Ultrathin mesoporous Co$_3$O$_4$ nanosheets with excellent photo-/thermo-catalytic activity

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Experimental

Co$_3$O$_4$-O preparation

Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, A. R.) and oxalic acid dihydrate (C$_2$H$_2$O$_4$·2H$_2$O, A. R.) were purchased from Shanghai Chemical Company. All of the materials were used without further purification.

Co$_3$O$_4$-O nanoparticles were synthesized through a template-free strategy of decomposing self-made bimetal oxalate as previously reported. In a typical process, 0.01 mol Co(NO$_3$)$_2$·6H$_2$O was dissolved in 40 mL deionized water under magnetic stirring. 0.01 mol H$_2$C$_2$O$_4$·2H$_2$O was dissolved in 15 mL deionized water at 60 °C. The latter solution was added dropwise to the former under vigorous magnetic stirring, resulting in a precipitation forming. After stirring for another 1 h in an ice bath, the solid residue was separated by filtration, washed copiously with deionized water, and dried in air at 60 °C followed by calcinations in air at 250 °C for 2 h (at 1 °C min$^{-1}$ heating rate). The sample was denoted as Co$_3$O$_4$-O.

Electrophoresis of SS-Co$_3$O$_4$ (EP)

The electrophoretic deposition was performed on a DC power supply (HY3003) with stainless steel mesh (SS, approximately 2 cm × 3 cm) as both the cathode and anode. 40 mg Co$_3$O$_4$-O and 10mg iodine were added to 50 mL acetone, the whole solution were ultrasonic for 3 minutes. The voltage was set to 10 V and the whole electrophoretic deposition process lasted for 4 minutes, the as-obtained sample was denoted as SS-Co$_3$O$_4$ (EP) and washed with deionized water, then dried in air at 60 °C.

Electrochemical analysis

The photocurrent spectra were performed in a three-electrode cell (quartz window) with 0.1 M Na$_2$SO$_4$ as electrolyte at a potential of 0.5 V. A Pt ring was used
as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the catalyst as the working electrode. A CHI 660C electrochemical workstation (Shanghai Chenhua, China) was used for the photocurrent measurements. As for light sources, a 500W Xe lamp (CHF-XM500) was used.

**TG/DTA measurement**
Thermogravimetric/differential thermal analyzer (TG/DTA) measurements were conducted using a NETZSCH STA 449C apparatus with an air flow of 20 mL min\(^{-1}\) and a heating rate of 10 K min\(^{-1}\).

**Raman spectra** were recorded on a microscopic confocal Raman spectrometer (Renishaw 1000NR) with an excitation of 514 nm laser light.

Table S1 The amount of Co$_3$O$_4$ grown on each SS substrate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Co$_3$O$_4$ nanosheets scratched down from the SS</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Weight (mg)</td>
<td>6.4</td>
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</table>
Fig. S1 XRD patterns of Co(OH)$_2$ precursor and SS-Co$_3$O$_4$
As seen from Fig. S2A, the Co(OH)\(_2\) obtained by electrodeposition undergoes a two step weight loss due to dehydration and deposition, rather than a single step weight loss for the \(\beta\)-Co(OH)\(_2\).\(^2\) The weight loss below 152 °C is attributed to the removal of the absorbed water and the evaporation of the intercalated water molecules. And the weight loss above 152 °C is associated with the loss of water produced by the decomposition and dehydroxylation of Co(OH)\(_2\).\(^3\) After thermally oxidative transformation into Co\(_3\)O\(_4\), the net weight loss observed is ca. 19.52%, much larger than that of 13.6% of the \(\beta\)-Co(OH)\(_2\). These data further indicates the formed
precursor is $\alpha$-Co(OH)$_2$ phase rather than $\beta$-Co(OH)$_2$ and show the crystallization of Co$_3$O$_4$.$^4$

The sample scratched down from the SS clearly displayed five bands located at approximately 476 (E$_g$), 191 (F$_{2g}$), 513 (F$_{2g}$), 607 (F$_{2g}$), and 680 (A$_{1g}$) cm$^{-1}$, consonant with other references about Co$_3$O$_4$.$^5,6$

Fig. S3 UV-Vis-IR spectra of SS, SS-Co$_2$O$_4$ and Co$_2$O$_4$-O
Fig. S4 (A) XRD patterns of Co\textsubscript{3}O\textsubscript{4}-O. (B) TG and DTA curves of the Co-oxalate precursor. (C)(D) Transmission electron microscopy (TEM) images of Co\textsubscript{3}O\textsubscript{4}-O

Mainly, one endothermic peak and one exothermic peak can be found for the Co-oxalate precursor. The endothermic and exothermic peaks represent the loss of structural water (weight loss of 18.83\%) and decomposition of the C\textsubscript{2}O\textsubscript{4}\textsuperscript{2-} groups (weight loss of 36.85\%), respectively.\textsuperscript{1}
The Brunauer–Emmett–Teller (BET) specific surface area was measured to be 128.3 m²g⁻¹.
Fig. S6 Temporal change of the temperature on the Co$_3$O$_4$-O and SS under the irradiation of the Xe lamp.
Fig. S7 Blank experiments for C₃H₈ and C₃H₆ oxidation
Fig. S8 Consecutive cyclic tests for C$_3$H$_8$ oxidation over SS-Co$_3$O$_4$ under PTC conditions
Fig. S9 (A) Current–time (i–t) curves of SS, SS-Co$_3$O$_4$(EP), and SS-Co$_3$O$_4$ electrodes recorded at 0.5V vs. SCE. (B) Current–time (i–t) curves of SS-Co$_3$O$_4$ under different temperature.
Fig. S10 (A) FTO-Co$_3$O$_4$ (6.1 mg) (B) SS-Co$_3$O$_4$ (7.0 mg) (C) Ni-Co$_3$O$_4$ (6.8 mg) (D) (E)C$_3$H$_8$ and C$_3$H$_6$ oxidation over SS-Co$_3$O$_4$, Ni-Co$_3$O$_4$, FTO-Co$_3$O$_4$, and Co$_3$O$_4$ nanosheets scratched down from the SS substrate (50 mg) under simulated sunlight (Xe lamp).