Electronic Supplementary Material (ESI) for ChemComm.

# Electronic Supplementary Information

## Experimental section

### Materials

$SeO_2$, LiCl, HCl, $RuCl_3\cdot3H_2O$, KOH, and ethanol were purchased from Aladdin Ltd. (Shanghai, China). $Co(CH_3COO)_2\cdot4H_2O$ was purchased from Tianjin Chemical Corporation. Ti mesh was provided by Hongshan District, Wuhan Instrument Surgical Instruments business. Pt/C (20 wt% Pt on Vulcan XC-72R), and Nafion (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

### Preparation of *a*-CoSe/Ti:

Prior to the electrodeposition, Ti mesh was firstly washed with HCl, ethanol and water several times to remove the surface impurities. The electrodeposition solution contained 0.035 M $SeO_2$, 0.200 M LiCl and 0.065 M $Co(CH_3COO)_2\cdot4H_2O$. The electrodynamic deposition was carried out in a three-electrode cell using the cleaned Ti mesh (~ 1 cm x 2 cm) as the working electrode, a graphite plate as the counter electrode and Ag/AgCl (3 M KCl) as the reference electrode. Electrodeposition was performed by potentiostatically biasing the Ti mesh at a potential of -0.45 V vs. the Ag/AgCl reference electrode for 2 h at room temperature. After deposition, the Ti mesh was removed from the compression cell and rinsed first with ethanol, $H_2O$ and then dried at 60 °C for 8 h. The area of the Ti substrate that had not been covered by the electrodeposited film was then covered with nitrocellulose-based nail polish, to provide electrical insulation. The *a*-CoSe loading was determined with the use of a high precision microbalance. *a*-CoSe film with loading of 2.1 and 9.1 mg cm$^{-2}$ was also made by using a electrodeposition time of 1 and 3 h, respectively, under otherwise identical conditions.

**Preparation of Pt/C and $RuO_2$ loaded electrodes:**

$RuO_2$ catalyst was prepared according to reported method.[1] In brief, 0.01 mol of $RuCl_3 \cdot 3H_2O$ was dissolved in 100 mL deionized water and heated under air atmosphere at 100°C for 10 min, followed by the addition of 1 mL KOH solution (1.0 M). The reaction mixture was maintained at this temperature under stirring for 45 min. After that, the solution was centrifuged for 10 minutes and filtered. The precipitate was washed several times with deionized water to remove the remaining chlorides. The resulting Ru-hydroxide was dried for 5 h at 80°C and then calcined in air at 300°C for 3 h to obtain $RuO_2$. To prepare Pt/C and $RuO_2$ loaded electrodes, 20 mg Pt/C or $RuO_2$ and 10 μL 5 wt% Nafion solution were dispersed in 1 mL 1:1 v water/ethanol solvent by 30-min sonication to form an ink finally. Then 190 μL catalyst ink was loaded on a Ti mesh with a catalyst loading of 3.8 mg cm$^{-2}$.

**Structural Characterizations**

Electrochemical measurements are performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using *a*-CoSe/Ti as the working electrode, a graphite plate as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. $RuO_2$ or Pt/C was deposited on Ti mesh using Nafion solution. LSV measurements were conducted in

1.0 M KOH with a scan rate of 5 mV $s^{-1}$. All the potentials reported in this work were vs. RHE in 1.0 M KOH. E (RHE) = E (SCE) + 1.068 V. The RHE scale was calibrated using two Pt electrodes in a $H_2$ purged electrolyte. The long-term durability test was performed using chronopotentiometric measurements. All currents presented are corrected against the ohmic potential drop and no activation process was involved in all electrochemical tests. To reflect the real catalytic currents, all polarization curves were extracted by subtracting the capacitive currents.[2]

**Electrochemical characterization**

XRD data were acquired on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of 1 point per second. Raman spectra were collected with a Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter (Renishaw Ltd., Gloucestershire, U.K.) at ambient conditions. Radiation of 514.5 nm from an air-cooled argon ion laser was used for the SERS excitation. The laser beam was focused to a spot with a diameter of approximately 1 μm using a 20× microscope objective. The data acquisition time was

60 s for one accumulation. The Raman band of a silicon wafer at 520 $cm^{-1}$ was used to calibrate the spectrometer.

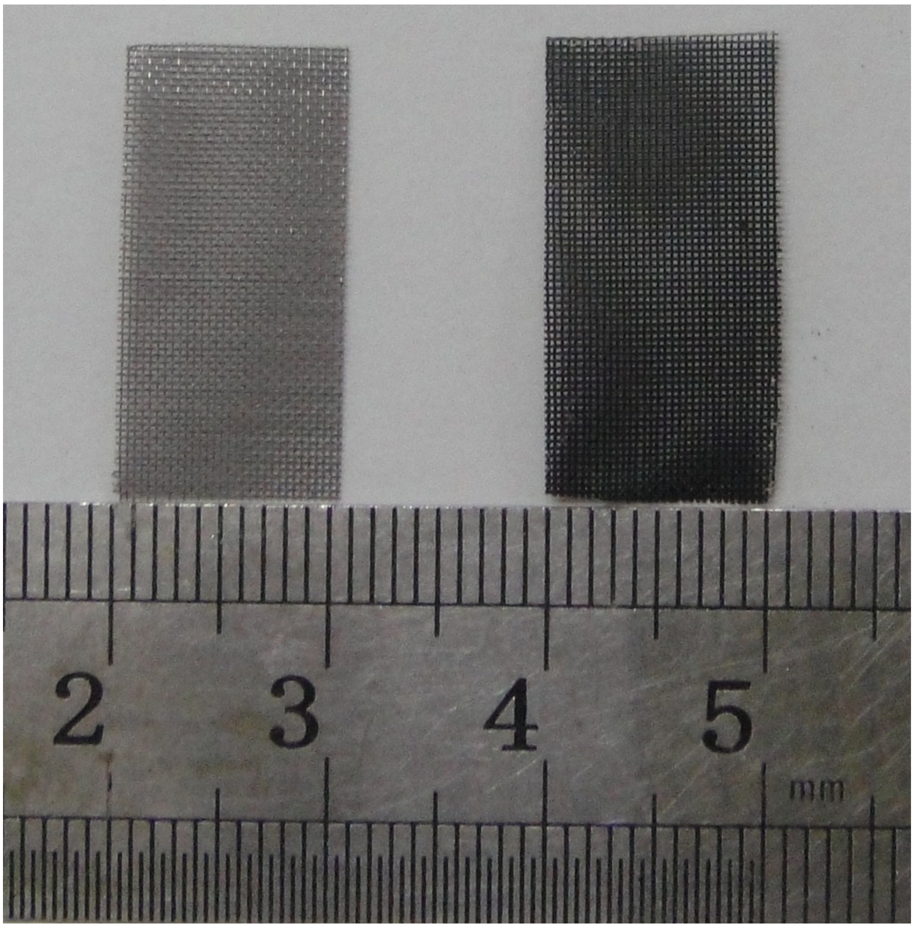

**Fig. S1.** Photograph of Ti mesh before (left) and after (right) electrochemical deposition.

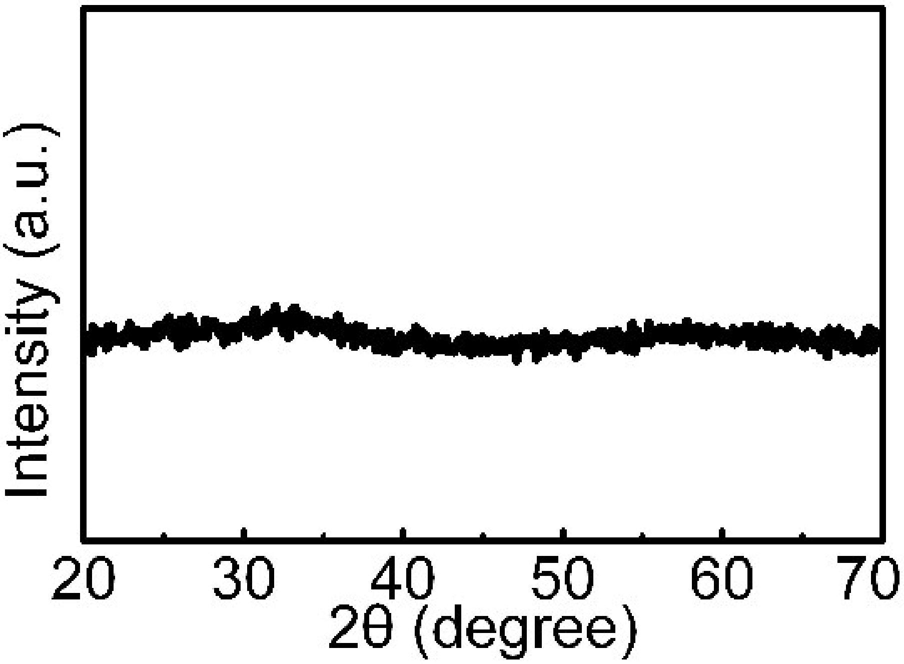

**Fig. S2.** XRD pattern for the deposit.

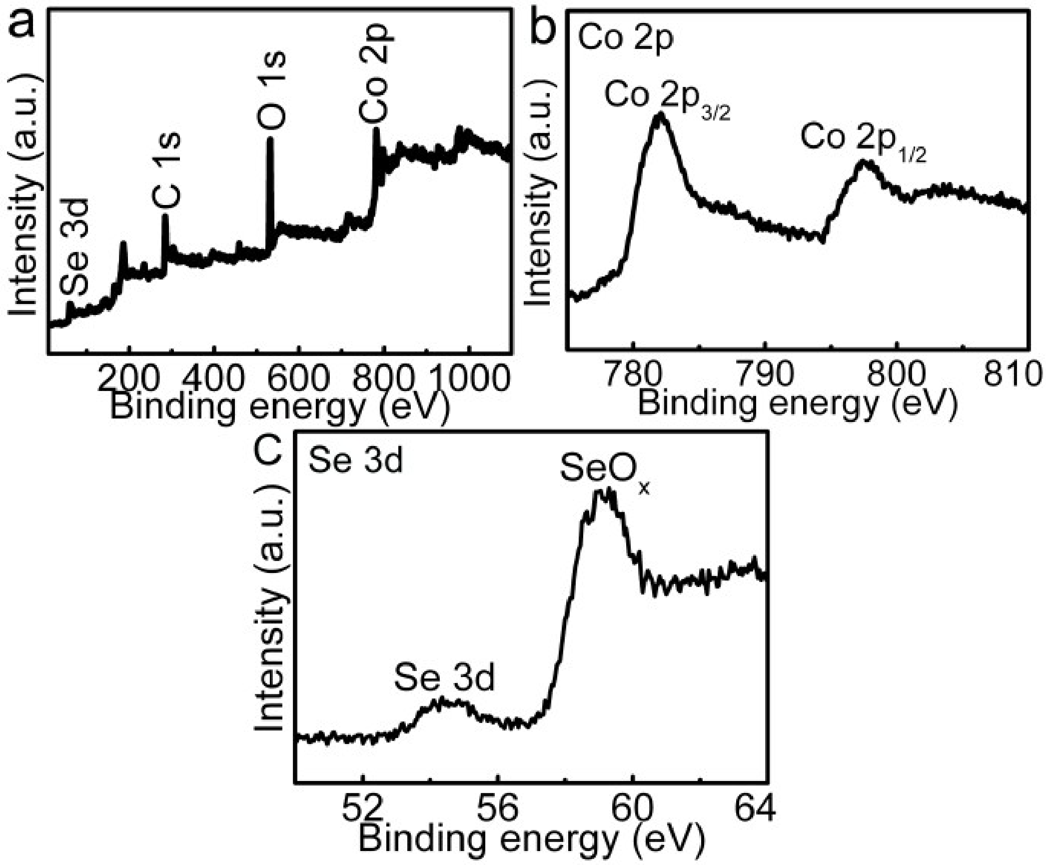

**Fig. S3.** (a) XPS survey spectrum of the *a*-CoSe/Ti. High-resolution XPS spectra in the (b) Co 2p and (c) Se 3d regions for *a*-CoSe.

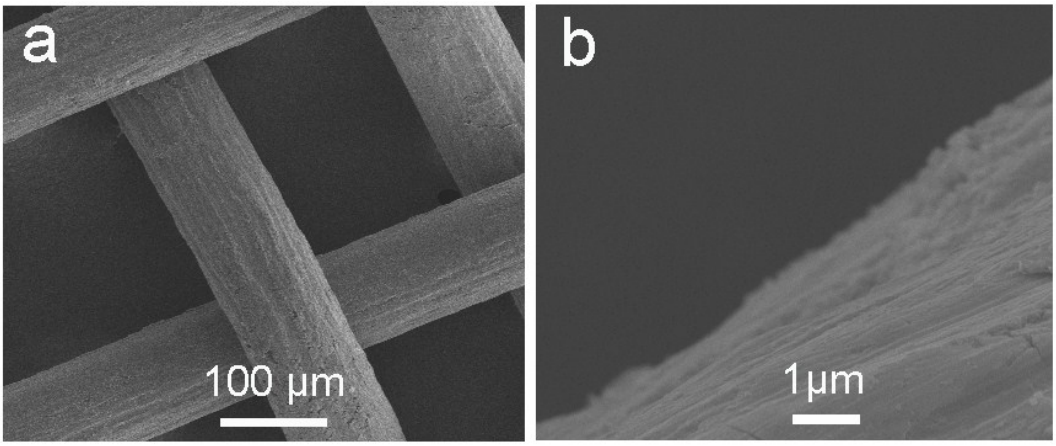

**Fig. S4.** (a) Low- and (b) high-magnification SEM images of Ti mesh.

**Table S1.** Comparison of OER performance for *a*-CoSe/Ti with other non-noble metal OER electrocatalysts in alkaline media.

| **Catalyst** | **Mass loading (mg cm$^{-2}$)** | **Electrolyte** | **Tafel slope (mV dec$^{-1}$)** | **$\eta$@10 mA cm$^{-2}$ (mV)** | **Ref.** |
|---|---|---|---|---|---|
| *a*-CoSe/Ti | 3.8 | 1.0 M KOH | 69 | 292 | This work |
| NiFe LDH | - | 1.0 M NaOH | - | 240 | *Science*, 2014, **345**, 1593-1596 |
| $CoO_x$@CN | 0.42 | 1.0 M KOH | - | 260 | *J. Am. Chem. Soc.*, 2015, **137**, 2688-2694 |
| PCPTF | 0.10 | 1.0 M KOH | 65 | ~300 | *Adv. Mater.***,** 2015, **27**, 3175-3180 |
| $Co_3O_4$/rm-GO | 0.17 | 1.0 M KOH | 67 | 310 | *Nat. Mater.*, 2011, **10**, 780-786 |
| $Zn_xCo_{3-x}O_4$ nanowire array | ~1 | 1.0 M KOH | 51 | 320 | *Chem. Mater.* 2014, **26** 1889-1895 |
| $Ni_{0.33}Co_{0.67}S_2$ nanowires | 0.30 | 1.0 M KOH | 51 | 330 | *Adv. Energy Mater.*, **2015**, *5*, 1402031 |
| Co-P film | 2.71 | 1.0 M KOH | 47 | 345 | *Angew. Chem. Int. Ed.*, 2015**,** **54**, 6251-6254 |
| N-doped graphene-CoO | - | 1.0 M KOH | 71 | 340 | *Energy Environ. Sci.*, 2014**,** **7**, 609-616 |
| $Ni_xCo_{3-x}O_4$ nanowire array | 2.3 | 1.0 M KOH | 59-64 | 370 | *Adv. Mater.*, 2010, **22** 1926-1929 |
| CoCo LDH | 0.07 | 1.0 M KOH | 59 | 393 | *Nat. Commun.*, 2014, **5**, 4477 |
| CoMn LDH | 0.142 | 1.0 M KOH | 43 | 324 | *J. Am. Chem. Soc.*, 2014, **136**, 16481-16484 |
| NiCo LDH | ~0.17 | 1.0 M KOH | 40 | 367 | *Nano Lett.*, 2015, **15**, 1421-1427 |
| PCN-CFP | ~0.20 | 0.1 M KOH | 61.6 | 400 | *Angew. Chem. Int. Ed.*, 2015, **54**, 4646-4650 |
| G-$C_3N_4$ nanosheets | ~0.10 | 0.1 M KOH | 128 | 414.5 | *Adv. Sci.*, 2015, **2**, 1400015 |
| NG-CNT | ~1.75 | 0.1 M KOH | 141 | ~480 | *Adv. Mater.*, 2014, **26**, 2925-2930 |

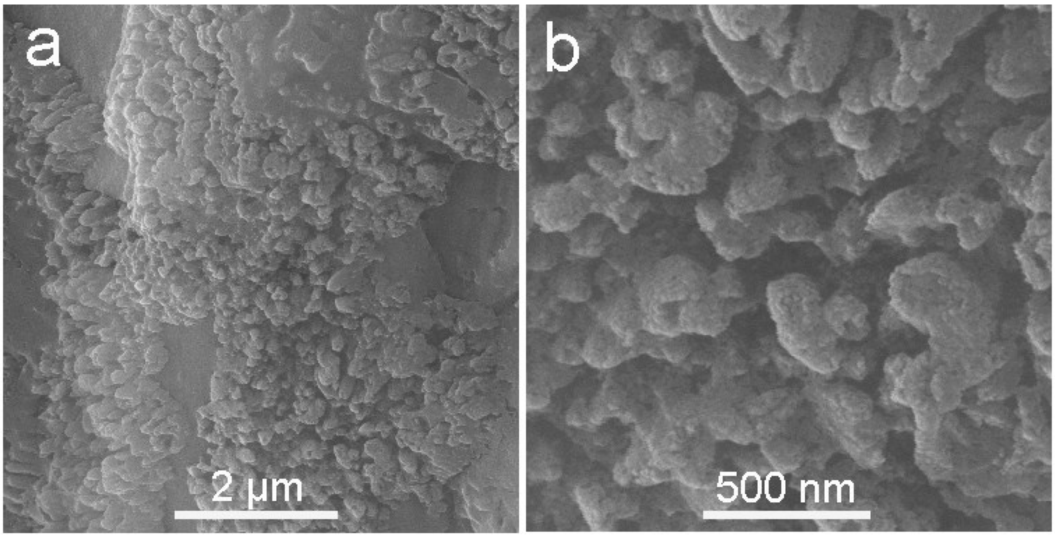

**Fig. S5.** (a) Low- and (b) high-magnification SEM images of *a*-CoSe/Ti after 2-h OER electrolysis at $\eta = 388$ mV.

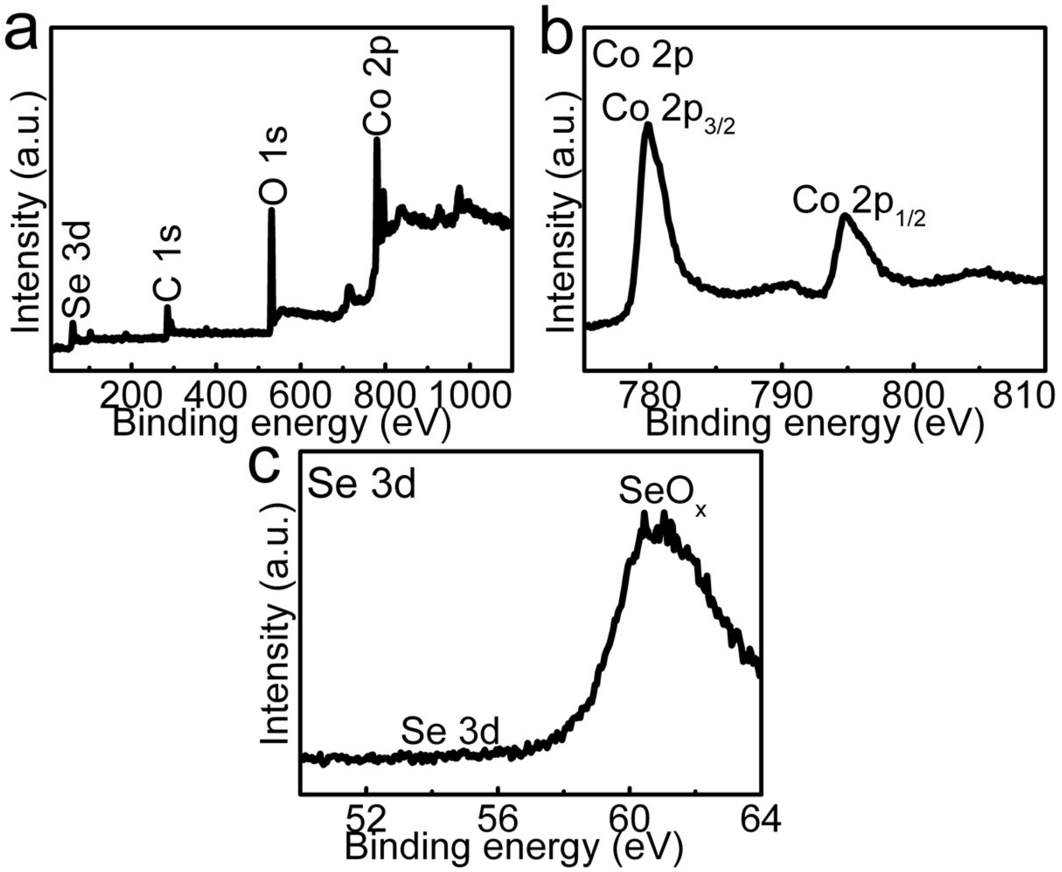

**Fig. S6.** (a) XPS survey spectrum for *a*-CoSe/Ti after OER electrolysis. XPS spectra for the post-OER *a*-CoSe/Ti in the (b) Co 2p and (c) Se 3d regions.

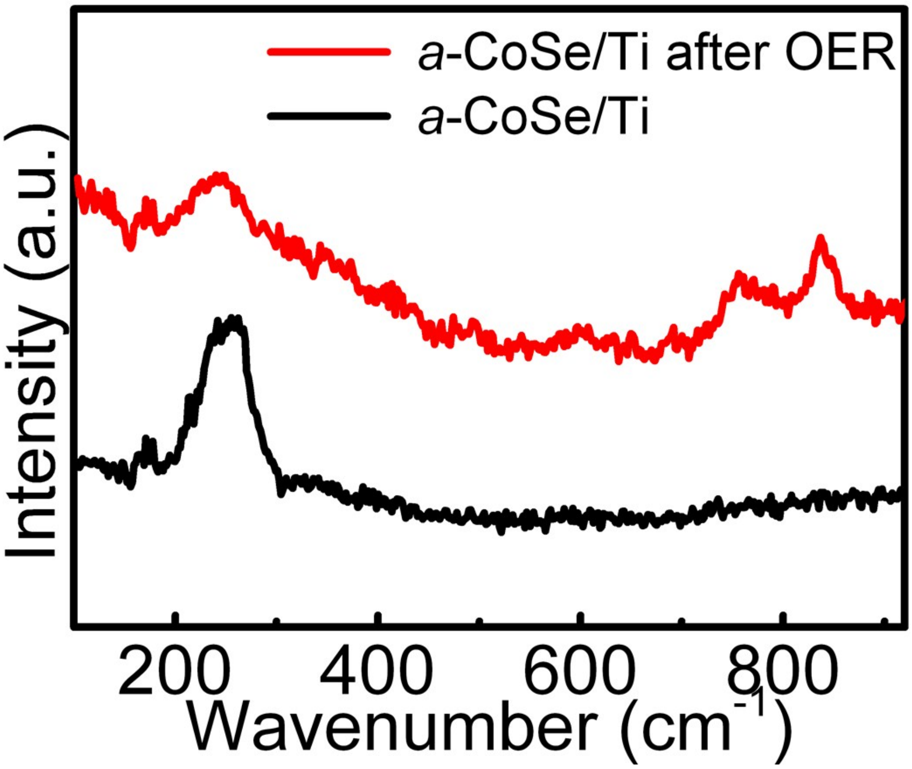

**Fig. S7.** Raman spectra of *a*-CoSe/Ti before and after OER electrolysis in 1.0 M KOH.

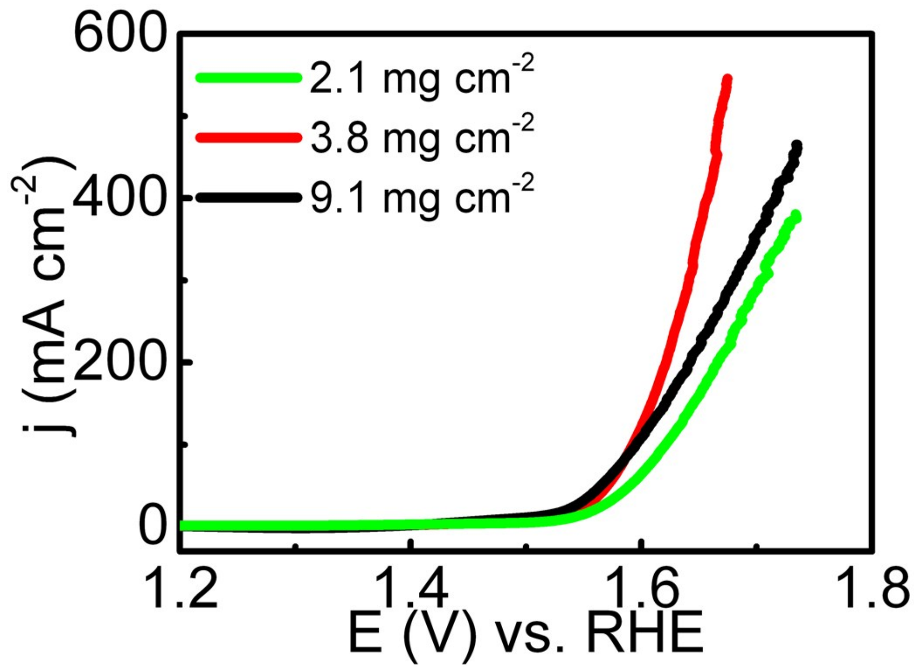

**Fig. S8.** Polarization curves of CoSe/Ti at different loading, suggesting the optimized loading is 3.8 mg $cm^{-2}$.

**Table S2.** Comparison of HER performance for *a*-CoSe/Ti with other non-precious metal HER electrocatalysts in alkaline media.

| **Catalyst** | **Mass loading (mg cm$^{-2}$)** | **Electrolyte** | **Tafel slope (mV dec$^{-1}$)** | ***η*@10 mA cm$^{-2}$ (mV)** | **Ref.** |
|---|---|---|---|---|---|
| *a*-CoSe/Ti | 3.8 | 1.0 M KOH | 84 | 121 | This work |
| $Ni_{0.33}Co_{0.67}S_2$ nanowires | 0.3 | 1.0 M KOH | 118 | 88 | *Adv. Energy Mater.*, **2015**, *5*, 1402031 |
| Co-P film | 2.71 | 1.0 M KOH | 42 | 94 | *Angew. Chem. Int. Ed.*, 2015, **54**, 6251-6254 |
| Co-N film | 3.4 | 1.0 M KOH | 193 | 180 | *ChemSusChem,* 2015, **8**, 1850-1855 |
| CoP/CC | 0.92 | 1.0 M KOH | 129 | 209 | *J. Am. Chem. Soc.*, 2014, **136**, 7587-7590 |
| NiFe LDH | - | 1.0 M NaOH | - | 210 | *Science*, 2014, **345**, 1593-1596 |
| $CoO_x$@CN | 0.42 | 1.0 M KOH | - | 232 | *J. Am. Chem. Soc.*, 2015, **137**, 2688-2694 |
| PCPTF | 0.1 | 1.0 M KOH | - | 375 | *Adv. Mater.*, 2015, **27**, 3175-3180 |
| Co-NRCNTs | 0.28 | 1.0 M KOH | - | ~370 | *Angew. Chem. Int. Ed.*, 2014, **126**, 4461-4465 |
| $CoSe_2$ NP/CP | 2.8 | 0.5 M $H_2SO_4$ | 42.1 | 139 | *J. Am. Chem. Soc.*, 2014, **136**, 4897−4900 |
| $WS_2$@P, N, O-graphene film | 0.113 | 0.5 M $H_2SO_4$ | 52.7 | 125 | *Adv. Mater.*, 2015*,* **27**, 4234-4241 |
| PCN@N-graphene-750 | 0.57 | 0.5 M $H_2SO_4$ | 49.1 | 80 | *ACS Nano*, 2015, **9**, 931-940 |

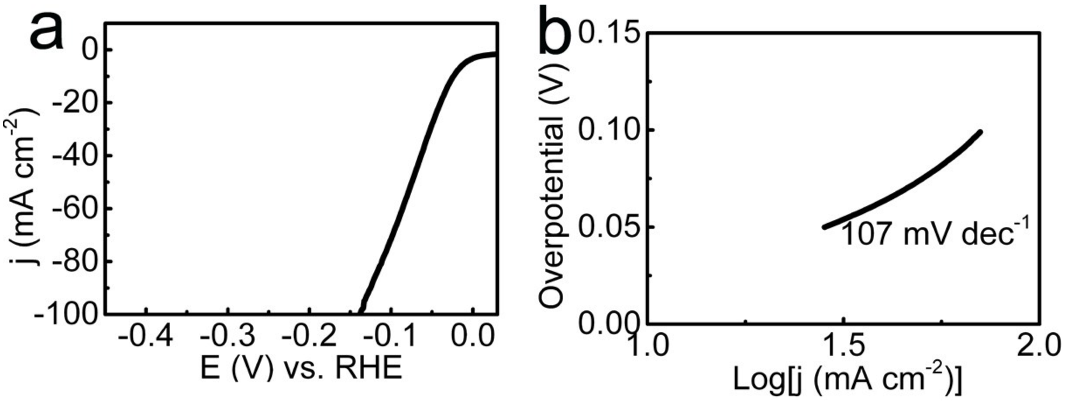

**Fig. S9.** (a) LSV curve and (b) the corresponding Tafel plot for Pt/C on GCE in 1.0 M KOH at a scan rate of 5 mV s$^{-1}$ for HER.

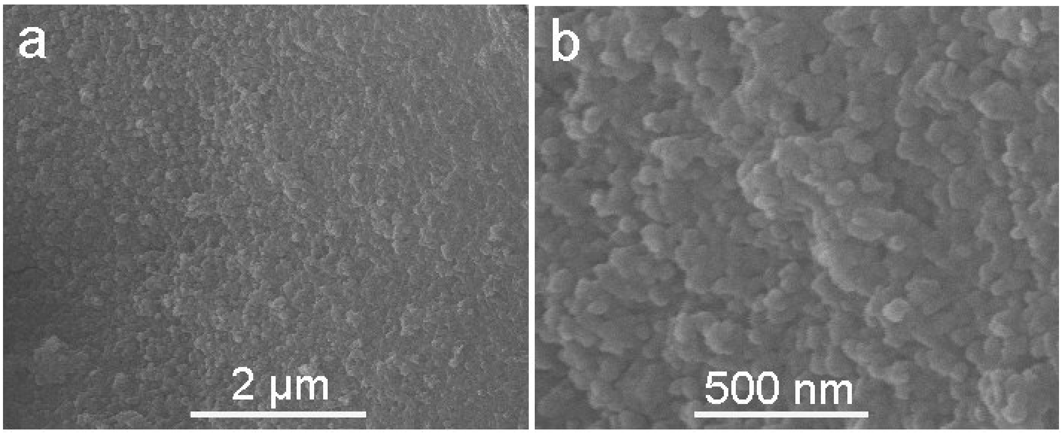

**Fig. S10.** (a) Low- and (b) high-magnification SEM images of *a*-CoSe/Ti after 2-h HER electrolysis at $\eta$ =135 mV.

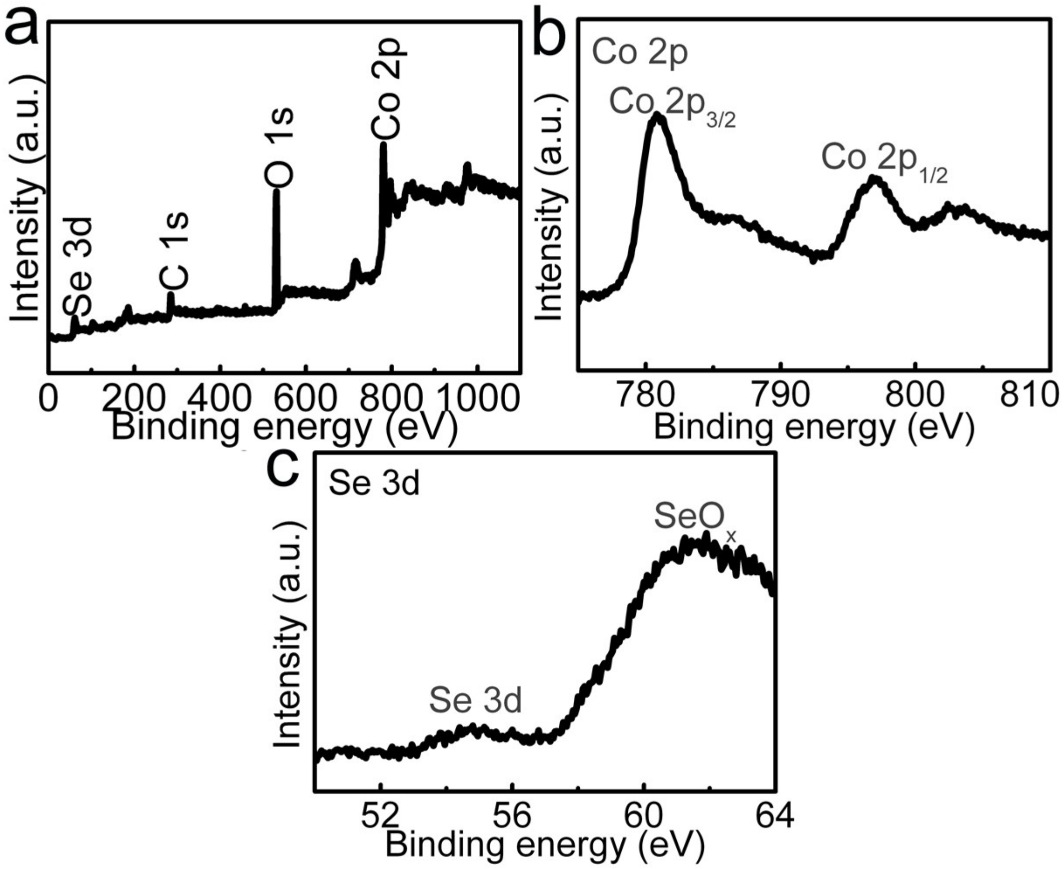

**Fig. S11.** (a) XPS survey spectrum for *a*-CoSe/Ti after HER electrolysis. XPS spectra for the post- HER a-CoSe/Ti in the (b) Co 2p and (c) Se 3d regions.

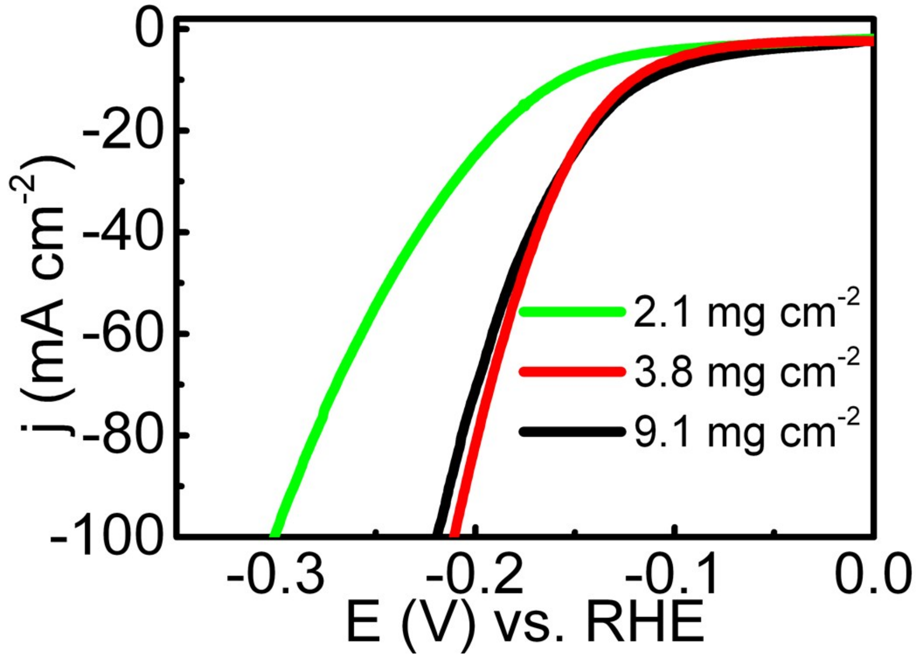

**Fig. S12.** Polarization curves of CoSe/Ti at different catalyst loading, suggesting the optimized loading for HER is 3.8 mg cm$^{-2}$.

**Movie S1.** This movie shows $H_2$ and $O_2$ evolution on *a*-CoSe/Ti electrodes in a two-electrode setup driven by a DC power supply with a cell voltage of 1.60 V in 1.0 M KOH.

## References

1 J. C. Cruz, V. Baglio, S. Siracusano, V. Antonucci, A. S. Aric, R. Ornelas, L. Ortiz-Frade, G. Osorio-Monreal, S. M. Durn-Torres and L. G. Arriaga, *Int. J. Electrochem. Sci.,* 2011, **6**, 6607-6619.

2 R. Mohamed, X. Cheng, E. Fabbri, P. Levecque, R. Kotz, O. Conrad and J. Schmidt, *J. Electrochem. Soc.,* 2015, **162**, 579-582.