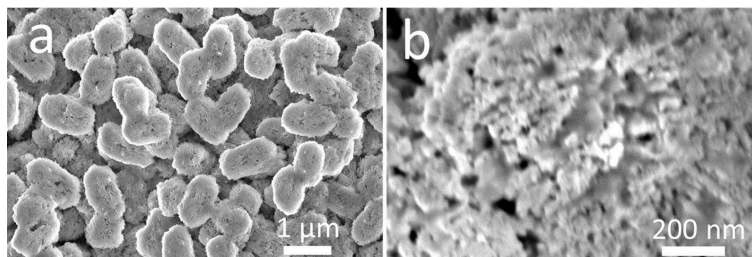


Fig. S3. (a, b) SEM images of AMO-CoO with different magnifications after durability test.

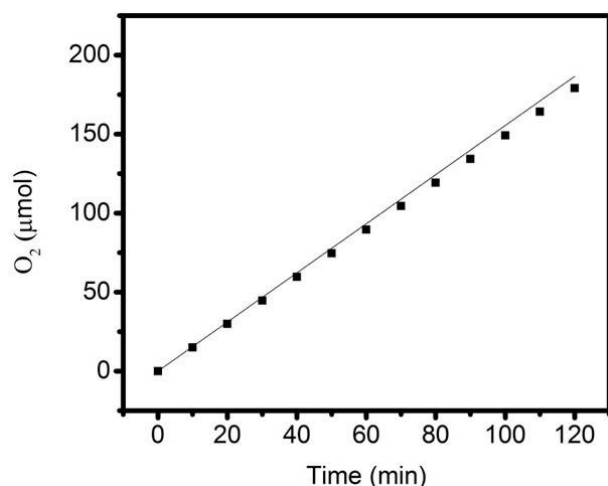


Fig. S4. The quantity of oxygen theoretically calculated and experimentally obtained versus time for AMO-CoO/CC in 1.0 M KOH.