

## Supporting information

### **Interface Engineering of Cobalt-Sulfide-Selenium Core-Shell Nanostructures as Bifunctional Electrocatalysts toward Overall Water Splitting**

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#### **Experimental Section**

**Synthesis of Co(OH)Cl umbrella type nanorods:** In a typical synthesis, 2 mmol CoCl<sub>2</sub> or CoCl<sub>2</sub>•6H<sub>2</sub>O, 7 mmol NH<sub>4</sub>Cl, and 9 mmol urea were dissolved in 35 mL deionized water. After being thoroughly dissolved, the solution was transferred into a 50 mL autoclave. Afterwards, the autoclave was placed in an oven at 140°C for 6-12 h. After cooling to room temperature, the resulting product was collected by centrifugation and then washed with absolute ethanol for several times. Finally, the product was dried overnight under vacuum at 60°C.

**Preparation of Cobalt Sulfide nanotubes:** The sulfurization process is described as in our previous work:<sup>33</sup> A ceramic boat containing 0.01 g of the as-prepared Co(OH)Cl-U samples was located at the high-temperature zone of a quartz tube and another ceramic boat containing S powder (0.1g) located at the upstream zone of the quartz tube. The distance between these two positions was about 15 cm. The upstream zone was heated to 250°C at a rate of 6°C/min, and the downstream zone was heated to 400°C at a rate of 10°C/min. The whole sulfurization process maintained at 400°C for 1h in the Ar/H<sub>2</sub> atmosphere to obtain the final products.

**Preparation of Cobalt-Sulfide-Selenium Core-shell nanotubes:** In a typical sulfurization-selenylation process, a ceramic boat containing 0.01 g of the as-prepared Co(OH)Cl-U samples was located at the high-temperature zone of a quartz tube, and another ceramic boat containing S powder (0.08g) and Se powder (0.02g) located at the upstream zone of the quartz tube. The distance between these two positions was about 15 cm. The upstream zone was heated to 250°C at a rate of 6°C/min, and the downstream zone was heated to 400°C at a rate of 10°C/min. The whole sulfurization-selenylation process maintained at 400°C for 1h in the Ar/H<sub>2</sub> atmosphere to obtain the final products.

**Preparation of Cobalt-Selenium pore-like nanorod:** The selection process is described as follows: A ceramic boat containing 0.01 g of the as-prepared Co(OH)Cl-U samples was located at the high-temperature zone of a quartz tube and another ceramic boat containing Se powder (0.1g) located at the upstream zone of the quartz tube. The distance between these two positions was about 15 cm. The upstream zone

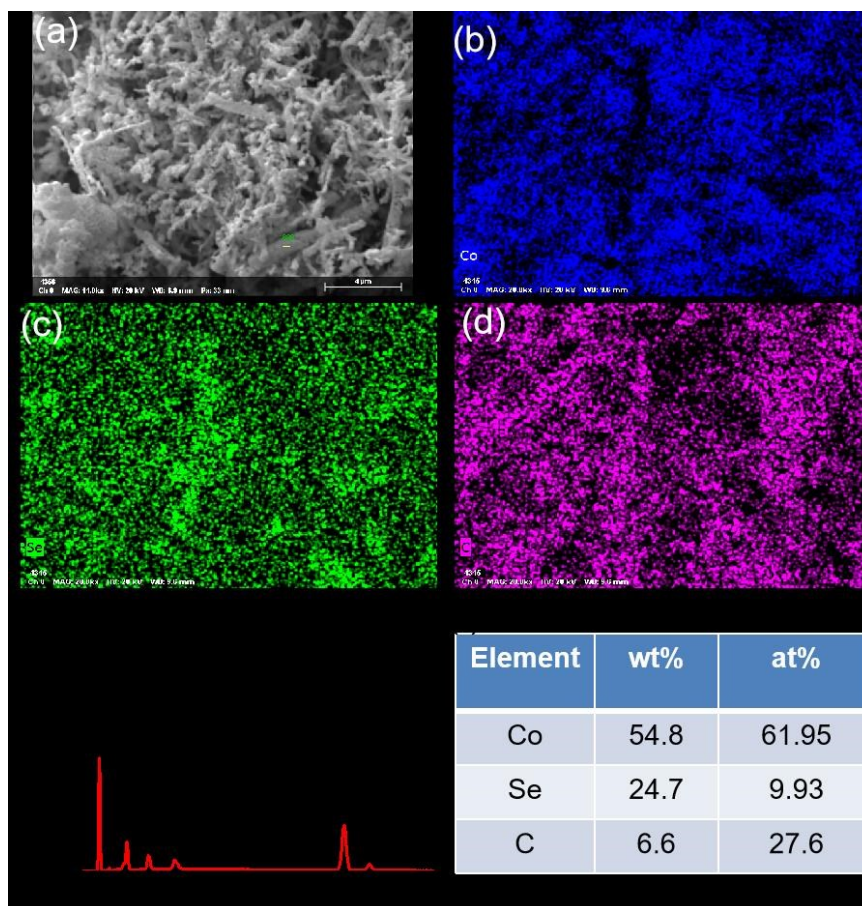
was heated to 250°C at a rate of 6°C/min, and the downstream zone was heated to 400°C at a rate of 10°C/min. The whole selection process maintained at 400°C for 1h in the Ar/H<sub>2</sub> atmosphere to obtain the final products.

**Characterization:** The morphologies of as-prepared samples were characterized by Field emission scanning electron microscopy (FE-SEM) images performed by SU8010 (Hitachi Japan and MIRA3 TESCAN). Field emission transmission electron microscopy (FETEM) was carried out using a JEM2100F operated at 200 kV with samples made by evaporating a drop of dispersions of the submicron wires in butanol onto holey-carbon-coated Cu grids. X-ray photoelectron spectroscopy (XPS) was performed in a Thermo Scientific Escalab 250Xi surface analysis system (Al K $\alpha$ , Waltham, Massachusetts, USA). The fractions were determined by using X-ray diffraction (XRD), with a Xpert Pro MPD diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

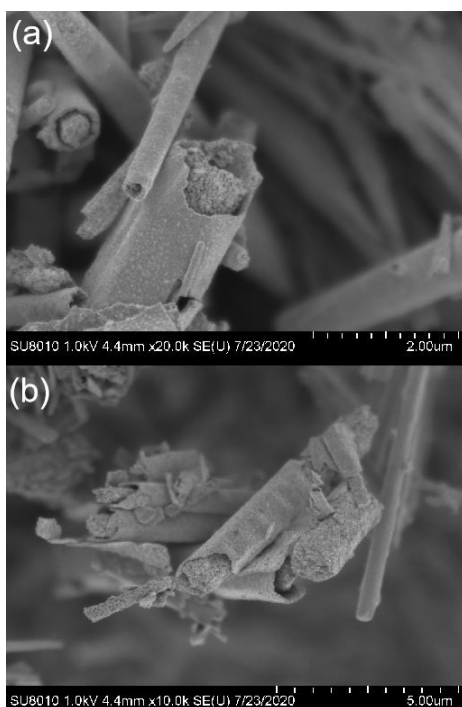
**Electrochemical Measurement:** The typical electrode preparation process was similar to previous work,<sup>33</sup> where 4 mg sample and 30  $\mu\text{L}$  Nafion solution (5 wt%) were dispersed in 0.2 mL water / 0.8 mL ethanol solution by sonicating for 1h to form a homogeneous catalyst ink. Then 15  $\mu\text{L}$  of the dispersion (containing 60  $\mu\text{g}$  of catalyst) was loaded onto a glassy carbon electrode (GCE) (diameter  $d=3 \text{ mm}$ ). The catalyst loading is about  $0.855 \text{ mg cm}^{-2}$ . All the electrochemical catalytic properties were tested on a Zara electrochemical station in a three-electrode system. Linear sweep voltammetry was conducted in 1 M KOH (pure N<sub>2</sub>) using a Ag/AgCl (saturated KCl) electrode as the reference electrode, a graphite rod as the counter electrode, and

the glassy carbon electrode as the working electrode. And the potentials were calibrated with respect to a reversible hydrogen electrode (RHE) according to the formula: 1 M KOH,  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.217\text{V}$ .<sup>33</sup> All the potentials reported in the manuscript were against RHE. Before the electrochemical test, the working electrode was activated at  $500\text{ mV s}^{-1}$  for several cycles. Linear sweep voltammetry was measured at  $5\text{ mV s}^{-1}$ . The double-layer capacitances ( $C_{\text{dl}}$ ) were estimated by CV in the range of 0.9-1.0 V versus RHE region at various scan rates ( $10\text{-}300\text{ mV s}^{-1}$ ) to evaluate the effective surface area of various catalysts. The ohmic resistance used for iR-correction was obtained from EIS measurements with frequencies ranging from 0.1 Hz to  $10^5$  Hz, with an AC voltage of 0.5 V.

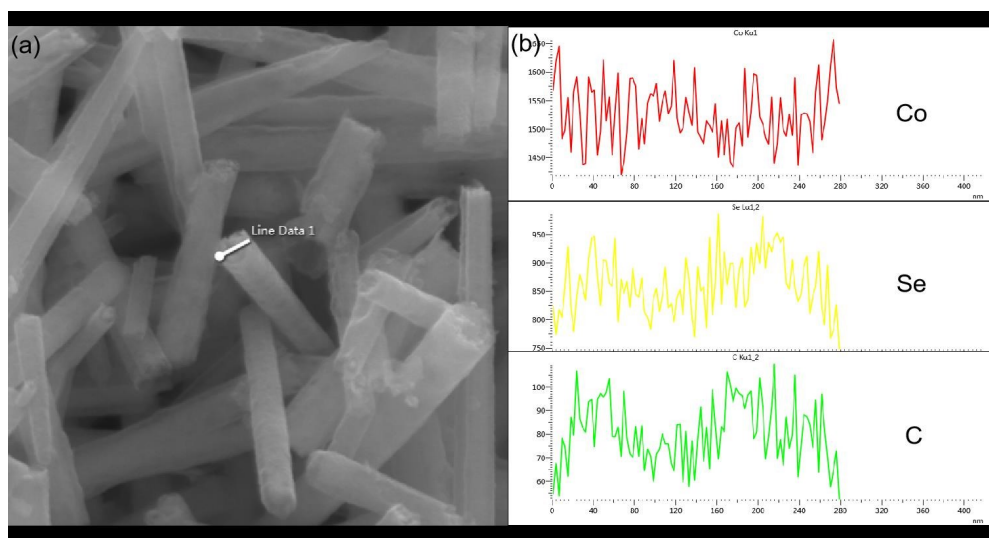
**DFT calculations:** The geometry optimizations and electronic structures calculations were carried through density functional theory (DFT) with the projector-augmented wave (PAW) method, performed by Vienna ab-initio simulation package (VASP) program<sup>15,44</sup>. The exchange and correlation interactions were described by the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional.<sup>64</sup> The electronic wave functions were expanded in plane wave basis with the cutoff energy of 500 eV. In the calculation, a Monkhorst-Pack grid was set to be  $7\times 7\times 7$  for the bulk systems and  $7\times 7\times 1$  for the surface systems, respectively. The top layers of surface systems were fully relaxed in order to make the maximum force acting on every atom in the unit cell less than  $0.02\text{ eV/\AA}$ . And energy convergence criterion was set to be  $10^{-5}\text{ eV}$ .



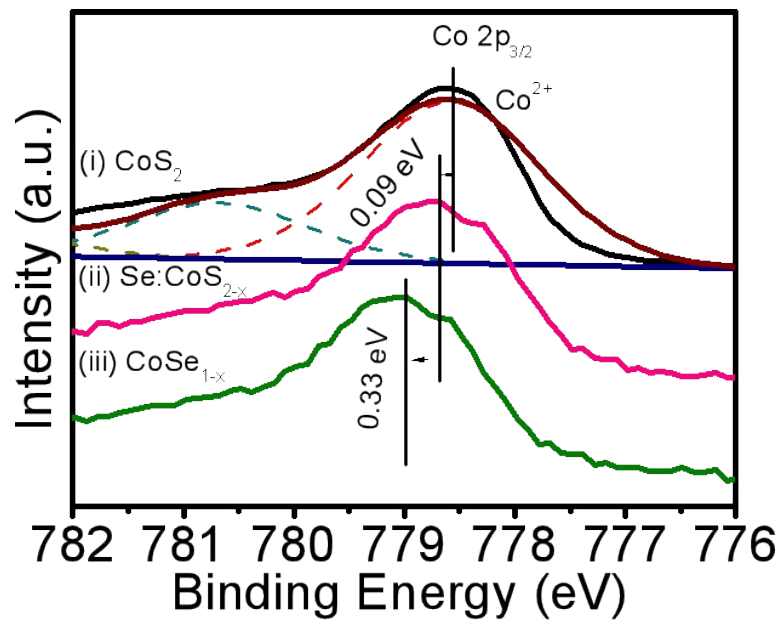
**Fig. S1.** (a-f) EDS elemental mapping of  $\text{CoSe}_{1-x}$  obtained after selenization in pure Ar at  $400^\circ\text{C}$ .



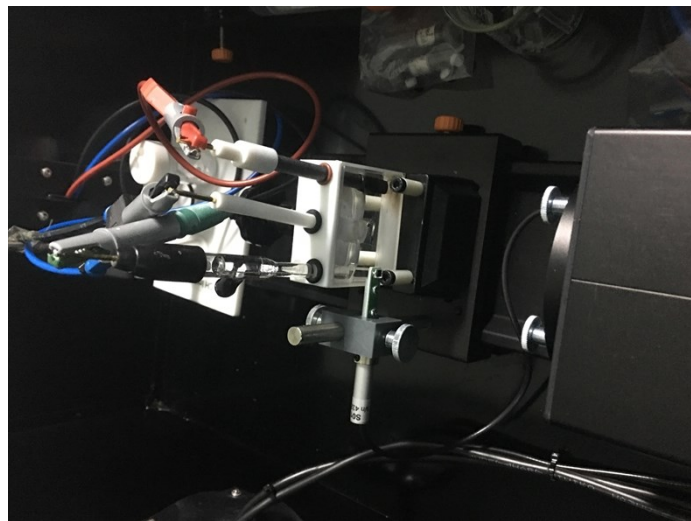
**Fig. S2.** SEM images of products obtained after selenylation in Ar/H<sub>2</sub> at 400°C.



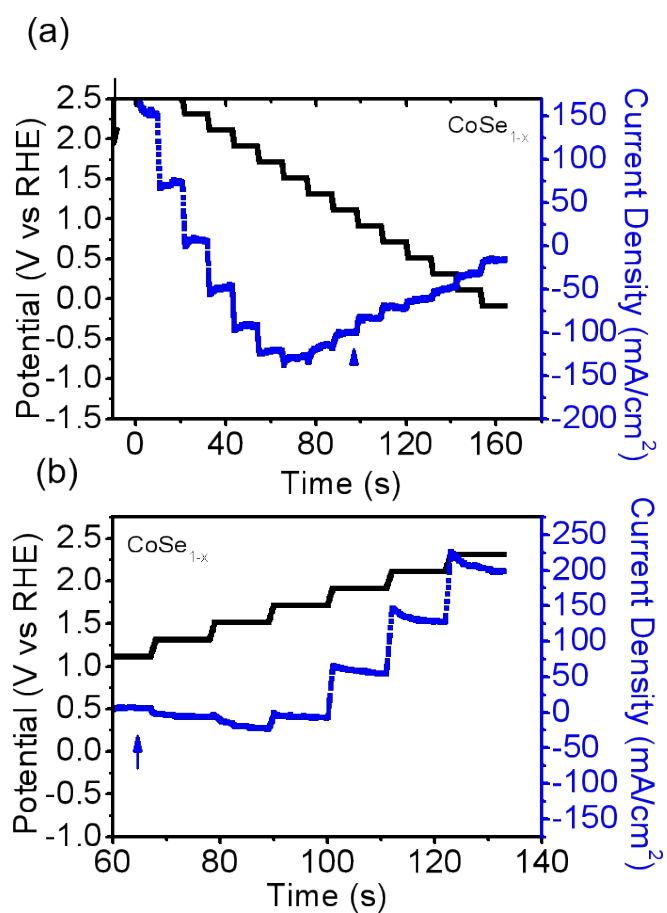
**Fig. S3.** EDS line elemental mapping of CoSe<sub>1-x</sub> obtained after sulfuration and selenization in pure Ar/H<sub>2</sub> at 400°C.



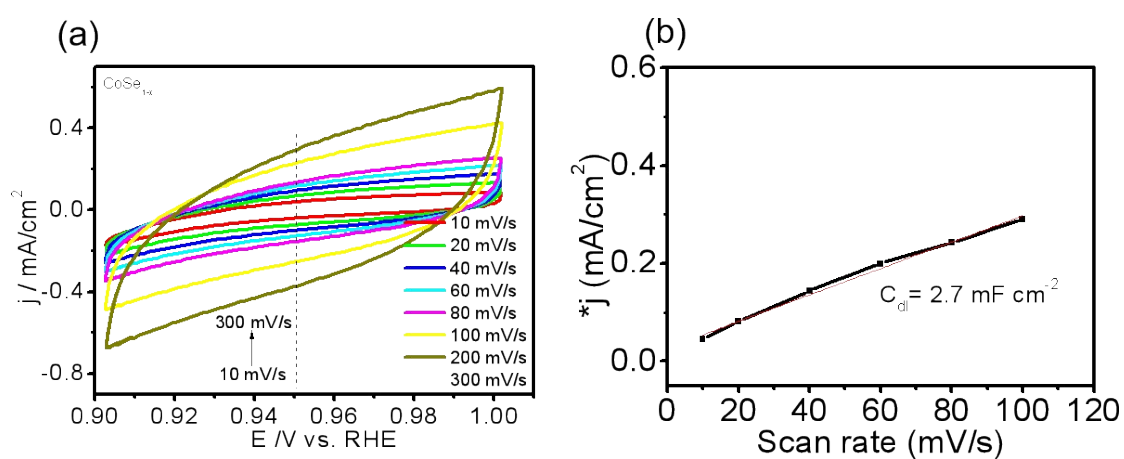
**Fig. S4.** Enlarged XPS survey Co 2p spectra of CoS<sub>2</sub> nanotubes, Se:CoS<sub>2-x</sub> core-shell nanotubes, and CoSe<sub>1-x</sub> nanorods.



**Fig. S5.** Optical photograph of the photochemical test system.

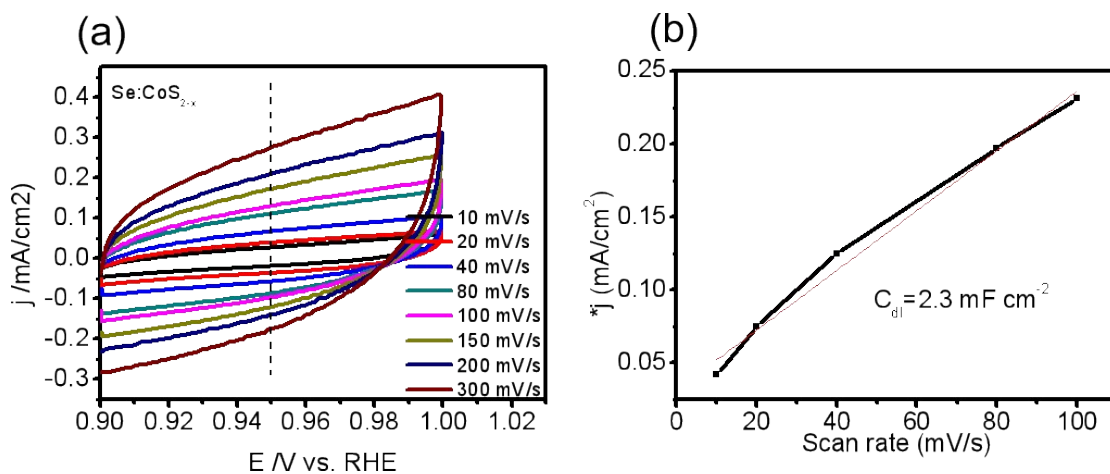


**Fig. S6.** The multi-step chronopotentiometric curve of CoSe<sub>1-x</sub> electrode.

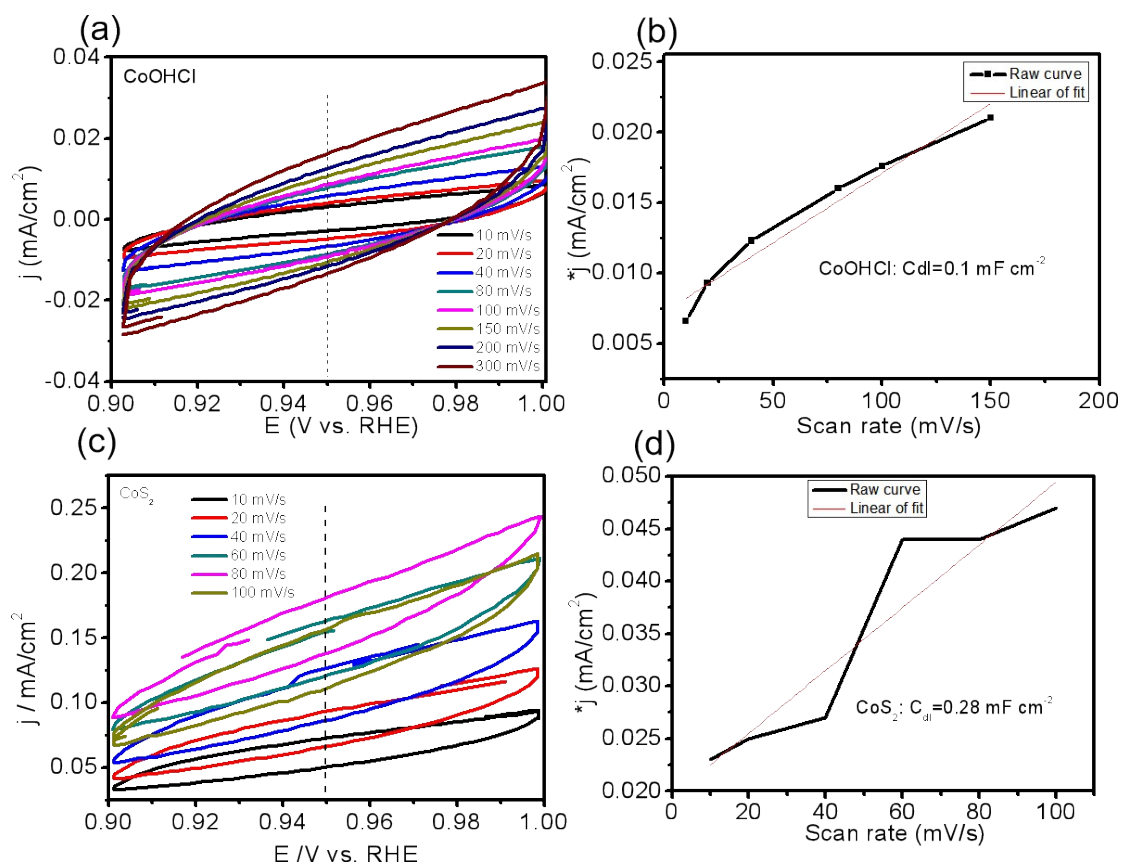


**Fig. S7.** Measured capacitive currents plotted of CoSe<sub>1-x</sub> electrode.

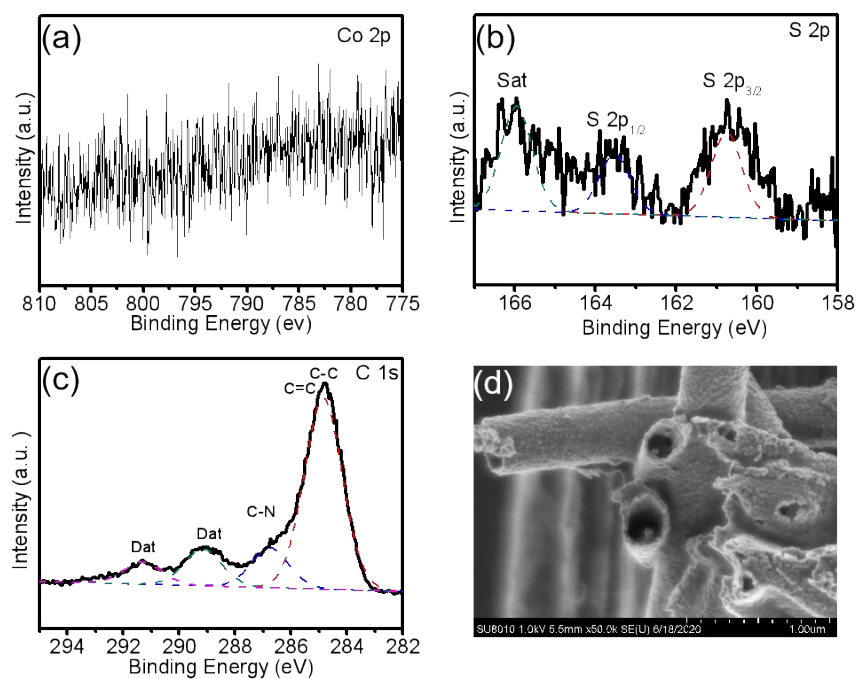




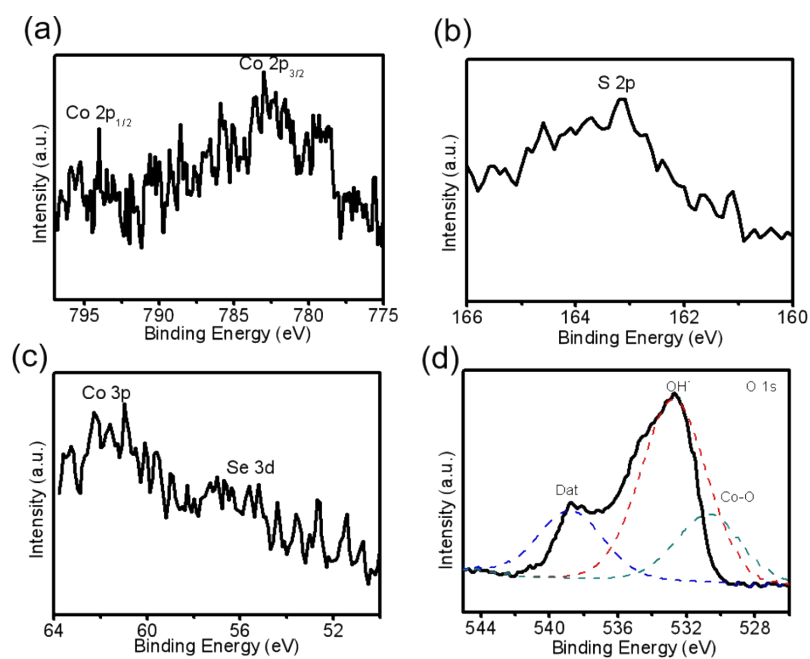
**Fig. S8.** Measured capacitive currents plotted of Se:CoS<sub>2-x</sub> electrode.



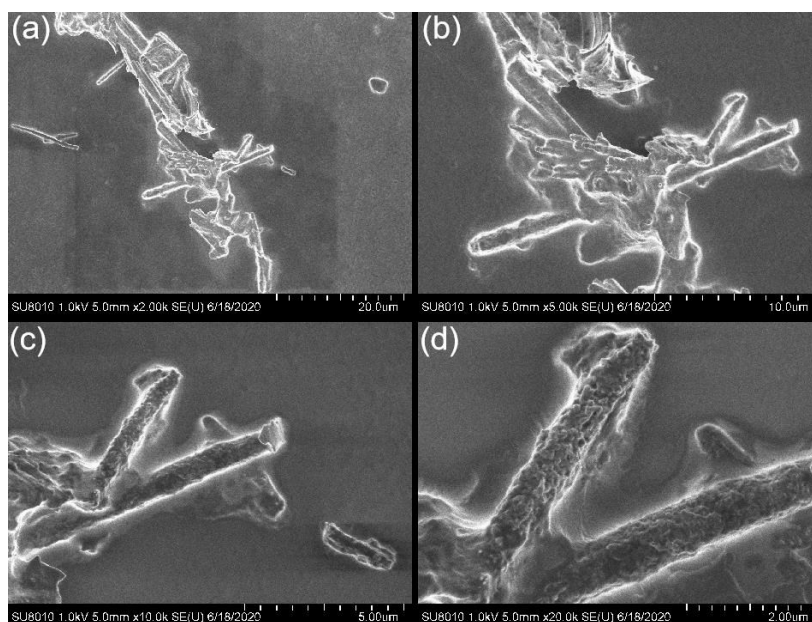
**Fig. S9.** Measured capacitive currents of CoOHCl, CoS<sub>2</sub> electrode, respectively.



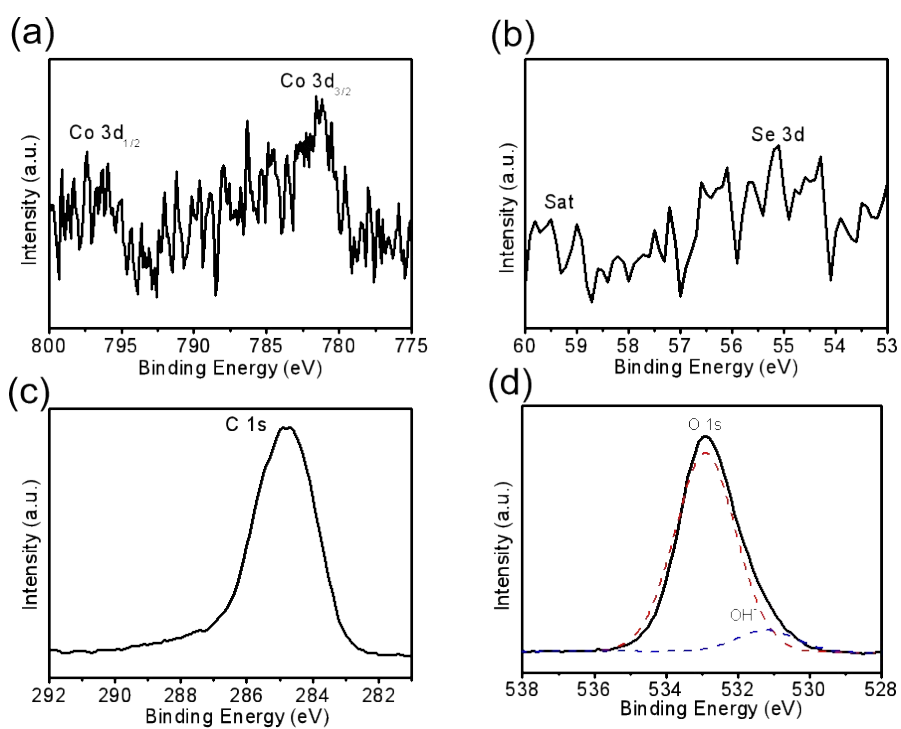
**Fig. S10.** (a) Co 2p; (b) S 2p; (c) C 1s of XPS spectra of CoS<sub>2</sub> after OER, respectively; (d) SEM image of CoS<sub>2</sub> after OER.



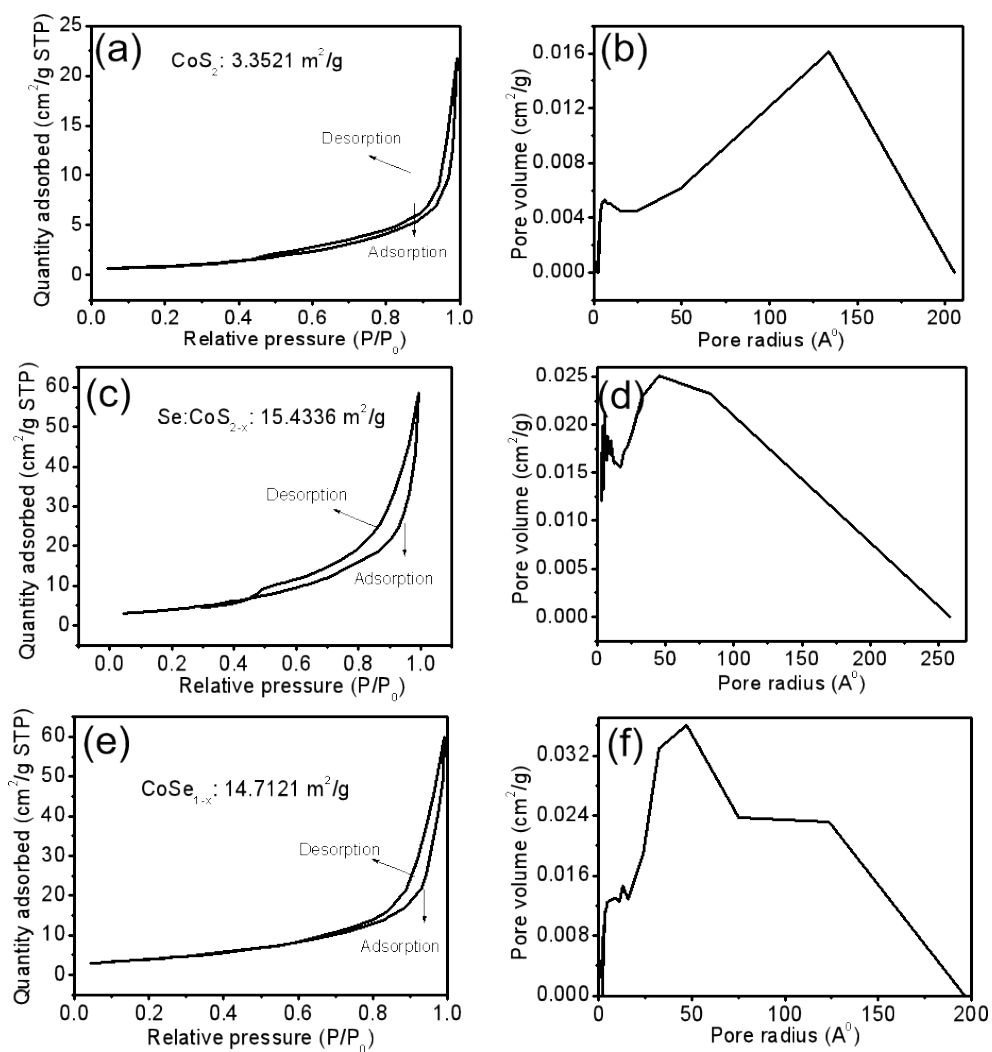
**Fig. S11.** (a) Co 2p; (b) S 2p; (c) Se 3d; (d) O 1s; of XPS spectra of Se:CoS<sub>2-x</sub> after OER, respectively.



**Fig. S12.** (a-d) SEM images of  $\text{CoSe}_{1-x}$  after OER.



**Fig. S13.** (a) Co 3d; (b) Se 3d; (c) C 1s; (d) O 1s; of XPS spectra of  $\text{CoSe}_{1-x}$  after OER, respectively.



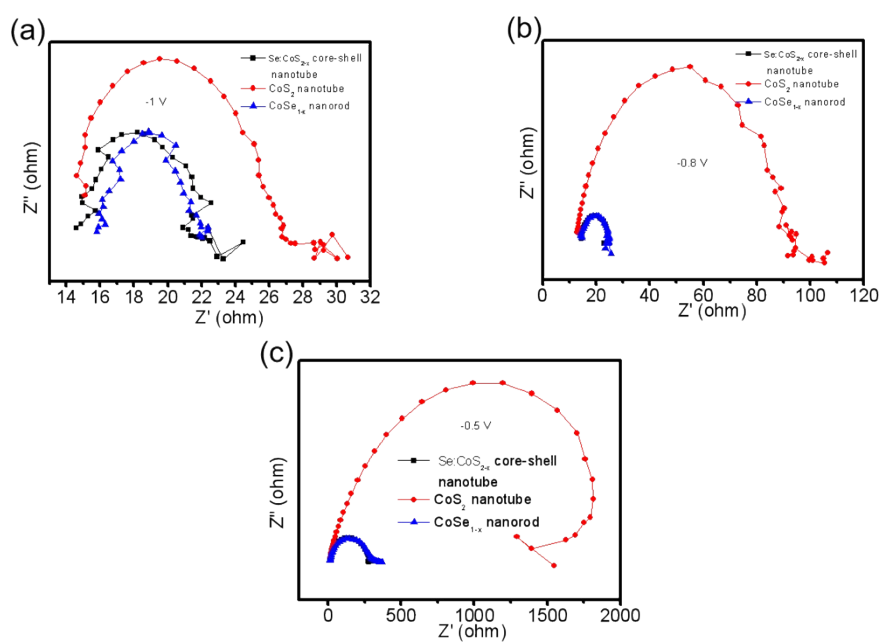
**Fig. S14.** N<sub>2</sub> adsorption–desorption isotherms of (a-d) CoS<sub>2</sub>, Se:CoS<sub>2-x</sub>, and CoSe<sub>1-x</sub>.

Properties	CoS <sub>2</sub>	Se:CoS <sub>2-x</sub>	CoSe <sub>1-x</sub>
BET surface area	3.3521 m <sup>2</sup> g <sup>-1</sup>	15.4336 m <sup>2</sup> g <sup>-1</sup>	14.7121 m <sup>2</sup> /g
Total pore volume (single point)	0.0338 ml/g	0.0908 ml/g	0.0927 ml/g

**Table S1.** Surface properties of the samples.

Electrodes	$\eta$ /mV@HER	Tafel slope/ mV dec <sup>-1</sup> @HER	$\eta$ /V@OER	Tafel slope/ mV dec <sup>-1</sup> @OER
CoOHCl	>800	189.2	1.63	657.1
CoS <sub>2</sub>	530	114.1	1.67	286.7
Se:CoS <sub>2-x</sub>	280	58.4	1.32	156.9
CoSe <sub>1-x</sub>	240	82.2	1.67	289.5

**Table S2.** The HER and OER performance ( $\eta$ ) and the double-layer capacitance in the non-faradaic region ( $C_{dl}$ ) of different catalysts.



**Fig. S15.** (a-c) Electrochemical impedance spectroscopy of the Se:CoS<sub>2-x</sub>, and CoSe<sub>1-x</sub> at different bias voltages.