

Supporting Information

Fabrication of superaerophobic Ru-doped *c*-CoSe₂ for efficient hydrogen production

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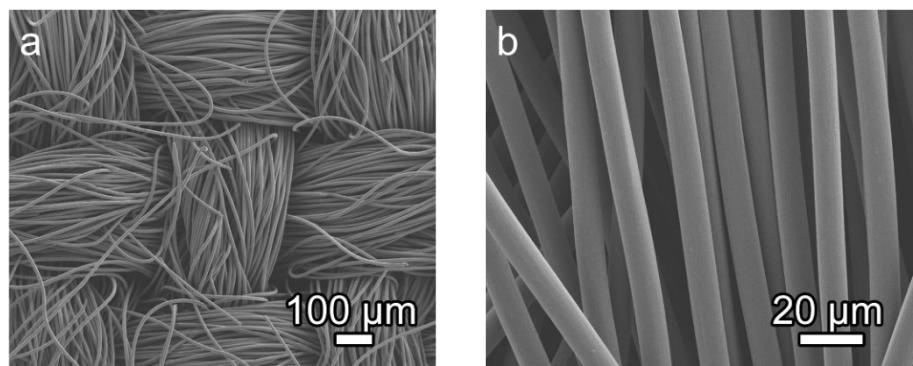


Figure S1. SEM images of CC at different magnifications.

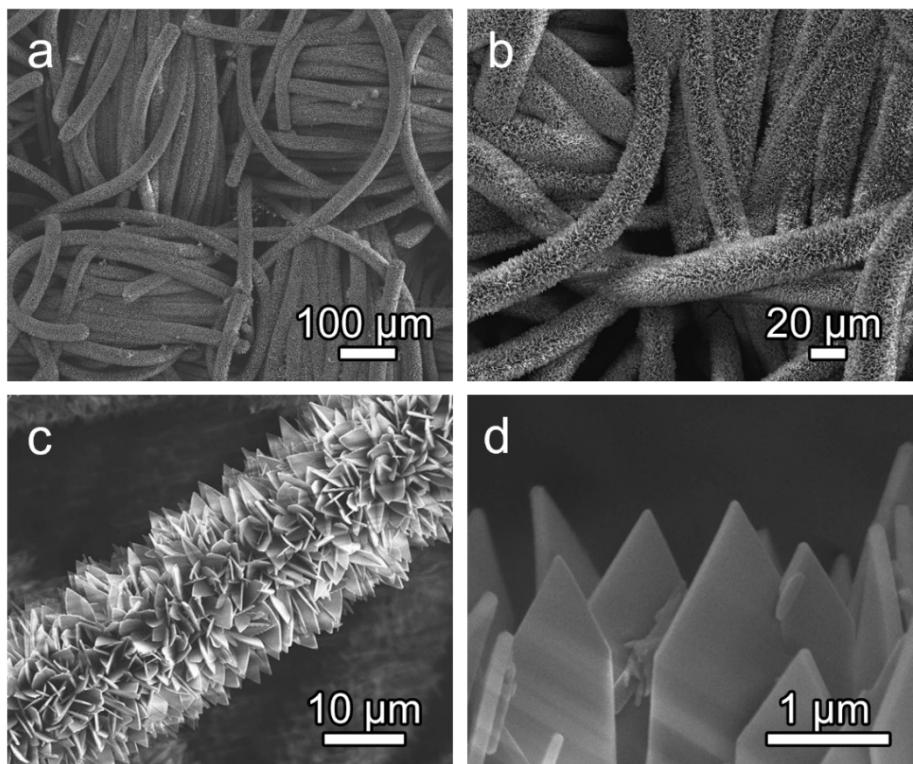


Figure S2. SEM images of Co-ZIF/CC at different magnifications.

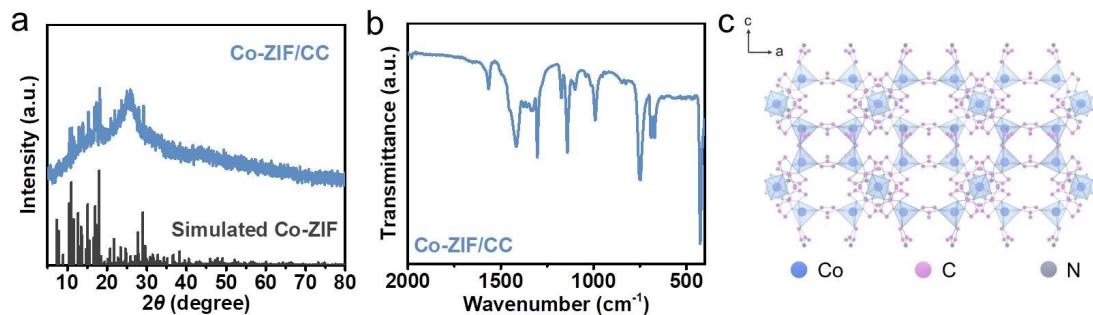


Figure S3. (a) XRD pattern and (b) FT-IR spectrum of Co-ZIF/CC. (c) Crystal structure of Co-ZIF.

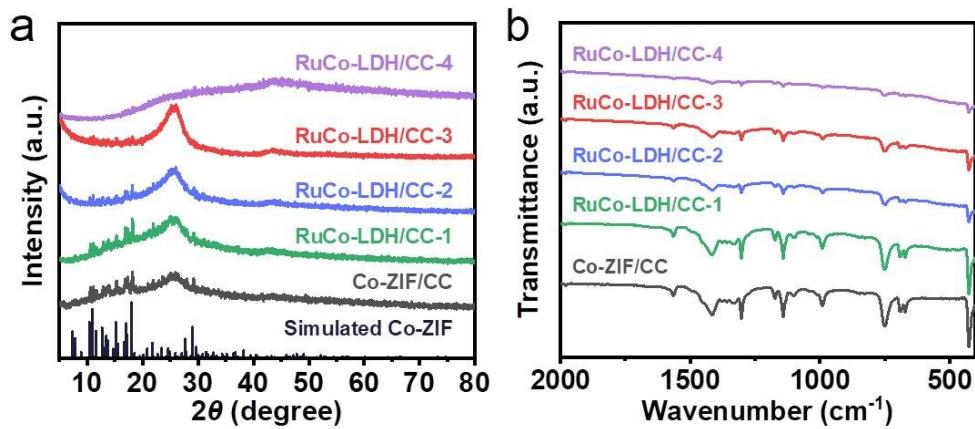


Figure S4. (a) XRD patterns and (b) FT-IR spectra of Co-ZIF/CC and RuCo-LDH/CC-x series samples.

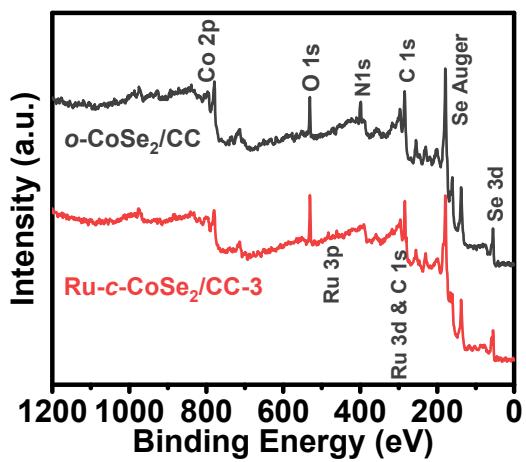


Figure S5. XPS survey spectra of *o*-CoSe₂/CC and Ru-*c*-CoSe₂/CC-3.

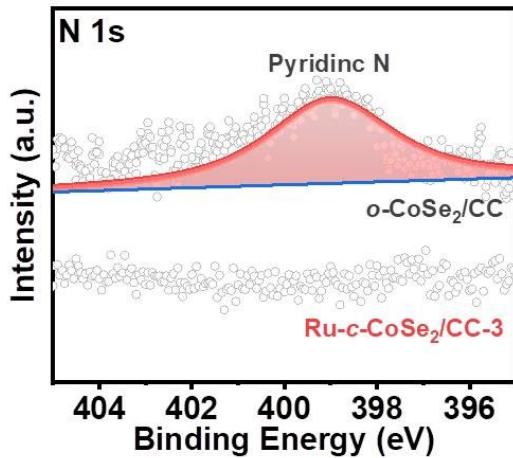


Figure S6. High-resolution N 1s XPS spectra of *o*-CoSe₂/CC and Ru-*c*-CoSe₂/CC-3.

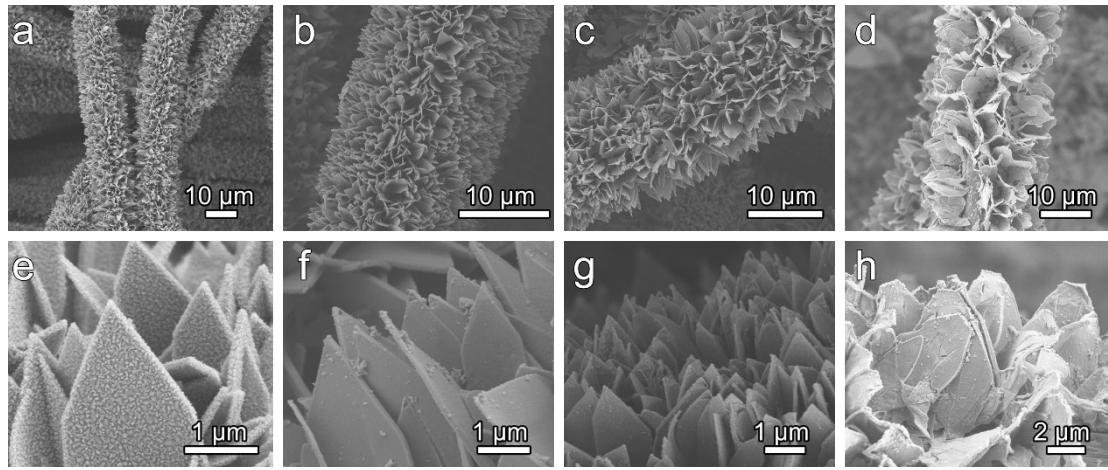


Figure S7. SEM images of (a, e) *o*-CoSe₂/CC, (b, f) Ru-*c,o*-CoSe₂/CC-1, (c, g) Ru-*c,o*-CoSe₂/CC-2, and (d, h) Ru-*c*-CoSe₂/CC-4.

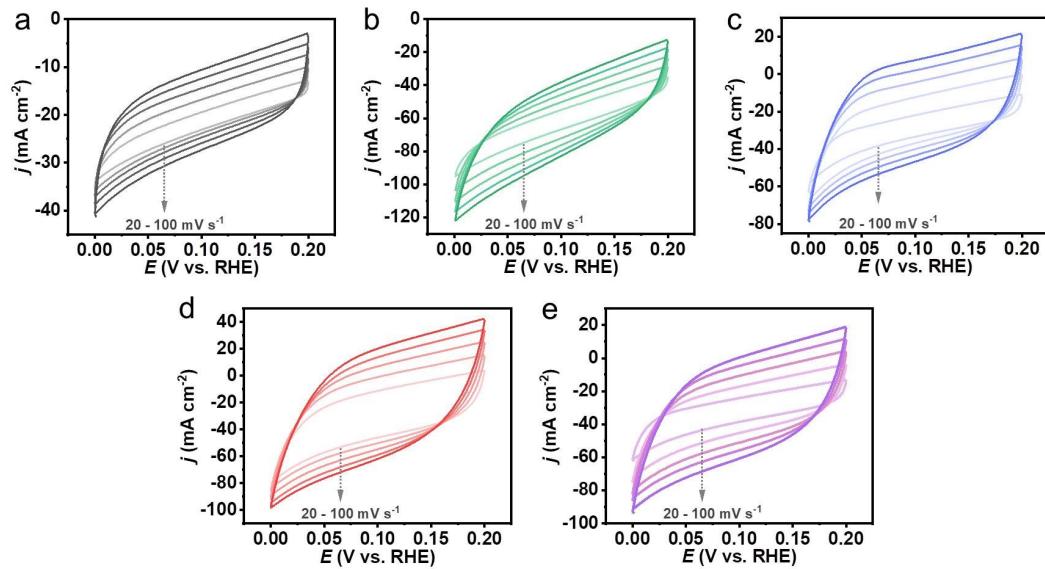


Figure S8. CV curves of (a) *o*-CoSe₂/CC, (b) Ru-*c,o*-CoSe₂/CC-1, (c) Ru-*c,o*-CoSe₂/CC-2, (d) Ru-*c*-CoSe₂/CC-3 and (e) Ru-*c*-CoSe₂/CC-4 at different scan rates from 20 to 100 mV s⁻¹ within the potential range of 0 – 0.2 V vs. RHE in 0.5 M H₂SO₄.

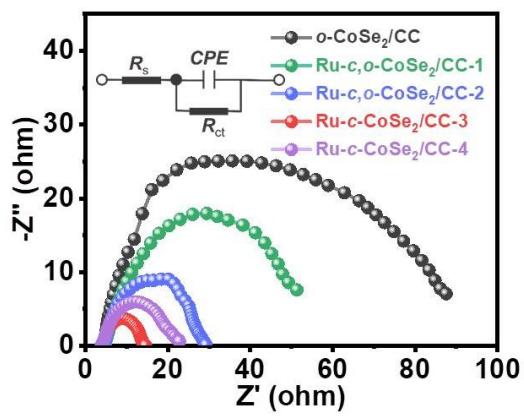


Figure S9. Nyquist plots of the samples in 1 M KOH under an overpotential of 110 mV.

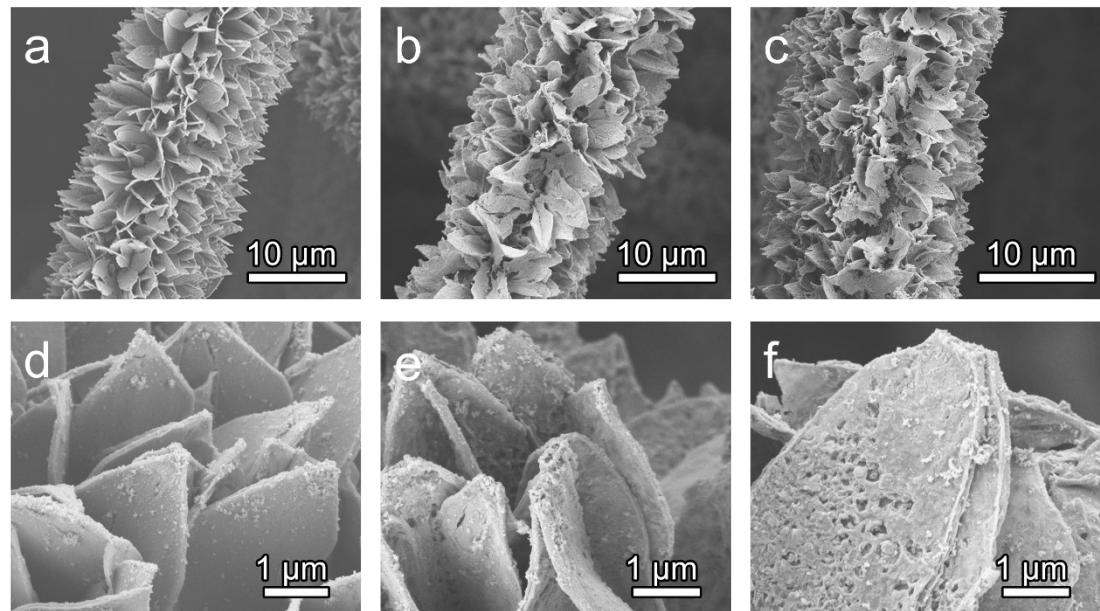


Figure S10. SEM images of (a, d) $\text{Ru-}c\text{-}\text{CoSe}_2/\text{CC-}3$, (b, e) $\text{Ru-}c\text{-}\text{CoSe}_2/\text{CC-}450$ and (c, f) $\text{Ru-}c\text{-}\text{CoSe}_2/\text{CC-}500$.

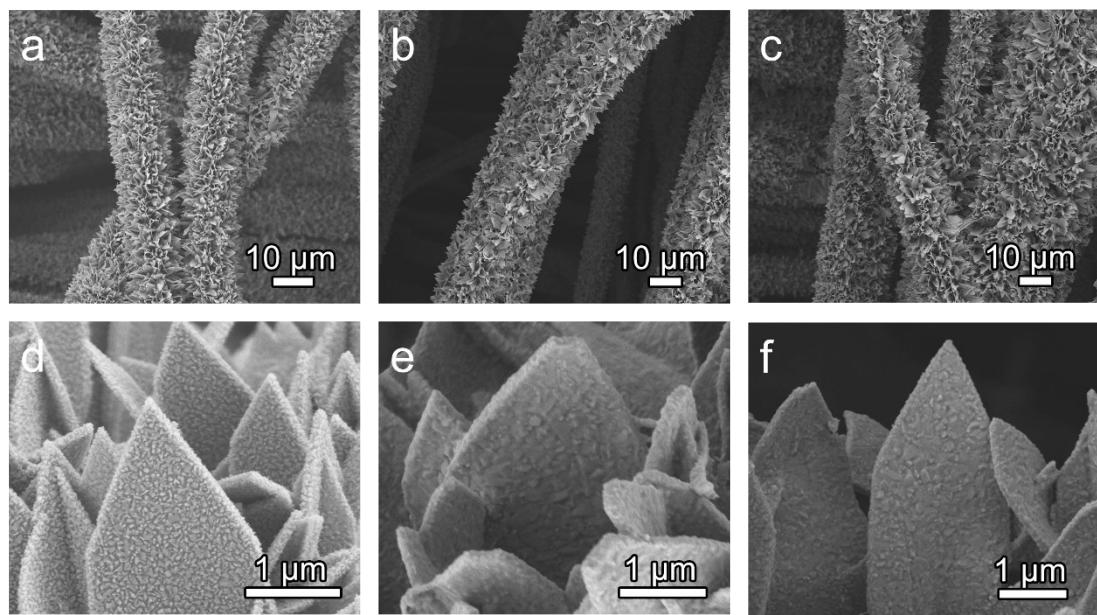


Figure S11. SEM images of (a, d) *o*-CoSe₂/CC, (b, e) *c,o*-CoSe₂/CC-450 and (c, f) *c*-CoSe₂/CC-500.

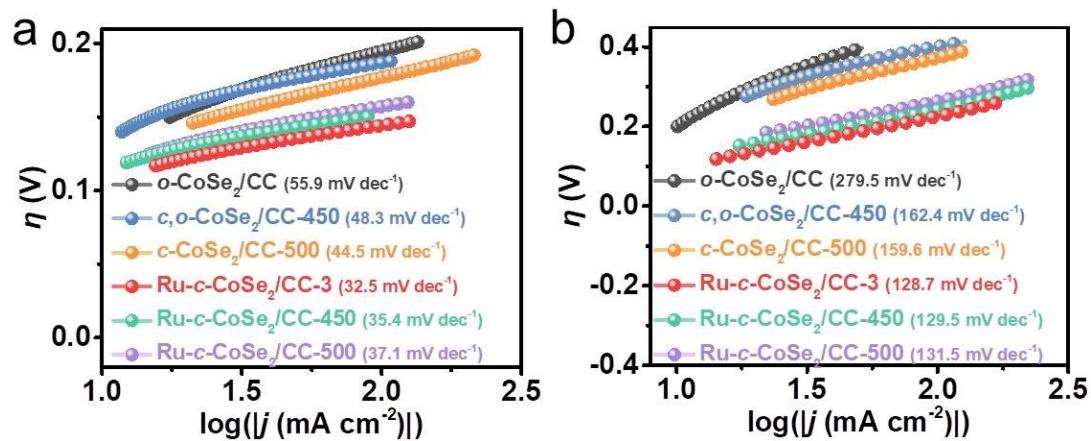


Figure S12. Tafel plots of *o*-CoSe₂/CC, *c,o*-CoSe₂/CC-450, *c*-CoSe₂/CC-500, Ru-*c*-CoSe₂/CC-3, Ru-*c*-CoSe₂/CC-450 and Ru-*c*-CoSe₂/CC-500 in (a) 0.5 M H₂SO₄ and (b) 1 M KOH.

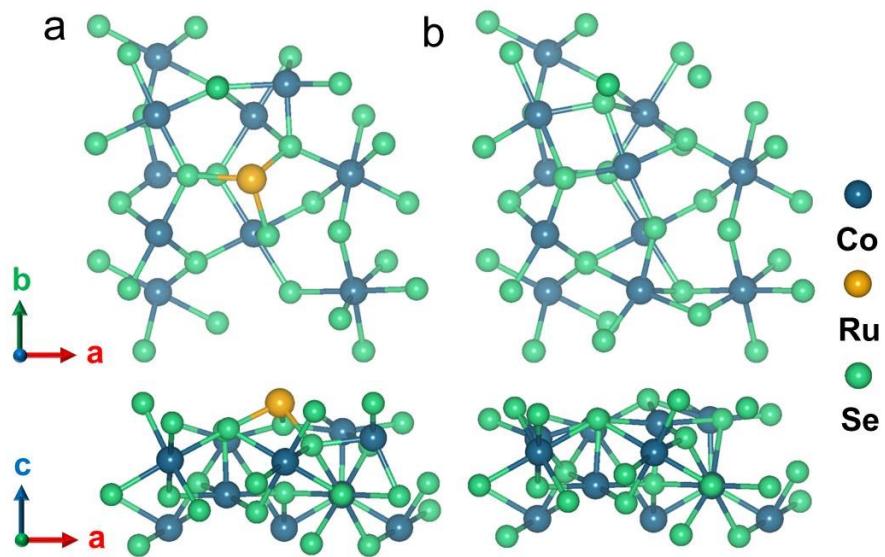


Figure S13. Top and side views of schematic models for (a) Ru-*c*-CoSe₂(211) and (b) *c*-CoSe₂(211).

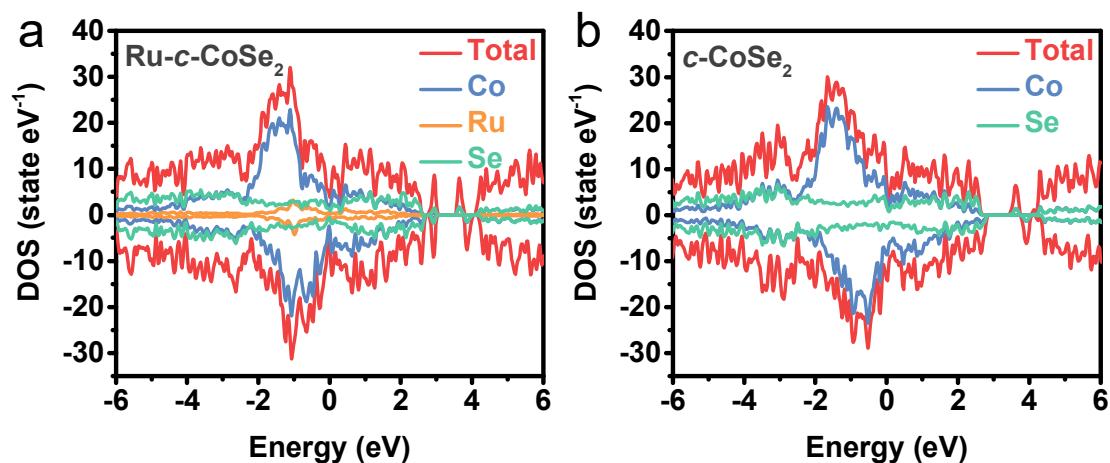


Figure S14. The electronic density of states calculated for (a) Ru-*c*-CoSe₂ and (b) *c*-CoSe₂.

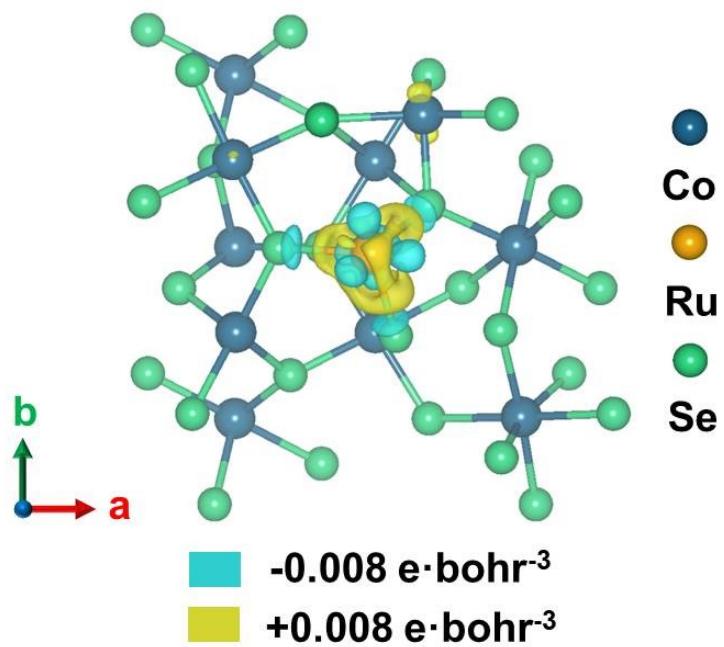


Figure S15. Top view of schematic model of charge density-difference for Ru-*c*-CoSe₂.

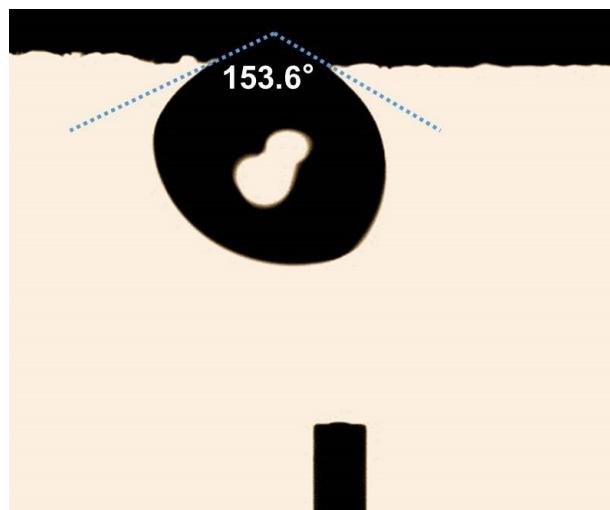


Figure S16. Contact angle of a H₂ bubble on Ru-*c*-CoSe₂/CC-3.

Table S1. Comparison of the HER catalytic performance of Ru-*c*-CoSe₂/CC-3 with the reported CoSe₂-based electrocatalysts in 0.5 M H₂SO₄.

Electrocatalysts	η_{10} (mV)	η_{100} (mV)	b (mV dec ⁻¹)	Ref.
Ru-<i>c</i>-CoSe₂/CC-3	105	144	32.5	<i>This work</i>
Fe-CoSe ₂ @NC	143	184	40.9	<i>ACS Sustain. Chem. Eng.</i> 2018 , <i>6</i> , 8672
CoSe ₂ @DC	132	260	82	<i>Nano Energy</i> 2016 , <i>28</i> , 143
pure CoSe ₂	209	-	72.2	<i>Electrochim. Acta</i> 2019 , <i>322</i> , 134739
m-CoSe ₂	124	-	60	<i>Nat. Commun.</i> 2019 , <i>10</i> , 5338
CoSe ₂ /CNTAs-3	204	229	36.7	<i>Electrochim. Acta</i> 2018 , <i>285</i> , 254
CoSe ₂ /SDGC-60	203	-	55.8	<i>Int. J. Hydrogen Energy</i> 2019 , <i>44</i> , 13424
CoSe ₂	115	235	115	<i>Small</i> 2020 , <i>16</i> , 1906629
<i>o</i> -CoSe ₂ -NC	147	-	39.8	<i>ACS Sustain. Chem. Eng.</i> 2022 , <i>10</i> , 4022
CoSe	242.8	-	58	<i>Angew. Chem. Int. Ed.</i> 2020 , <i>59</i> , 22743
c-CoSe ₂ @HC	189.2	-	50.8	<i>Chem. Eng. J.</i> 2021 , <i>424</i> , 130341
CoSe ₂ NPs	169	-	56	<i>J. Mater. Chem. A</i> 2018 , <i>6</i> , 7842
MOF-D CoSe ₂	195	-	43	<i>Sustain. Energy Fuels</i> 2021 , <i>5</i> , 4992
CoSe ₂ -CNT	174	-	37.8	<i>Small</i> 2017 , <i>13</i> , 1700068
1D-CoSe ₂ (tex-48h) nanoarray	216	-	78	<i>Dalton Trans.</i> 2020 , <i>49</i> , 14191

Table S2. Comparison of the HER catalytic performance of Ru-*c*-CoSe₂/CC-3 with the reported CoSe₂-based electrocatalysts in 1 M KOH.

Electrocatalysts	η_{10} (mV)	η_{100} (mV)	b (mV dec ⁻¹)	Ref.
Ru-<i>c</i>-CoSe₂/CC-3	97	226	128.7	<i>This work</i>
c-CoSe ₂ /CC	190	-	85	<i>Adv. Mater.</i> 2016 , <i>28</i> , 7527
N- <i>c</i> -CoSe ₂	98	-	63.4	<i>Angew. Chem. Int. Ed.</i> 2021 , <i>60</i> , 21575
CoSe ₂ /CC	136	380	58	<i>Chin. Chem. Lett.</i> 2023 , <i>34</i> , 107364
MOF-CoSe ₂ -160°	156	-	40	<i>Inorg. Chem.</i> 2020 , <i>59</i> , 12778
B-CoSe ₂ /CC	153	260	85	<i>Colloids Surf. A Physicochem. Eng. Asp.</i> 2022 , <i>646</i> , 128903
Annealed c-CoSe ₂	248	-	155	<i>Nat. Commun.</i> 2018 , <i>9</i> , 2533
o-CoSe ₂	220	-	107	<i>ACS Omega</i> 2022 , <i>7</i> , 15901
MoS ₂ @CoSe ₂ -CC	101	-	67	<i>Nanoscale</i> 2022 , <i>14</i> , 2490
c-CoSe ₂	149	-	79.1	<i>J. Mater. Chem. A.</i> 2017 , <i>5</i> , 4513
CoSe ₂ NPs	278	-	120	<i>J. Mater. Chem. A.</i> 2018 , <i>6</i> , 7842
o-CoSe ₂ /c-CoSe ₂ / MoSe ₂	112	-	96.9	<i>Mater. Today Chem.</i> 2022 , <i>23</i> , 100724
CoSe/Co(OH ₂)- CM(AE)	207	-	126	<i>Compos. B. Eng.</i> 2022 , <i>236</i> , 109823
CoSe ₂ ⁽⁴⁰⁰⁾ -NC-800	234	-	95	<i>ACS Appl. Mater. Interfaces</i> 2019 , <i>11</i> , 3372
p-CoSe ₂ /CC	138	-	83	<i>ACS Sustain. Chem. Eng.</i> 2018 , <i>6</i> , 15374