Supporting information for

Electrochemical Partial Reforming of Ethanol into Ethyl Acetate Using Ultrathin Co$_3$O$_4$ Nanosheets as a Highly Selective Anode Catalyst

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Chemicals: cobalt chloride (CoCl$_2$, analytical grade), ammonium hydroxide (NH$_3$·H$_2$O, 25%). All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. The deionized water used in all experiments with a resistivity of 18.2 was prepared using an ultrapure water system.

Preparation of ultrathin Co$_3$O$_4$ nanosheets. In a typical synthesis, 50mg CoCl$_2$ were dissolved in 10.0 mL of deionized water to form homogeneous solution. Then 8 mL of NH$_3$·H$_2$O was added dropwise to the mixed solution with constant stirring in air for about 10 min. The mixture was sealed in a 50 mL glass pressure vessel and heated at 140 °C for 5 h. The dark products were rinsed three times with deionized water.

Preparation of ultrathin Co$_3$O$_4$ nanocubes (ref. 42). In a typical synthesis, 50mg CoCl$_2$ were dissolved in 10.0 mL of 0.1M KOH solution to form suspension solution. The mixture was sealed in a 50 mL glass pressure vessel and heated at 140 °C for 5 h. The resulting product was filtered and washed with water for several times, and finally calcined in air at 350 °C for 3h.
Preparation of ultrathin Co$_3$O$_4$ nanosheets growing on carbon cloth. Adding a 2x5 cm$^2$ carbon cloth in the synthesis system of ultrathin Co$_3$O$_4$ nanosheets.

Characterizations. Transmission electron microscopic investigation was carried out using a high-resolution transmission electron microscope (JEOL, JEM-2100F) operated at 200 kV and TECNAI F-30 operated at 300 kV. All samples were dispersed in absolute ethanol solution and then dropped on a copper grid. Atomic force microscopy in the present work was performed using a Veeco DI Nano-scope MultiMode V system. The phase purity of the as-prepared sample was characterized by X-ray diffraction (D/max 2550VL/PC) with Cu KR radiation from 10 to 80° at a scanning rate of 10°/min. The X-ray tube voltage and current were set at 40 kV and 30 mA, respectively. UV-Vis absorption spectra were recorded on a Varian Carry 5000 spectrophotometer. Mass spectra were recorded on an Agilent Technologies ESI-TOF-MS. Zeta potentials were measured on Malvern Zetasizer (nano-ZS) with the ethanol solution of Co$_3$O$_4$ nanosheets.

XPS data were acquired using a Kratos AXIS Ultra X-ray photoelectron spectroscopic instrument incorporating a 165 mm hemispherical electron energy analyzer. The incident radiation was monochromatic Al KR X-rays at 150 W. Survey (wide) scans were taken at an analyzer pass energy of 160 eV and multiplex (narrow) high-resolution scans of Co 2p, O 1s, and C 1s at a pass energy of 40 eV. Survey scans were carried out over 1200 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.1 eV steps and 162 ms dwell time.

Temperature program desorption-MS (TPD-MS) measurements were carried out in an in-situ pyrolysis TPD-MS apparatus. The samples were heated from room temperature to 630°C with a heating rateing rate of 5°C/min. the mass spectrum and sample temperature were recorded simultaneously. Each spectrum is an accumulation of 1000 spectra gathered at intervals of 100us. The typical pressure of the pyrolytic furnace is kept at 2x10$^{-4}$ Pa to prevent secondary reactions. Before the test, the sample was dried in a vacuum oven at 80°C for 24 hours.

$^1$H-NMR spectra were recorded on an Advance III 500 MHz Unity plus spectrometer (Bruker). In which 0.5 ml electrolyte was mixed with 0.1 ml D$_2$O (deuterated water) and 0.015 μl dimethyl sulfoxide (DMSO, Sigma, 99.99%) was added as an internal standard. In all the $^1$H-NMR spectra, the singlet at chemical shift of 2.54 ppm was corresponded to the DMSO.

GC-MS was performed on a GCMS-QP2010 Plus (SHIMADZU), which has a detection limit of 5 ppb.
**Electrochemical Measurements.** All electrochemical properties were investigated on a CHI 760e electrochemical workstation in a three-electrode configuration cell using as-prepared sample loading on carbon paper (1×1 cm²) as the working electrode, platinum plate (1×1 cm²) as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode in 1M KOH aqueous electrolyte (pH=13.6). It was calibrated with respect to reversible hydrogen electrode (RHE). In 1M KOH, E (RHE) = E (SCE) + 0.2412 + pH×0.0592 = E (SCE) +1.045.

OER polarization curves were collected at a scan rate of 1.0 mV/s. The long-term stability was examined via applying in the current density of 10mA/cm² on the working electrode for 10 h in 1M KOH aqueous electrolyte. In all measurements, saturated calomel electrode (SCE) was as the reference. Overpotentials were calculated by E (RHE) – 1.23V

The TOF values of the OER catalysts were calculated by the following equation: TOF=Js/4Fm, where J is the current density at different potential (A/cm²), s is the area of electrode (1cm²), F is the faraday constant (a value of 96485 C mol⁻¹), m is the number of moles of the active materials that are deposited onto the electrode.

The ethanol oxidation polarization curves were collected at a scan rate of 1.0 mV/s in 1.0 M KOH and 1.0 M ethanol aqueous solution. In all measurements, we used saturated calomel electrode (SCE) as the reference.

The values of solution resistances were derived from the impedance measurements with the working electrodes immersed into the electrolyte solutions. 85% of the values were used for iR corrections.

The Nyquist plots were measured with frequencies ranging from 100 kHz to 0.1 Hz, and the amplitude of the applied voltage was 1 mV. The impedance data were fitted to a simplified Randles circuit to extract the charge-transfer resistances.

The Faradaic efficiency towards ethyl acetate was calculated from the total amount of charge Q (in units of coulombs) passed through the sample and the total amount of formate produced n (Ethyl acetate, in moles). Q = J × S × t, where J (A/cm²) is the reduction current density at a specific applied potential, S is the electrode area (cm²) and t is the time (seconds) for the constant reduction current. The total amount of ethyl acetate produced was measured using NMR (Bruker AVANCE AV III 400) spectroscopy. Assuming that four electrons are needed to produce one ethyl acetate, the Faradaic efficiency can be calculated as follows: Faradaic efficiency = 4F × n (ethyl acetate) /Q = 4F×n( ethyl acetate)/(J×S×t), where F is the Faraday constant.
Figure S1 TEM images of the ultrathin Co$_3$O$_4$ nanosheets.

Figure S2 The powder XRD of the Co$_3$O$_4$ nanosheets.
Figure S3 (a) UV–vis absorption spectra of the CoCl$_2$ solution before and after adding NH$_3$·H$_2$O in the N$_2$ and air. (b) ESI-MS spectra of the CoCl$_2$ solution after adding NH$_3$·H$_2$O and stirring in the air for 10 min.
Figure S4 Representative TEM images obtained from the contrast experiments under different conditions: (a) conducted under N\textsubscript{2} atmosphere instead of air while keeping other experimental condition constant; (b) CH\textsubscript{3}NH\textsubscript{2} instead of NH\textsubscript{3}·H\textsubscript{2}O; (c) Co(Ac)\textsubscript{2} and (d) Co(NO\textsubscript{3})\textsubscript{2} as precursors.

Figure S5 XRD patterns of obtained from the contrast experiments under different conditions: (a) conducted under N\textsubscript{2} atmosphere instead of air while keeping other experimental condition constant; (b) CH\textsubscript{3}NH\textsubscript{2} instead of NH\textsubscript{3}·H\textsubscript{2}O; (c) Co(Ac)\textsubscript{2} and (d) Co(NO\textsubscript{3})\textsubscript{2} as precursors.
**Figure S6** TEM image of Co$_3$O$_4$ nanocrystals collected from the reaction with the same condition used in the synthesis of Co$_3$O$_4$NS but prepared by supplying different amount of NH$_3$·H$_2$O: (a) 1.0 mL, (b) 2.0 mL, (c) 4.0 mL and (d) 8.0 mL.

**Figure S7** TEM images of the product under the same reaction conditions. Used 0.01M KOH (a) and 0.1M KOH (b) to instead of NH$_3$·H$_2$O.
Figure S8 Zeta-potentials of the Co3O4 nanosheets.

Figure S9 HAADF-STEM image (a) and EDS-mapping (b) of Co3O4 nanosheets. The scale bar is 20nm.
Figure S10 XRD patterns of products obtained at hydrothermal time. (a) 0 h, (b) 0.5 h, (c) 1 h, and (d) 3 h.

Figure S11 TEM images of the products with a hydrothermal time of (a) 0 h, (b) 0.5 h, (c) 1 h, and (d) 3 h.
Figure S12 Schematic of the formation of the Co$_3$O$_4$ nanosheets.

Figure S13 (a), (b) TEM images and (c) HR-TEM image of the Co$_3$O$_4$ nanocubes, (d) XRD patterns of the Co$_3$O$_4$ nanocubes.
Figure S14 (a) The TOFs for the ultrathin $\text{Co}_3\text{O}_4$ nanosheets and $\text{Co}_3\text{O}_4$ nanocubes under the low potential. (b) The polarization curves after 3000 CV cycles with the $\text{Co}_3\text{O}_4$ nanosheets electrode.

![Graphs showing TOFs and polarization curves](image)

Figure S15 TEM of the catalysts after electrochemical tests: (a) $\text{Co}_3\text{O}_4$ nanosheets; (b) $\text{Co}_3\text{O}_4$ nanocubes; (c) XRD spectrum. The above process was performed on 5 similar working electrodes with larger mass loading (1 mg/cm²) and all the samples collected were used to conduct the above characterizations.

![TEM images and XRD spectrum](image)
Figure S16 CVs of the Co$_3$O$_4$ in 1.0 M KOH solution before and after 1.0 M ethanol addition. Both Co$_3$O$_4$ catalysts modified carbon paper electrode showed an amperometric response to ethanol. Compared with OER, electrooxidation of ethanol can be achieved on Co$_3$O$_4$ at a lower potential. While Co$_3$O$_4$ nanosheets showed better electrocatalytic towards OER and electrooxidation of ethanol. Scan rate: 1.0 mV/s.

Figure S17 Carbon paper show little catalytic in both OER and ethanol reforming.
Figure S18 (a) Chronoamperometry curves of ultrathin Co$_3$O$_4$ multilayer nanosheets and nanocubes at 1.545V vs. RHE for 1h. (b) Chronopotentiometry curves of multilayer nanosheets at a constant current density of 20 and 50 mA/cm$^2$.

Figure S19 GC-MS of the product obtained after chronoamperometry curves tests at 1.545V vs. RHE. (a) MS spectrum of ethanol; (b) MS spectrum of ethyl acetate. GC-MS results confirmed that the product is ethyl acetate, a product of four-electron oxidation processes.
Figure S20 $^1$H NMR spectra of ethyl acetate (dark cyan line), product after bulk electrolysis (BE) at a potential of 1.545 V (vs. RHE) within 1.0 h on Co$_3$O$_4$ nanosheets modified carbon paper electrode (blue line), ethanol (red line) and the spectrum of the solution before BE with 15 mM added ethyl acetate (black line) to further confirm the characteristic peak at 1.72 ppm assignments for ethyl acetate.
Figure S21 N$_2$ adsorption isotherm of Co$_3$O$_4$ nanosheets and nanocubes. Based on the BET analysis, the surface areas of the Co$_3$O$_4$ nanosheets and nanocubes were 43.4 m$^2$/g and 10.7 m$^2$/g, respectively (a). The normalized polarization curves of multilayer ultrathin Co$_3$O$_4$ nanosheets and Co$_3$O$_4$ nanocubes by the BET surface area of electrocatalysts in OER (b) and ethanol reforming (c).

Figure S22 Top views of the proposed terminations of Co$_3$O$_4$ (111) and (100). Dark gray, silver, and red spheres are Co$_{\text{oct}}$, Co$_{\text{tet}}$, and O atoms, respectively. Large and small spheres refer to atoms on the surface and in inner layers, respectively.
Figure S23 The high-resolution XPS spectra of Co2p the Co$_3$O$_4$ nanosheets and nanocubes. In the NS, the area of the peak at 799.6 eV (Co$^{3+}$) was much larger than that at 781.5 eV (Co$^{2+}$), and the molar ratio of Co$^{3+}$/Co$^{2+}$ is higher than that in the NCs.

Figure S24 Cyclic voltammetry of Co$_3$O$_4$ nanocrystals in 0.1M KOH and the scan rate was 100 mV/s.
Figure S25 Nyquist plots of ultrathin Co₃O₄ nanosheets and nanocubes under the potential of 1.50 V (vs. RHE). Z′ is real impedance and -Z″ is imaginary impedance. Co₃O₄ nanosheets exhibited superior electrical conductivity and ion transport kinetics over nanocubes (the mass loading is about 0.1 mg/cm²). The electrochemical interface can be modeled by an equivalent circuit containing the total Ohmic resistance of the cell (RΩ); charge-transfer resistance (Rct) and the double-layer capacitance (Cdl).
Figure S26 (a) SEM image of Co$_3$O$_4$ Nanosheets. The nanosheets were grown on carbon cloth to form a flexible anode electrode (the mass leading about 0.5 mg/cm$^2$), the NSs still maintained their ultrathin multilayer structure. (b) TEM image of Ni-Mo nanopowders (mass leading 0.1mg/cm$^2$). Both of the anode and cathode electrode area was 10 cm$^2$.

Figure S27 (a) $^1$H NMR spectra of the product obtained at different reaction times. (b) Gas chromatograms of product obtained in the ethanol reforming cells after 48h.
Table S1 The analysis of the XPS spectra.

| Catalysts            | Molar content of $\text{Co}^{3+}$ | Molar content of $\text{Co}^{2+}$ | $\text{Co}^{3+}/\text{Co}^{2+}$ |
|----------------------|-----------------------------------|-----------------------------------|---------------------------------|
| Co$_3$O$_4$ nanosheets | 73.6%                             | 26.4%                             | 2.79                            |
| Co$_3$O$_4$ nanocubes | 65.7%                             | 34.3%                             | 1.92                            |