

Electronic Supplementary Information

**Beaded-Stream-like CoSe₂ Nanoneedles Array for Efficient
Hydrogen Evolution Electrocatalysis**

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Table S1. Comparison of overpotential, mass activity and charge transfer resistance of cobalt selenide catalysts and reported non-precious metal catalysts in acid electrolyte.

Catalysts	η_{20} (mV) ^a	j_0 (mA cm ⁻²) ^b	$j@ \eta=150$ mV (mA cm ⁻²) ^c	Loading (mg cm ⁻²)	Mass activity @ $\eta=150$ mV (mA mg ⁻¹)	R_{ct} (Ω)	ref
CoSe ₂ -BSND	125	4.3×10 ⁻²	35.0	1.60	21.90	74 @ $\eta=150$ mV	this work
CoSe ₂ -PA	220	5.2×10 ⁻³	1.40	1.50	0.93	310@ $\eta=150$ mV	this work
Co-BSND	325	2.1×10 ⁻³	0.13	0.45	0.29	--	this work
MoS ₂ /RGO	140	N.A.	10.00	1.00	10.00	250@ $\eta=120$ mV	28
Mo ₂ C nanowires	150	N.A.	20.00	0.21	95.20	90@ $\eta=150$ mV	29

	η @current density	j_0 (mA cm ⁻²) ^b	Loading (mg cm ⁻²)	Tafel slop (mV dec ⁻¹)	R_{ct} (Ω)	Ref
MoS ₂ nanosheets	190 mV@10 mA cm ⁻²	3.89 × 10 ⁻²	0.285	68.0	N.A.	S1 ^d
Vertically aligned MoSe ₂ layers	450 mV@8 mA cm ⁻²	2.0 × 10 ⁻³	0.135	108.0	N.A.	S2 ^d
CoSe ₂ nanoparticles on carbon fiber	137 mV@10 mA cm ⁻²	4.9 × 10 ⁻³	2.8	42.1	N.A.	23
CoSe ₂ nanoparticles on Ti foil	135 mV@10 mA cm ⁻²	6.4 × 10 ⁻²	3.0	62.0	N.A.	26
CoSe ₂ nanoparticles on graphite disk	193 mV@10 mA cm ⁻²	N.A.	2.8	42.2	8.8@ $\eta=240$ mV	S3 ^d
CoS ₂ nanosheets/RGO-CNT	153 mV@20 mA cm ⁻²	6.26× 10 ⁻²	1.15	51.0	N.A.	S4 ^d
CoS ₂ thin film	192 mV@10 mA cm ⁻²	3.53 × 10 ⁻³	N.A.	52.0	N.A.	S5 ^d

^a The overpotential for driving a current density at 20 mA cm⁻². ^b The exchange current density. ^c The cathodic current density at fixed overpotential of 150 mV.

^d Reference:

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S2. D. Kong, H. Wang, J. J. Cha, M. Pasta, K. J. Koski, J. Yao, Y. Cui *Nano Lett.*, **2013**, *13*, 1341–1347.

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S4. S. Peng et al. *Angew. Chem. Int. Ed.*, **2014**, *53*, 12594-12599.

S5. M. S. Faber, M. A. Lukowski, Q. Ding, N. S. Kaiser, S. Jin *J. Phys. Chem. C*, **2014**, *118*, 21347-21356.

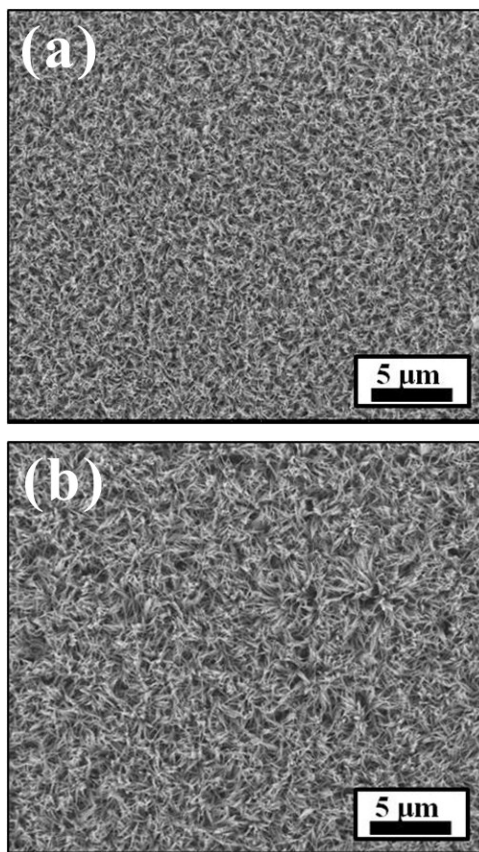


Fig. S1 SEM images of (a) Co₃O₄ and (b) CoSe₂ nanoneedle arrays taken at a magnification of 5,000x.

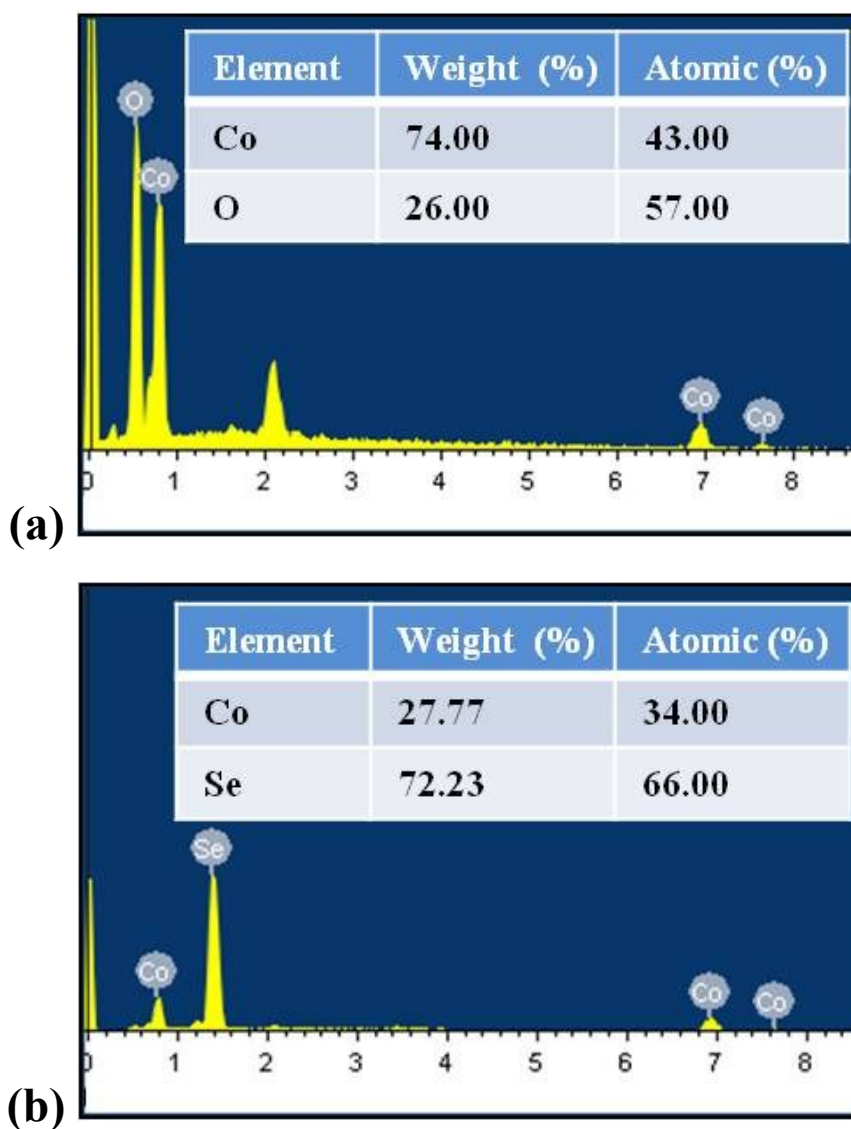


Fig. S2 Energy-dispersive X-ray spectra of (a) Co₃O₄ nanoneedles (Co₃O₄-ND) array and (b) CoSe₂ beaded-stream-like nanoneedles (CoSe₂-BSND) array.

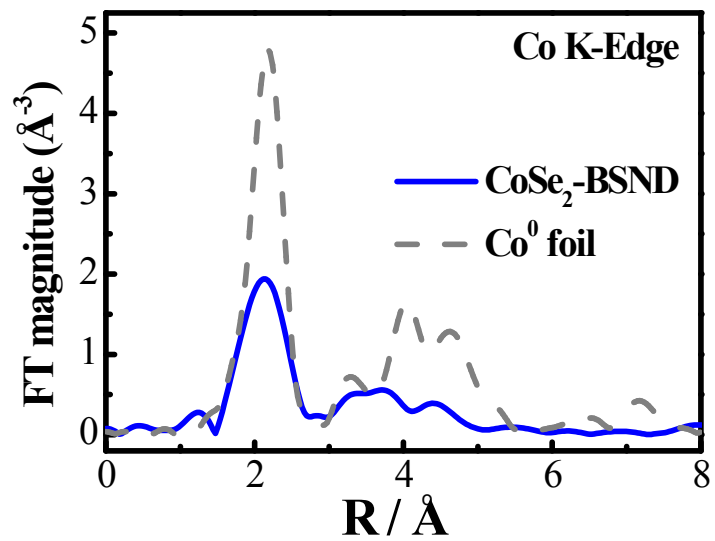


Fig. S3 Fourier transformed magnitudes of the k^2 -weighted Co K-edge EXAFS data for CoSe₂-BSND and the Co foil (k =the photoelectron wavenumber).

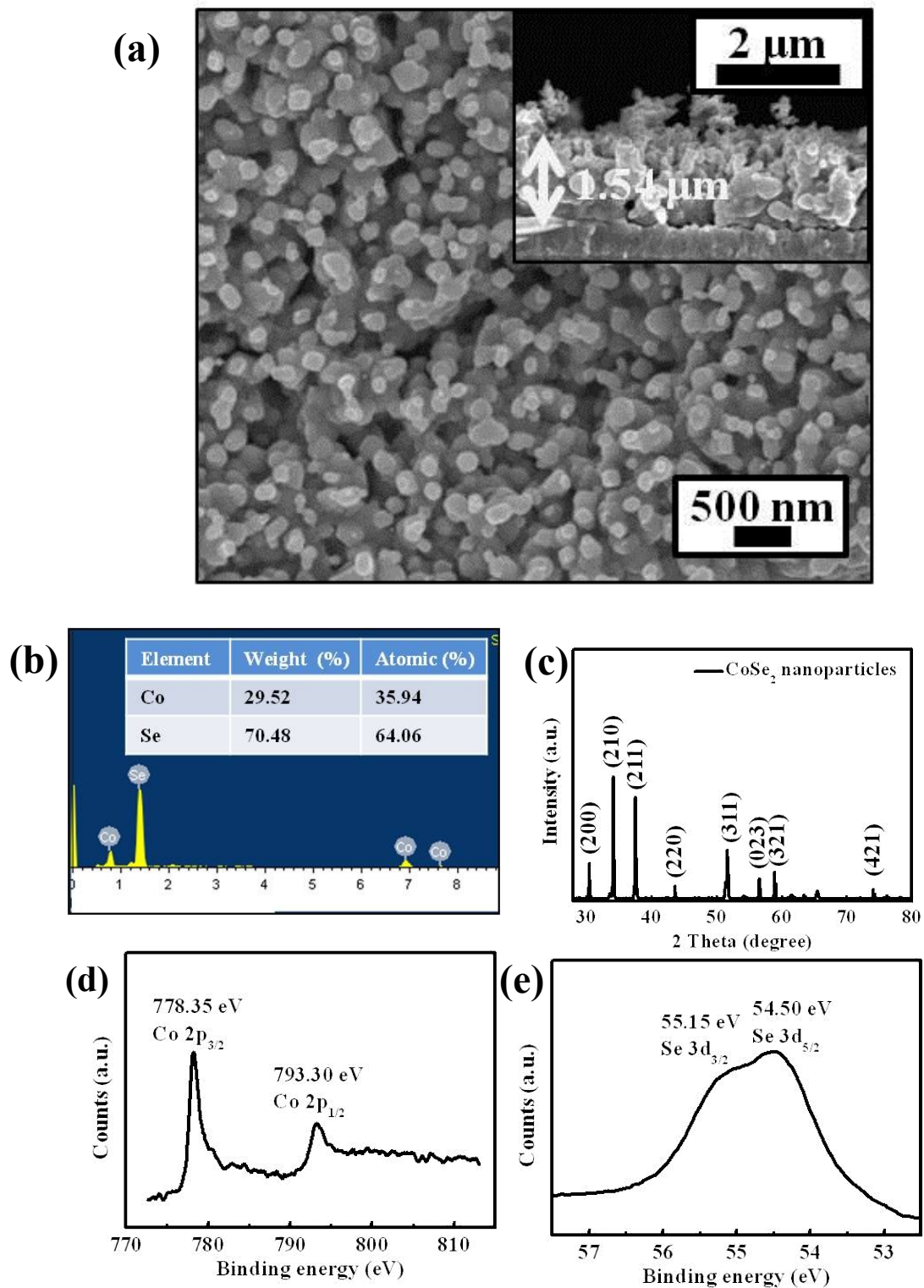


Fig. S4 (a) The SEM image, (b) EDX spectra, (c) XRD pattern and XPS spectra of (d) Co 2p and (e) Se 3d region of CoSe₂ particles (CoSe₂-PA) film prepared by using cobalt sulfate heptahydrate as the precursor.

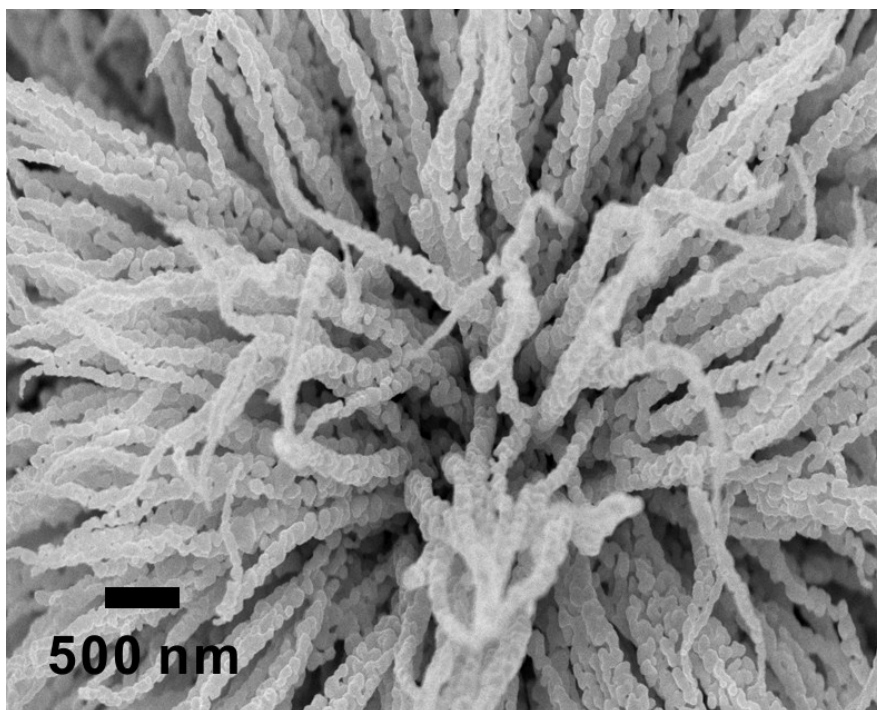


Fig. S5 The SEM image of beaded stream-like nanoneedle Co (Co-BSND) array formed by treating the Co_3O_4 -ND template under H_2 at 400 °C.

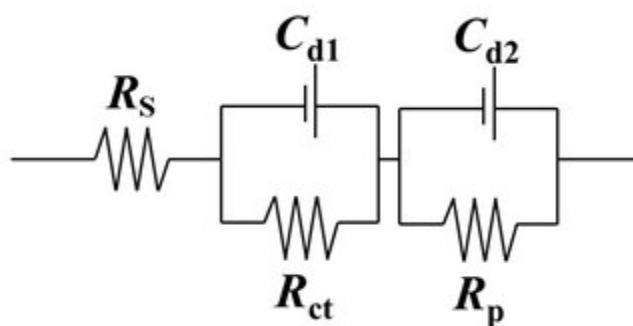


Fig. S6 Two-time constant equivalent circuit models for fitting the EIS response of hydrogen evolution reaction on CoSe_2 electrodes, where R_s is the series resistance, R_{ct} is the charge transfer resistance, R_p related to the porosity of the electrode surface, and the double layer capacitance is represented by the elements C_{d1} and C_{d2} . Here R_s contains components arising from the resistance in the wiring (R_{wiring}), the resistance of the Ti foil (R_{cp}), the resistance of cobalt selenide (R_{CoSe}), the resistance between the interface of CoSe_2 and Ti foil (R_{int}), and the solution resistance (R_{soln}).

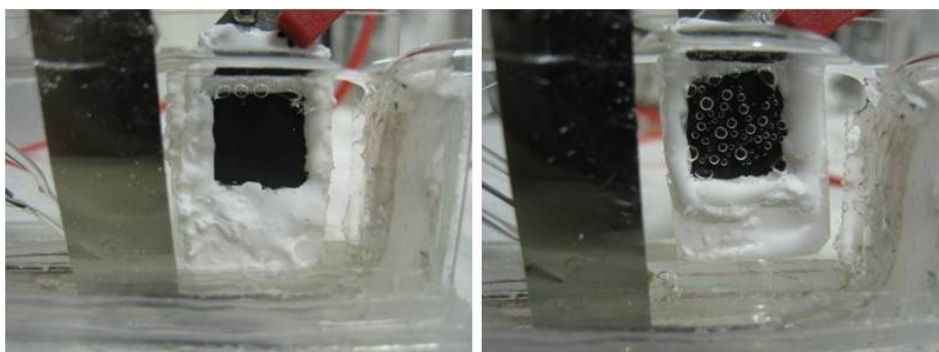


Fig. S7 Optical images depicting the H₂ bubbles pinning level on the surfaces of CoSe₂-BSND (left) and CoSe₂-PA (right) electrodes after electrolysis.

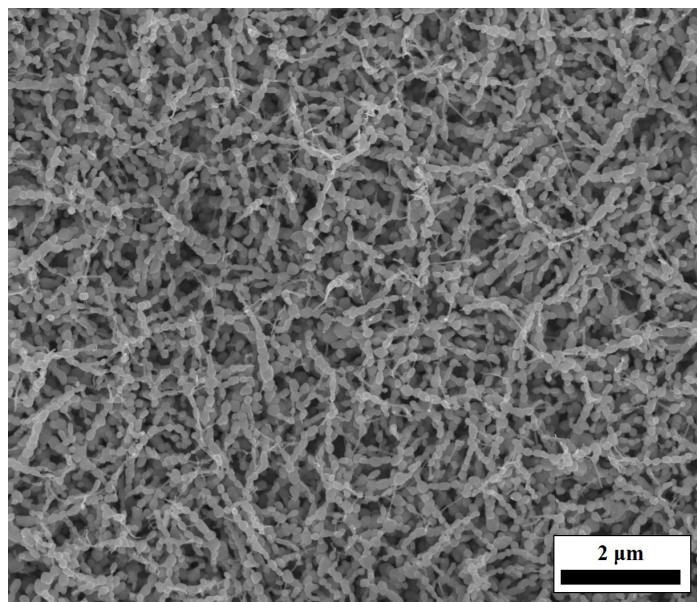


Fig. S8 A SEM micrograph of CoSe₂-BSND electrode after the durability test for 18h.