Supplementary information for

Ultrathin cobalt oxide nanostructures with morphology-dependent electrocatalytic oxygen evolution activity

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I. Additional Experimental Details

Materials

All reagents were used as received without further purification. Cobalt sulfate (CoSO₄), cobalt nitrate [Co(NO₃)₂], and urea [CO(NH₂)₂] were purchased from Sinopharm (China). Hypophosphorous acid (H₃PO₂, 50 wt.% in H₂O) were purchased from Aladdin (China). Nafion (5 wt.%) was purchased from Sigma-Aldrich (USA). Absolute ethanol was purchased from Beijing chemical works (China). Carbon cloth (CC, CeTech) or carbon paper (CP, Toray) was processed with potassium permanganate (0.125 g, dissolved in 10 mL of water) and concentrated nitric acid (5 mL) at 100 °C for 8h. Deionized (DI) water was used in all experimental procedures.

Preparation of CoO_x UTNS and NPs

In a typical synthesis, 0.20 mmol of $CoSO_4$, 0.125 mmol of H_3PO_2 and 0.60 mmol of urea were dissolved in 12 mL of DI water under magnetically stirring for 30 min. The obtained homogeneous solution was then transferred into a 25 mL Teflon-lined stainless-steel autoclave. A piece of pre-treated CC (*ca.* 2×2 cm²) was vertically immersed in the above solution. The autoclave was sealed tightly and put into an oven of 120 °C for 6 h. After being cooled to room temperature naturally, the CC was taken out, washed by DI water/ethanol for several times, and dried in a vacuum oven at 60 °C. The preparation procedure of CoO_x NPs was similar to that for UTNS, except for the use of $Co(NO_3)_2$ as precursors instead of $CoSO_4$. The preparation of CoO_x UTNS/CP was similar to that for CoO_x UTNS/CC, except for the use of CP instead of CC as carbon supports.

Composition and structure characterizations

Scanning electron microscopy (SEM) was performed on a JSM-7500F SEM (JEOL, Japan). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a JEM-2100 TEM (JEOL, Japan). Atomic force microscopy (AFM) was performed with a Dimension FastScan Bio (Bruker). X-ray powder diffraction (XRD) patterns were recorded on a MiniFlex 600 diffractometer (Rigaku, Japan). X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALAB 250Xi spectrometer (Thermo). Inductively coupled plasma-optical emission spectrometry (ICP-OES) was measured on an ICAP-9000 spectrometer (Thermo Jarrell Ash).

Electrochemical measurements

The electrocatalytic properties of the materials were studied with a three-electrode system in 1.0 mol L⁻¹ aqueous KOH solution using an electrochemical workstation (CHI660D). A Ag/AgCl (saturated KCl) electrode and a

platinum plate were used as the reference and the counter electrodes, respectively, CoO_x/CC as the working electrode. The polarization curves were recorded at a scan rate of 5 mV/s. The working electrodes were scanned for several times until the signals were stabilized, and then the data for polarization curves were collected, corrected for the 95% *iR*-compensation within the cell. The current density was normalized to the geometrical surface area and the measured potentials *vs*. Ag/AgCl were converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation (where pH = 14 in 1.0 mol L⁻¹ KOH solution): $E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + E^{\theta}_{Ag/AgCl}$ (0.197).

The overpotential was calculated as follows: $\eta = E$ (*vs.* RHE) – 1.23 (V) considering O₂/H₂O equilibrium at 1.23 V *vs.* RHE. The Tafel slope was calculated according to the Tafel equation as follows: $\eta = b \cdot \log (j/j_0)$ where η denotes the overpotential, *b* denotes the Tafel slope, *j* denotes the current density, and j_0 denotes the exchange current density. The C_{dl} was determined by measuring the capacitive current associated with double-layer charging from the scanrate dependence of cyclic voltammetric stripping. The potential window of the cyclicvoltammetric stripping was set to 0.933–0.983 V *vs.* RHE. The scan rates were 10, 20, 30, 40 and 50 mV s⁻¹, respectively. The C_{dl} was estimated by plotting $\Delta j = (j_a - j_c)$ at 0.958 V *vs.* RHE (where j_c and j_a are the cathodic and anodic current densities, respectively) against the scan rate. The slope was twice that of the C_{dl} .

To study the electrocatalytic durability, chronoamperometry measurements were carried out at 50 mA cm⁻² without any *iR*-compensation in 1.0 mol L⁻¹ KOH aqueous solution. Commercial IrO₂/C catalysts were also applied onto the CC support to test their OER properties. About 1.6 mg of commercial 20 wt.% IrO₂/C was dispersed into 0.97 mL of ethanol solution containing 30 μ L of 5 wt.% Nafion solution with the assistance of ultrasonication for at least 1 h to form a homogeneous ink. The ink was then dropped evenly onto the carbon cloth (1 × 1 cm²) and dried. All the tests were carried out at room temperature.

II. Supplementary data



Fig. S1 XRD pattern for the CoO_x ultrathin nanosheets (UTNS), #: diffraction peaks for the carbon cloth.



Fig. S2 XRD pattern for the CoO_x nanoplates (NPs).



Fig. S3 XPS spectra for the P 2p core levels for (a) CoO_x UTNS and (b) CoO_x NPs.



Fig. S4 XPS spectra for the N 1s core levels for (a) CoO_x UTNS and (b) CoO_x NPs.



Fig. S5 SEM images for CoO_x nanoplates obtained at the reaction temperature of 140 °C with cobalt sulfate as cobalt precursors.



Fig. S6 TEM and HRTEM images for CoO_x nanoplates obtained at the reaction temperature of 140 °C with cobalt sulfate as cobalt precursors.



Fig. S7 XRD patterns for CoO_{x} samples obtained at 120 and 140 $^{\circ}\text{C}.$



Fig. S8 (a) XRD patterns for the CoO_x UTNS and the control sample obtained without the presence of H_3PO_2 in the reaction mixture. SEM (b, c), TEM (d), HRTEM (e) images for the control sample. (f) SEM image for the control sample prepared without the addition of urea into the reaction mixture.



Fig. S9 CV curves over a potential range of 0.05-1.6 V (vs. RHE) at a scan rate of 50 mV s⁻¹ in 1.0 M KOH.



Fig. S10 Cyclic voltammograms at scan rates from 10 to 50 mV s⁻¹ in the region between 0.933 and 0.983 V (*vs.* RHE) for different samples: (a) CoO_x UTNS, (b) CoO_x NPs, (c) IrO_2 , and (d) carbon cloth (CC).



Fig. S11 Linear sweep voltammetry (LSV) curves for CoO_x UTNS and CoO_x NPs in 1.0 mol L⁻¹ KOH electrolytes.



Fig. S12 OER electrocatalytic properties of CoO_x UTNS and control samples in 1.0 M KOH electrolytes. (a) LSV curves for CoO_x UTNS (reaction temperature: 120 °C), nanoplates (reaction temperature: 140 °C), IrO₂, and CC; sweep rate: 5 mV s⁻¹. (b) Tafel plots obtained from LSV curves. (c) Charging current density differences plotted against scan rates. The linear slop, equivalent to twice the double-layer capacitance, C_{dl} was used to represent the ECSA for CoO_x UTNS (reaction temperature: 120 °C), nanoplates (reaction temperature: 140 °C), IrO₂, and CC.



Fig. S13 Cyclic voltammograms at the scan rates from 10 to 50 mV s⁻¹ in the region between 0.933 and 0.983 V (*vs.* RHE) for the CoO_x nanoplates prepared at the reaction temperature of 140 °C with sulfate as cobalt precursors.



Fig. S14 SEM and TEM images for the CoO_x UTNS and CoO_x NPs after long-time (22 h) water-oxidation process. (a) SEM and (b) TEM images for CoO_x UTNS; (c) SEM and (d) TEM images for CoO_x NPs.



Fig. S15 XRD patterns for CoO_x UTNS before (black) and after (red) the electrochemical test.



Fig. S16 XRD patterns for CoO_x NPs before (black) and after (red) the electrochemical test.



Fig. S17 XPS full survey spectrum for CoO_x UTNS after water-oxidation tests.



Fig. S18 XPS full survey spectrum for CoO_x NPs after water-oxidation tests.



Fig. S19 XRD patterns for the carbon paper (CP) and CoO_x UTNS/CP.



Fig. S20 SEM images for CP (**a**,**b**) and CoO_x UTNS/CP (**c**–**f**).



Fig. S21 TEM and HRTEM images for CoO_x UTNS exfoliated from the CP supports.



Fig. S22 OER performances for CoO_x UTNS/CP in 1.0 mol L⁻¹ KOH electrolytes. (a) Linear sweep voltammetry (LSV) curve for CoO_x UTNS/CP, Scan rate, 5 mV s⁻¹. (b) Chronopotentiometric (CP) curve for CoO_x UTNS/CP with constant current density.

Table S1 The inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis results for CoO_x UTNS and CoO_x NPs (1 × 1 cm² CC).

	m _{Co} (μg)	m _P (μg)
CoO _x UTNS	147.1±0.5	1.4±0.05
CoO _x NPs	111.0±0.2	2.9±0.04

Table S2 Comparison in catalytic performance for CoO_x UTNS to some previously reported cobalt oxide catalysts.

Material	Overpotential	Overpotential	Tafel slope
	(at 10 mA·cm ⁻² , mV)	(at 50 mA·cm ⁻² , mV)	(mV/dec)
Co ₃ O ₄ -B ¹	318	~363	57.6
Co_3O_4/CoS_2^2	280	~345	63
CoO _x @NC ³	348	-	-
CoO _x @C ³	397	-	-
Co ₃ O ₄ /N-CNTAs ⁴	430	-	79.65
CoO _x nanoplates ⁵	306	~370	65
Co ₃ O ₄ @C-MWCNTs ⁶	320	~400	62
CoO _x @CN ⁷	-	~360	-
Co ₃ O ₄ nanocubes/N-rGo ⁸	318	~340	69
CC@Co ₃ O ₄ ⁹	380	-	75
Co ₃ O ₄ NSs ¹⁰	330	-	69
Co ₃ O ₄ NPs ¹⁰	380	-	96
Calcinated Co ₃ O ₄ NSs ¹⁰	360	-	85
Reduced Co ₃ O ₄ NWs ¹¹	~400	-	72
meso-Co ₃ O ₄ -35 ¹²	411	-	80
meso-Co ₃ O ₄ -100 ¹²	426	-	66
CoO _x (4.3)/CNTs ¹³	394	-	69
CoO _x (6.3)/CNTs ¹³	405	-	69
$CoO_x(7.5)/CNTs^{13}$	416	-	73
$CoO_x(9.5)/CNTs^{13}$	445	-	80
This work	-	315	76

References

- 1 R. J. Wei, M. Fang, G. F. Dong, C. Y. Lan, L. Shu, H. Zhang, X. M. Bu and J. C. Ho, *ACS Appl. Mater. Interfaces*, 2018, **10**, 7079–7086.
- 2 M. M. Guo, K. Xu, Y. H. Qu, F. Y. Zeng and C. L. Yuan, *Electrochim. Acta*, 2018, 268, 10–19.
- 3 Y. C. Hao, Y. Q. Xu, N. N. Han, J. F. Liu and X. M. Sun, J. Mater. Chem. A, 2017, 5, 17804–17810.
- 4 W. L. Tian, H. Y. Li, B. C. Qin, Y. Q. Xu, Y. C. Hao, Y. P. Li, G. X. Zhang, J. F. Liu, X. M. Sun and X, Duan, *J. Mater. Chem. A*, 2017, **5**, 7103–7110.
- 5 W. J. Xu, F. L. Lyu, Y. C. Bai, A. Q. Gao, J. Feng, Z. X. Cai and Y. D. Yin, *Nano Energy*, 2018, 43, 110–116.
- 6 X. Z. Li, Y. Y. Fang, X. Q. Lin, M. Tian, X. C. An, Y. Fu, R. Li, J. Jin and J. T. Ma, *J. Mater. Chem. A*, 2015, **3**, 17392–17402.
- 7 H. Y. Jin, J. Wang, D. F. Su, Z. Z. Wei, Z. F. Pang and Y. Wang, J. Am. Chem. Soc., 2015, 137, 2688–2694.
- 8 S. K. Singh, V. M. Dhavale and S. Kurungot, ACS Appl. Mater. Interfaces, 2015, 7, 442–451.
- 9 C. Guan, X. Liu, W. Ren, X. Li, C. Cheng and J. Wang, Adv. Energy Mater., 2017, 7, 1602391.
- 10 S. C. Du, Z. Y. Ren, Y. Qu, J. Wu, W. Xi, J. Q. Zhu and H. G. Fu, Chem. Commun., 2016, 52, 6705–6708.
- 11 Y. C. Wang, T. Zhou, K. Jiang, P. M. Da, Z. Peng, J. Tang, B. Kong, W. B. Cai, Z. Q. Yang and G. F. Zheng, *Adv. Energy Mater.*, 2014, **4**, 1400696.
- 12 Y. J. Sa, K. Kwon, J. Y. Cheon, F. Kleitz and S. H. Joo, J. Mater. Chem. A, 2013, 1, 9992–10001.
- 13 B. Seo, Y. J. Sa, J. Woo, K. Kwon, J. Park, T. J. Shin, H. Y. Jeong and S. H. Joo, ACS Catal., 2016, 6, 4347–4355.