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Electronic Supplementary Information

for

Synergistic tuning of oxygen vacancies and d-band centers of ultrathin cobaltous dihydroxycarbonate nanowires for enhanced electrocatalytic oxygen evolution

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Additional experimental data including possible reaction mechanism for Co-OH NWs and OER, XPS, BET, ECSA and water contact characterizations of Co-OH NWs, oxygen vacancy and band structure information of Co-OH NWs, and comprehensive characterizations of Co_3O_4 NPs.

Table of contents

Scheme S1 The possible reactions involved in the preparation of Co-OCH NWs.

Scheme S2 The general mechanism for electrochemical oxygen evolution reaction.

Fig S1 A representative AFM image of the Co-OCH NWs-8.7 nm.

- Fig S2 TEM image, XRD, full XPS spectrum and high-resolution O1s nd Co2p spectrum of Co₃O₄ nanoparticles.
- Fig S3 High-resolution Co2p spectra of Co-OCH NWs-8.7 nm and cubic Co₃O₄ nanoparticles.
- Fig S4 Nitrogen adsorption/desorption isotherms BET surface areas of the asprepared Co-OCH nanowires samples.
- Fig S5 CV and the corresponding linear plots of the current density of the asprepared Co-OCH nanowire samples measured in a non-Faradaic region at different scan rates.
- Fig S6 The specific activity (i.e., current normalized by BET surface area) of the as-prepared Co-OCH NWs samples.
- Fig S7 Current density plotted against the ECSA of all Co-OCH NWs samples and the estimated activities of the Co-OCH NWs-8.7 nm sample.
- Fig S8 Water contact angles measured at the surfaces coating with the as-prepared Co-OCH NWs samples.
- Table S1 Co, O, C, and N element content (at %) in the as-prepared Co-OCH NWs and Co₃O₄ nanoparticles.
- Table S2 Summary of area percentages of different oxygen species of the asprepared Co-OCH NWs samples.
- Table S3 The content of N_e , O_V and E_{FB} in Co-OCH nanowires.
- Table S4 The VBM and the 3d electron center of the as-prepared Co-OCH NWs samples.

$$Co(COOCH_3)_2 + 2H_2O = 2CH_3COOH + Co(OH)_2$$
(1)

$$CH_3COOH+2O_2=2CO_2+2H_2O$$
(2)

$$NH_2CH_2CH_2CH_3 + H_2O = NH_3 + CH_2CH_2CH_3OH$$
(3)

$$NH_3 + H_2O = NH_4^+ + OH^-$$

$$\tag{4}$$

$$CO_2 + 2OH^{-} = CO_3^{2^{-}} + H_2O$$
 (5)

$$Co^{2+} + OH^{-} + 0.5CO_3^{2-} + 0.11 H_2O = Co(CO_3)_{0.5}(OH) \cdot 0.11 H_2O$$
 (6)

Scheme S1 The possible reactions involved in the preparation of cobaltous dihydroxycarbonate nanowires



Fig. S1A representative AFM image of the Co-OCH NWs with an average size -8.7 nm.



Fig. S2 (a) TEM image, (b) XRD, (c) full XPS spectrum, (d) high-resolution O1s spectrum and (e) high-resolution Co2p spectrum of Co₃O₄ nanoparticles (the control sample).



Fig.S3 High-resolution Co2p spectra of Co-OCH NWs-8.7 nm (bottom) and cubic Co_3O_4 nanoparticles (top).



Fig. S4 (a) Nitrogen adsorption/desorption isotherms of the as-prepared Co-OCH NW samples and (b) their corresponding BET surface areas.



Fig. S5 (a, c, e) Cyclic voltammograms and (b, d, f) the corresponding linear plots of the current density variation vs. scan rates at 0.1 – 0.2 V of the as-prepared Co-OCH NWs samples measured in a non-Faradaic region at different scan rates in 1.0 M KOH: (a-b) Co-OCH NWs-8.7 nm sample, (c-d) Co-OCH NWs-12.5 nm sample, (e-f) Co-OCH NWs-16.7 nm sample.



Fig. S6 The specific activity (i.e., current normalized by BET surface area) of the asprepared Co-OCH NWs samples at a potential of 1.55 V (vs. RHE).



Fig. S7 Current density at 1.55, 1.57 and 1.60 V (vs. RHE) plotted against the ECSA of all Co-OCH NWs samples and the estimated activities of the Co-OCH NWs-8.7 nm sample with equal ECSA at such potentials.



Fig. S8 Water contact angles measured at the surfaces coating with the as-prepared Co-OCH NWs samples: (a) Co-OCH NWs-8.7 nm sample, (b) Co-OCH NWs-12.5 nm sample, (c) Co-OCH NWs-16.7 nm sample.

Table S1 Co, O, C, and N element content (at %) in the as-prepared Co-OCH nanowires and Co₃O₄ nanoparticles.

Sample	Со	0	С	Ν
Co-OCH NWs-8.7 nm	19.24%	51.03%	27.75%	1.98%
Co-OCH NWs-12.5 nm	19.88%	51.41%	27.18%	1.53%
Co-OCH NWs-16.7 nm	20.27%	52.51%	25.72%	1.50%
Co ₃ O ₄	35.06 %	47.96%	15.72%	1.26%

* The C signal in the Co₃O₄ sample was originated from the carbon substrate; while the N signal in all the sample was originated from the surface ligands.

Table S2 Summary of area percentages of different oxygen species obtained from thedeconvoluted spectra of the as-prepared Co-OCH NWs samples.

Samples	Ov	O _A	OL
Co-OCH NWs-8.7 nm	78.6 %	17.2%	4.2%
Co-OCH NWs-12.5 nm	75.7%	17.6%	6.7%
Co-OCH NWs-16.7 nm	70.3%	20.8%	8.9%
Co ₃ O ₄	65.4%	9.9%	24.7%

Samples	Ne	E _{FB}	O _V (estimated)
Co-OCH NWs-8.7 nm	$7.9 \times 10^{17} \text{ cm}^{-3}$	-0.74 V	$3.9 \times 10^{17} \mathrm{cm}^{-3}$
Co-OCH NWs-12.5 nm	$6.3 \times 10^{17} \mathrm{cm}^{-3}$	-0.78 V	$3.2 \times 10^{17} \mathrm{cm}^{-3}$
Co-OCH NWs-16.7 nm	$3.4 \times 10^{17} \text{cm}^{-3}$	-0.83 V	$1.7 \times 10^{17} \mathrm{cm}^{-3}$

Table S3 N_e and O_V content and E_{FB} position in the as-prepared Co-OCH NW samples

 E_{FB} : flat-band potentials, which was determined from the intercept of Mott-Schottky curve on the V axis (i.e., x axis).

Table S4 The VBM and the 3d electron center of the as-prepared Co-OCH NWs-8.7nm, Co-OCH NWs-12.5 nm and Co-OCH NWs-16.7nm samples.

Samples	VBM (relative to E _F)	D_{center} (relative to E_F)
Co-OCH NWs-8.7 nm	0.93 eV	-5.92 eV
Co-OCH NWs-12.5 nm	1.17 eV	-6.26 eV
Co-OCH NWs-16.7 nm	1.41 eV	-6.48 eV

*VBM: the valence band maximum, which was estimated by determining the edge of XPS valence band spectrum.



Scheme S2 The general mechanism for electrochemical oxygen evolution reaction occurring on the surfaces of metal-containing catalysts in an alkaline solution.

According to previous studies,³⁴ there are two different ways to form oxygen molecules from a MO intermediate. One possible path is to generate oxygen molecules from step (1) to (2) and then to (5): firstly, MOH* species are formed by adsorbing OH⁻ groups onto the surfaces of catalysts (M) with accompanying one electron generation; and the surface-absorbed MOH* species then react with an OH⁻ group to form surface-adsorbed atomic O (MO*); finally, two MO* species combine together to produce O₂. The other way involves the formation of MOOH* intermediates: the surface-adsorbed atomic O (MO*) species can react with an OH⁻ group to generate MOOH* species and releases an electron; the MOOH*species then continue to bind with an OH⁻ groups to generates O₂ finally.