



Supporting Information

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Anchoring CoO Domains on CoSe₂ Nanobelts as Bifunctional Electrocatalysts for Overall Water Splitting in Neutral Media

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Characterization of CoSe₂-DETA

The CoSe₂/DETA (DETA = diethylenetriamine) nanobelts grown on Ti mesh were synthesized by the reported method with slight modifications.^[1] We can see from Figure S1, that nanobelts were grown on Ti mesh on a large scale, with 30-300 nm in width and several dozens of micrometers in length. The TEM image further indicates the flexible nanobelt structure. The XRD patterns are consisted with that of the reported CoSe₂/DETA,^[2] further supporting the formation of CoSe₂-DETA precursors.

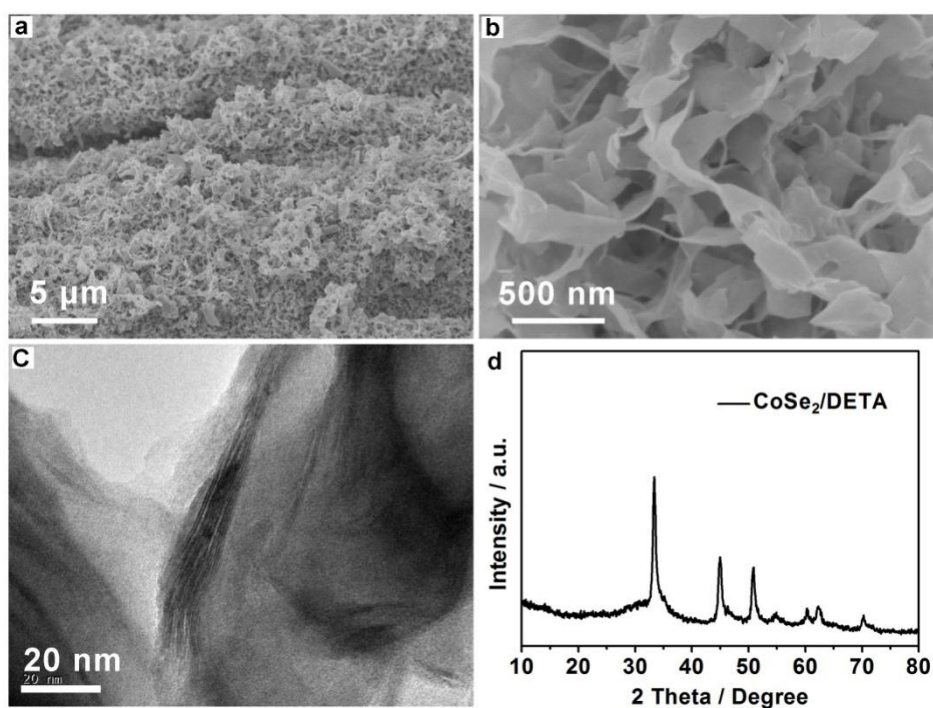


Figure S1. (a) Low- and (b) high-magnification SEM images of CoSe₂-DETA precursors. (c) A typical TEM image and (d) XRD pattern of CoSe₂-DETA precursors.

Elements in the as-prepared CoO/CoSe₂

Energy-dispersive X-ray spectroscopy (EDX) reveals that the sample on Ti mesh is composed of O, Co and Se elements.

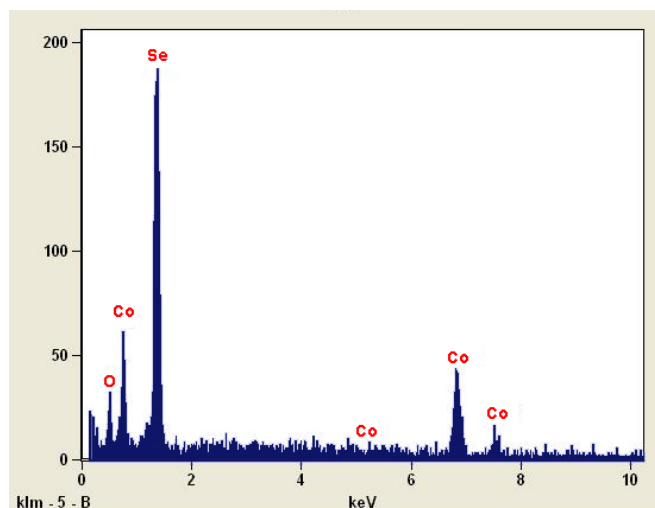


Figure S2. The EDX spectrum of the as-prepared CoO/CoSe₂ synthesized by one-step calcination of CoSe₂-DETA (DETA = diethylenetriamine) precursors at 450 °C in mixed O₂ (0.018 vol%)/Ar atmosphere.

HRTEM image of CoO/CoSe₂

The lattice spacing of 2.10 Å and 2.60 Å, as expected for CoO (200) planes and CoSe₂ (210) planes, are observed for domains and nanobelts, respectively. This observation reveals that small CoO domains were anchored on the CoSe₂ nanobelts.

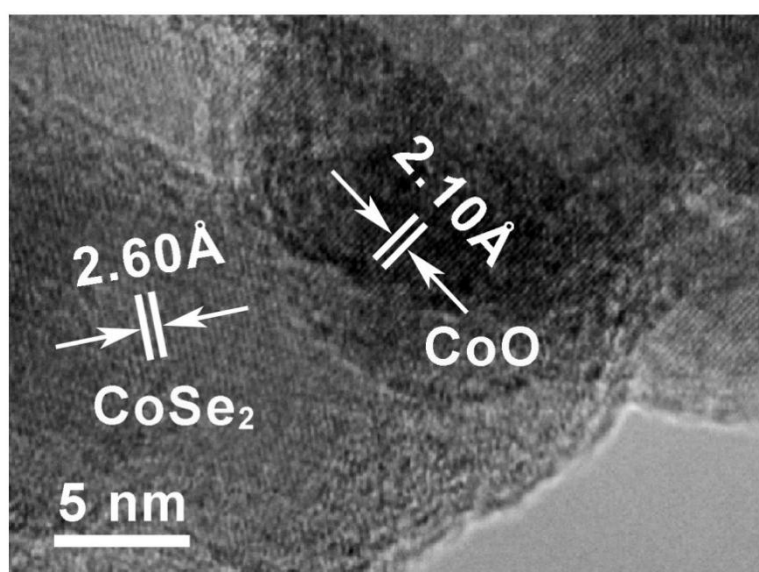


Figure S3. HRTEM image of the as-prepared CoO/CoSe₂ synthesized by one-step calcination of CoSe₂-DETA (DETA = diethylenetriamine) precursors at 450 °C in mixed O₂ (0.018 vol%)/Ar atmosphere.

Characterization of pure CoSe₂

For comparison, the pure CoSe₂ was obtained by annealing CoSe₂-DETA precursors in high-purity Ar atmosphere with other conditions remaining unchanged. As we can see from Figure S4, nanobelt-like morphology can be preserved, which is similar to that of the as-prepared CoO/CoSe₂. Additionally, all XRD patterns can be attributed to pure CoSe₂ (JCPDS no. 09-0234), suggesting that CoSe₂ can be synthesized in the absence of oxygen in the Ar atmosphere.

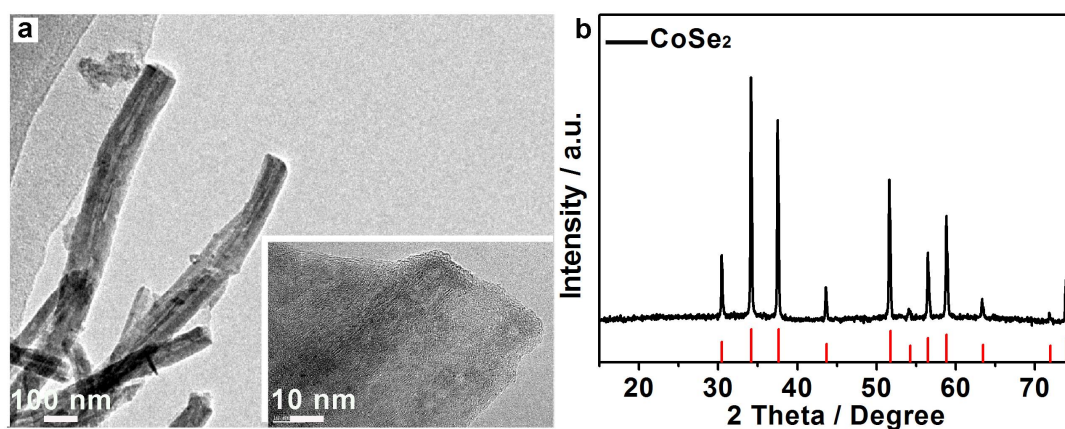


Figure S4. (a) TEM image and (b) XRD pattern of pure CoSe₂ nanobelts. Inset in (a) is the high-resolution TEM image.

Characterization of commercial CoO

CoO was purchased from Aladdin Industrial Corporation (AR) and was used as received without further treatment.

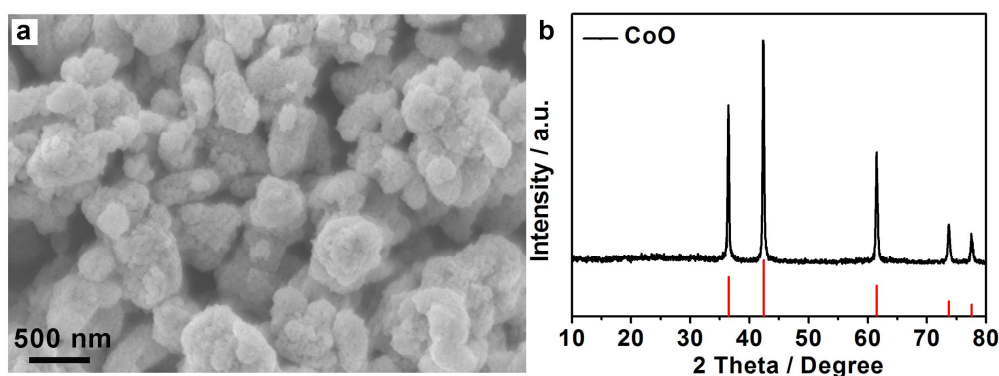
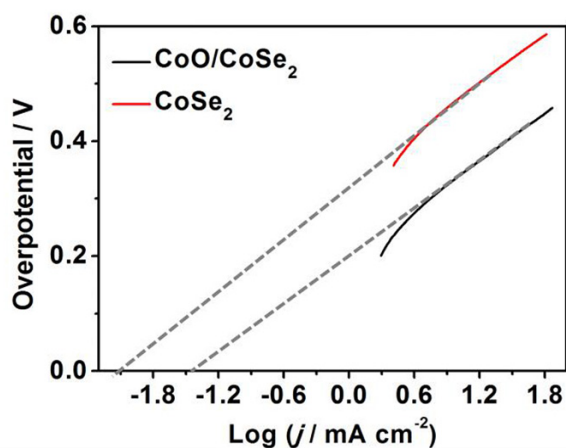
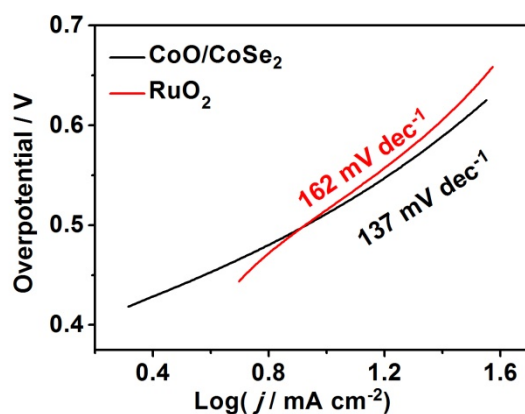


Figure S5. (a) SEM image of CoO. (b) XRD pattern of pure CoO sample corresponding to CoO (JCPDS no. 43-1004).

Calculation of exchange current density**Figure S6.** Calculated exchange current density by extrapolating the Tafel plot.**Characterization of commercial RuO₂**

RuO₂ was purchased from Aladdin Industrial Corporation (AR) and was used as received without further treatment. The measured Tafel slope of commercial RuO₂ is 162 mV dec⁻¹.

**Figure S7.** Tafel plots for CoO/CoSe₂ and commercial RuO₂.

Stability of CoO/CoSe₂ during HER and OER

The SEM and TEM images suggest that the CoO/CoSe₂ electrocatalyst still maintains the original nanobelt structure after HER and OER measurements.

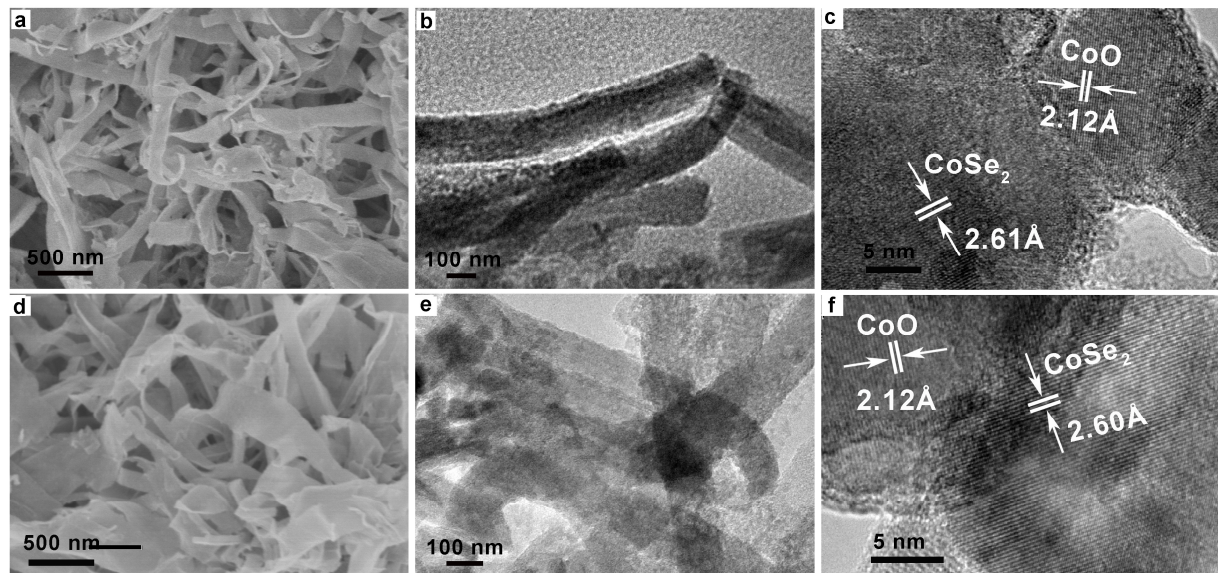


Figure S8. (a) SEM, (b) TEM and (c) HRTEM images of CoO/CoSe₂ after HER tests. (d) SEM, (e) TEM and (f) HRTEM images of CoO/CoSe₂ after OER tests.

The corresponding XPS spectra of Co 2p region indicate that a similar peak profile is displayed for post-HER (780.4 eV) or post-OER (780.2 eV) catalyst in spite of a slight positive shift compared with the as-prepared CoO/CoSe₂ electrocatalyst (779.6 eV).

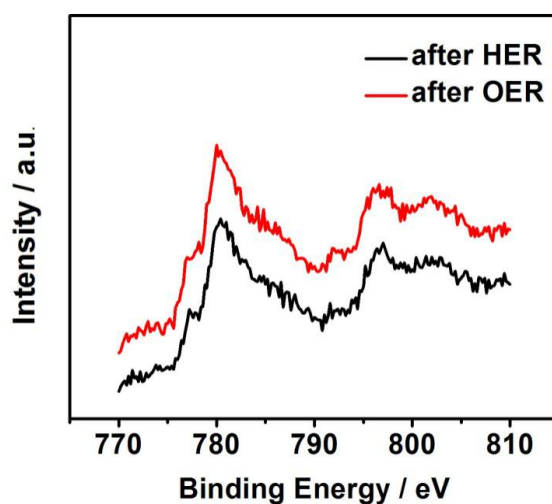


Figure S9. XPS spectra of the Co 2p region for CoO/CoSe₂ after HER and OER.

Characterization of Ti mesh

Ti mesh (diameter: 0.12 mm) was purchased from Hongyun Metal Products Co., Ltd.

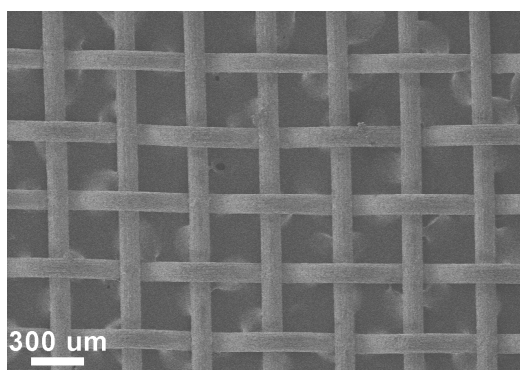


Figure S10. SEM image of Ti mesh.

Linear sweep voltammetry (LSV) curves (HER and OER) before and after I-R corrected

All the potential values measured were calibrated by using the following equation:

$E_{\text{after}} = E_{\text{before}} - IR$, where I was the current flowing through the cell and R was the ohmic resistance of the cell. The resistances, R , were measured by the IR compensation function available on the electrochemical workstation (CHI 660D, CH Instruments, Austin, TX).

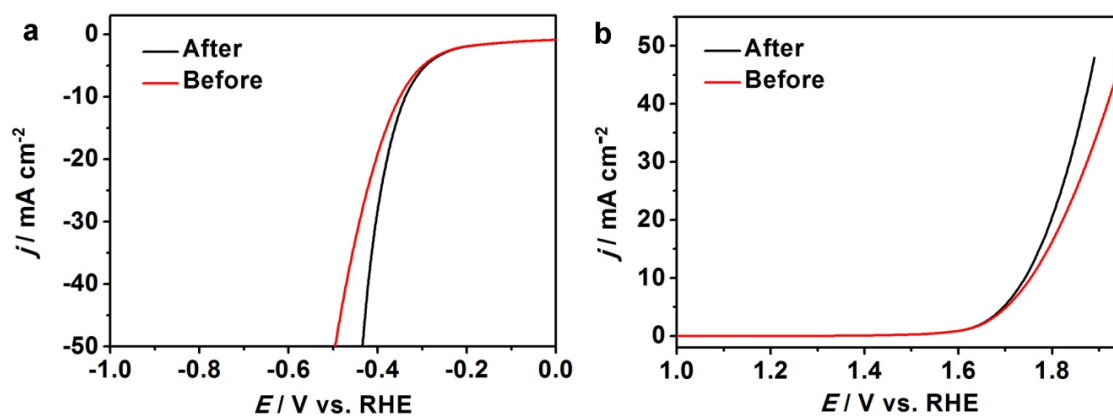


Figure S11. (a) HER polarization curves of CoO/CoSe₂ before and after I-R correction. (b) OER polarization curves of CoO/CoSe₂ before and after I-R correction.

Table S1. Comparison of the HER activity of CoO/CoSe₂ under neutral conditions with some representative HER catalysts recently reported.

Sample	Loading/substrate	electrolyte	Current density (<i>j</i>)/ mA cm ⁻²	Overpotential/mV at the corresponding <i>j</i>	Reference
Co@nitrogen-rich carbon nanotubes	0.28 mg/cm ²	0.1 M phosphate buffer (pH = 7)	2 10	380 540	<i>Angew. Chem.</i> 2014 , <i>126</i> , 4461
CoO/CoSe ₂	2 mg cm ⁻² Ti mesh	0.5 M phosphate buffer solution (pH = 6.86)	2 10 50	200 337 434	This work
Metallic cobalt @ cobalt-oxo / hydroxo phosphate	FTO	0.5M phosphate buffer (KPi, pH = 7)	2	385	<i>Nat. Mater.</i> 2012 , <i>11</i> , 802
Electrodeposited cobalt-sulfide	Co = 1.35 □ μmol/cm ² (79.6 μg/cm ²) FTO	1.0 M potassium phosphate buffer pH = 7	2	85	<i>J. Am. Chem. Soc.</i> 2013 , <i>135</i> , 17699
Co–Mo–S film	glassy carbon	phosphate buffer pH = 7	1.04	200	<i>Chem. Sci.</i> 2012 , <i>3</i> , 2515
Ni ₃ S ₂ nanosheet arrays / Ni foam	1.6 mg/cm ² Ni foam	phosphate buffer pH = 7	10	170	<i>J. Am. Chem. Soc.</i> 2015 , DOI: 10.1021/jacs.5b08186
Mo ₂ C	—	phosphate buffer pH = 7	1	200	<i>Angew. Chem. Int. Ed.</i> 2012 , <i>51</i> , 12703
Mo ₂ B	—	phosphate buffer pH = 7	1	250	<i>Angew. Chem. Int. Ed.</i> 2012 , <i>51</i> , 12703
CoP/CC	0.92 mg cm ⁻² carbon cloth	1.0 M phosphate buffer solution pH = 7	2 10	65 106	<i>J. Am. Chem. Soc.</i> 2014 , <i>136</i> , 7587

Table S2. Comparison of the OER activity of CoO/CoSe₂ under neutral conditions with some representative OER catalysts recently reported.

Sample	Loading/ substrate	electrolyte	Onset overpot ential /mV	Current density (j)/ mA cm ⁻²	Overpotentia l/ mV at the correspondin g j	Tafel slope /mV dec ⁻¹	Reference
Co ₃ S ₄ Nanosheets	0.28 mg/cm ²	phosphate buffer solution (pH = 6.86)	310	3.97	700	151	<i>Angew. Chem. Int. Ed.</i> 2015 , <i>54</i> , 11231
CoO/CoSe ₂	2 mg cm ⁻² Ti mesh	0.5 M phosphate buffer solution (pH = 6.86)	320	33.96	620	137	This work
Co-based phosphate/ITO	ITO	0.1 M potassium phosphate (pH = 7.0)	280	1	410	—	<i>Science</i> , 2008 , <i>321</i> , 1072
Mn ₃ (PO ₄) ₂ · 3H ₂ O/FTO	FTO	0.5M phosphate buffer (pH = 7)	450	0.316	680	120	<i>J. Am. Chem. Soc.</i> 2014 , <i>136</i> , 7435
LiCoPO ₄	0.10 mg/cm ²	0.1 M potassium phosphate (pH = 7.0)	370	—	—	120	<i>J. Am. Chem. Soc.</i> 2012 , <i>134</i> , 16959
LiMnP ₂ O ₇	0.25 mg/cm ² FTO	phosphate buffer (pH = 7.0)	450	0.5	680	120	<i>J. Am. Chem. Soc.</i> 2014 , <i>136</i> , 4201
Ni	17 nM FTO	0.5 M potassium borate (pH = 9.2)	—	1	540	—	<i>J. Am. Chem. Soc.</i> 2015 , <i>137</i> , 13980

References:

- [1] M. R. Gao, W. T. Yao, H. B. Yao, S. H. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 7486.
- [2] Y. R. Zheng, M. R. Gao, Q. Gao, H. H. Li, J. Xu, Z. Y. Wu, S. H. Yu, *Small* **2015**, *11*, 182.

