

## Supporting Information

### **Achieving Increased Electrochemical Accessibility and Lowered OER Activation Energy for Co<sup>2+</sup> Sites with a Simple Anion pre-Oxidation**

Sengeni Anantharaj\*<sup>1</sup>, Hisashi Sugime<sup>1</sup>, Bozhi Chen<sup>1</sup>, Natsuho Akagi<sup>1</sup> and Suguru Noda\*<sup>1,2</sup>

<sup>1</sup>Department of Applied Chemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

<sup>2</sup>Waseda Research Institute for Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

\* Correspondence should be addressed to: [anantharaj1402@gmail.com](mailto:anantharaj1402@gmail.com) and [noda@waseda.jp](mailto:noda@waseda.jp)

## EXPERIMENTAL

### Materials Used

Co(II) chloride, selenium metal powder and sodium borohydride were procured from Sigma Aldrich, USA. KOH was procured from Wako Chemicals, Japan. Carbon cloth (CC) substrate electrode was procured from Sainergy India Pvt. Ltd. Chennai, India. Deionized water was used for both synthesis and electrochemical characterizations. CC electrode was used as a counter electrode while Hg/HgO, 1 M OH<sup>-</sup> was used as a reference electrode. All electrochemical characterizations were carried out with Biologic electrochemical workstation.

### Electrode Fabrications

CC stripes of dimension 1 cm × 5 cm were acid functionalized to make them hydrophilic and the same were used as substrates. A catalyst ink of composition 0.75 mL water, 0.2 mL 2-propanol and 0.05 mL 5% Nafion solution was prepared by dispersing exactly 3 mg of catalyst powder. This was sonicated for 20 min to homogenize the mixture. The homogenized ink was later drop casted on CC stripes. The corresponding loading of the catalysts is 0.205 mg cm<sup>-2</sup>.

### Calculation of Charge ( $Q$ ) and Electrochemically Accessible Co<sup>2+</sup> Sites

#### For CoSeO<sub>3</sub>·2H<sub>2</sub>O before activation:

$$\text{Area under oxidation peak} = 0.364 \text{ V mA}$$

$$\text{Hence, charge } (Q) \text{ is} = 0.364 \text{ V mA} / 0.005 \text{ V s}^{-1}$$

$$= 72.8 \text{ mA s}$$

$$= 0.0728 \text{ A s}$$

$$= 0.0728 \text{ C } (Q = it)$$

Since,  $\text{Co}^{2+}$  to  $\text{Co}^{3+}$  oxidation is one-electron transfer reaction,

$$\begin{aligned}\text{number of electrochemically accessible } \text{Co}^{2+} \text{ is} &= 0.0728 \text{ C} / 1.602 \times 10^{-19} \text{ C} \\ &= 4.54 \times 10^{17}\end{aligned}$$

**For  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$  after activation:**

$$\text{Area under oxidation peak} = 0.12 \text{ V mA}$$

$$\text{Hence, charge } (Q) \text{ is} = 0.12 \text{ V mA} / 0.005 \text{ V s}^{-1}$$

$$= 24 \text{ mA s}$$

$$= 0.024 \text{ A s}$$

$$= 0.024 \text{ C } (Q = it)$$

Since,  $\text{Co}^{2+}$  to  $\text{Co}^{3+}$  oxidation is one-electron transfer reaction,

$$\begin{aligned}\text{Number of electrochemically accessible } \text{Co}^{2+} \text{ is} &= 0.024 \text{ C} / 1.602 \times 10^{-19} \text{ C} \\ &= 1.45 \times 10^{17}\end{aligned}$$

**For  $\text{CoSe}_2$  before activation:**

$$\text{Area under oxidation peak} = 0.064 \text{ V mA}$$

$$\text{Hence, charge } (Q) \text{ is} = 0.064 \text{ V mA} / 0.005 \text{ V s}^{-1}$$

$$= 12.8 \text{ mA s}$$

$$= 0.0128 \text{ A s}$$

$$= 0.0128 \text{ C } (Q = it)$$

Since,  $\text{Co}^{2+}$  to  $\text{Co}^{3+}$  oxidation is one-electron transfer reaction,

$$\text{number of electrochemically accessible } \text{Co}^{2+} \text{ is } = 0.0128 \text{ C} / 1.602 \times 10^{-19} \text{ C}$$

$$= 7.99 \times 10^{16}$$

**For  $\text{CoSe}_2$  after activation:**

$$\text{Area under oxidation peak} = 0.067 \text{ V mA}$$

$$\text{Hence, charge } (Q) \text{ is } = 0.067 \text{ V mA} / 0.005 \text{ V s}^{-1}$$

$$= 13.4 \text{ mA s}$$

$$= 0.0134 \text{ A s}$$

$$= 0.0134 \text{ C } (Q = it)$$

Since,  $\text{Co}^{2+}$  to  $\text{Co}^{3+}$  oxidation is one-electron transfer reaction,

$$\text{number of electrochemically accessible } \text{Co}^{2+} \text{ is } = 0.0134 \text{ C} / 1.602 \times 10^{-19} \text{ C}$$

$$= 8.36 \times 10^{16}$$

## Determination of Total Number of $\text{Co}^{2+}$ Sites in Loaded Catalyst and the Percentage

### Utilization of $\text{Co}^{2+}$ Sites

#### For $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ :

Molecular weight of  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$  = 222

Atomic weight of Co = 59

Hence, 222 g of  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$  has 59 g of Co

Therefore, weight of Co in 0.00205 g of  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$  =  $59/222 \times 0.00205 = 0.000545$  g

No. of Co in 0.00054482 g of Co =  $0.000545/59 = 9.23 \times 10^{-6}$

Now, no. of Co atom in  $9.23 \times 10^{-6}$  moles of Co =  $(9.23 \times 10^{-6}) (6.023 \times 10^{23})$   
=  $5.56 \times 10^{18}$

Electrochemically accessible  $\text{Co}^{2+}$  sites before activation =  $4.54 \times 10^{17}$

Utilization of  $\text{Co}^{2+}$  site in  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$  before activation = 8.17%

Electrochemically accessible  $\text{Co}^{2+}$  sites after activation =  $1.45 \times 10^{17}$

Utilization of  $\text{Co}^{2+}$  site in  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$  after activation = 2.61%

#### For $\text{CoSe}_2$ :

Molecular weight of  $\text{CoSe}_2$  = 217

Atomic weight of Co = 59

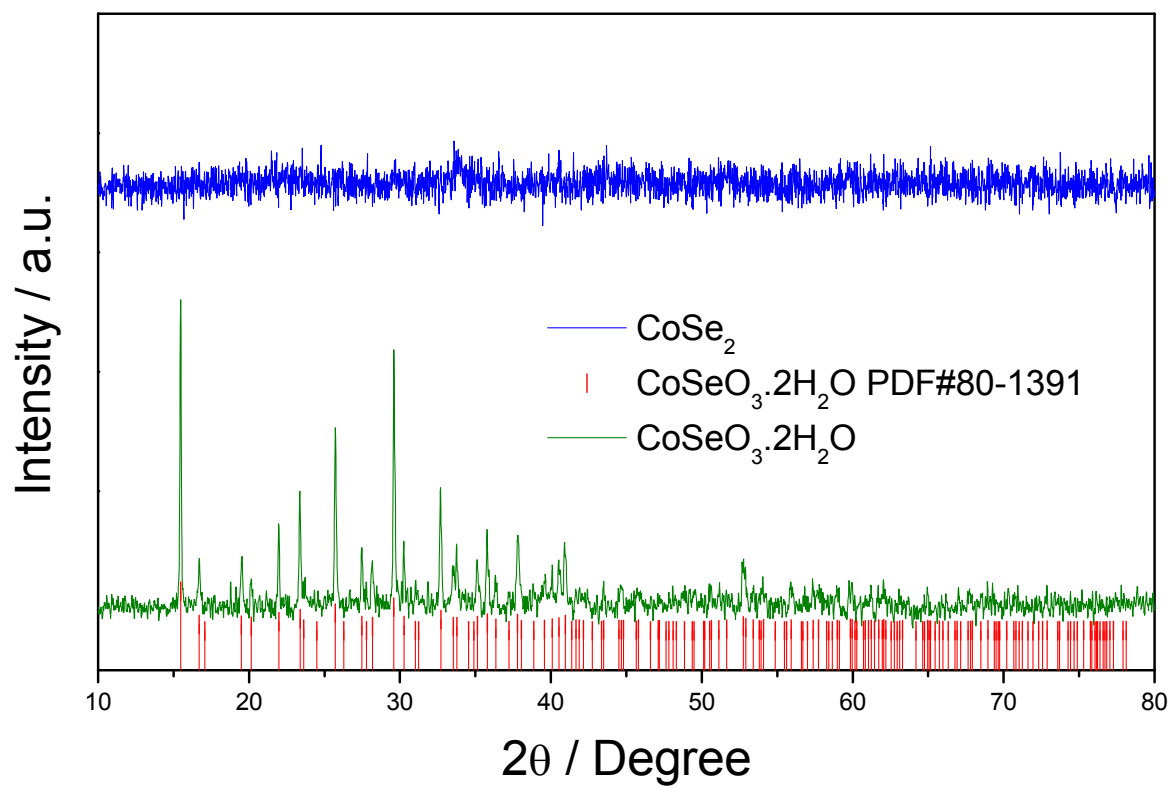
Hence, 217 g of  $\text{CoSe}_2$  has 59 g of Co

Therefore, weight of Co in 0.00205 g of  $\text{CoSe}_2$  =  $59/217 \times 0.00205 = 0.000557$  g

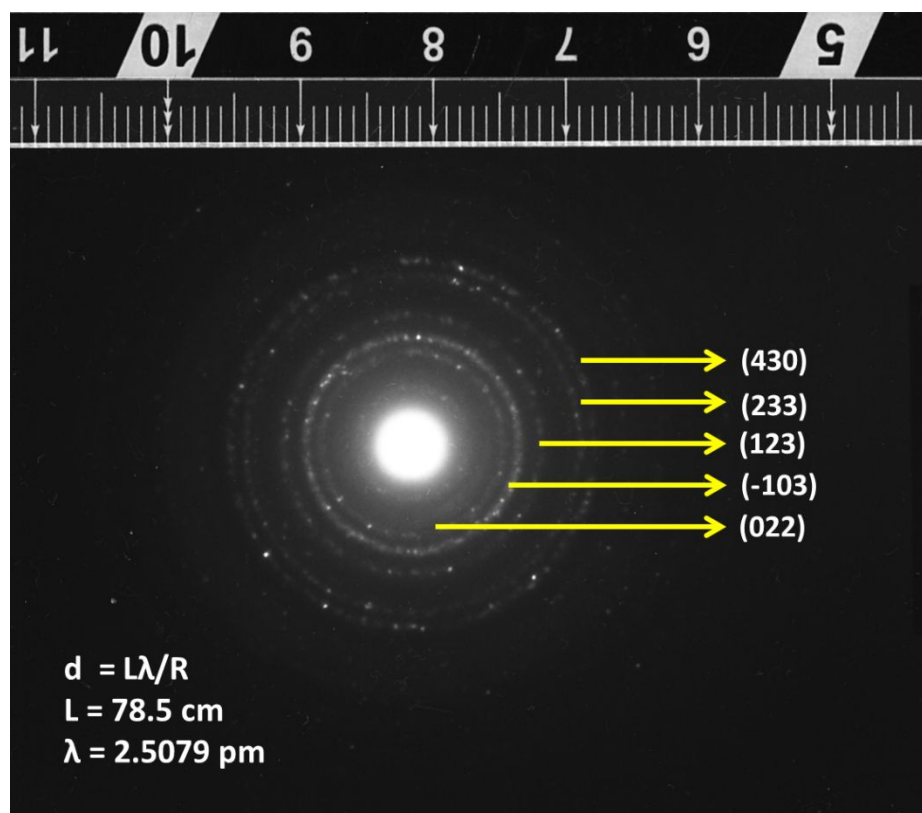
No. of moles of Co in 0.000557 g of Co =  $0.000557/59 = 9.45 \times 10^{-6}$

Now, no. of Co atom in  $9.45 \times 10^{-6}$  moles of Co =  $(9.45 \times 10^{-6}) (6.023 \times 10^{23})$   
=  $5.69 \times 10^{18}$

Electrochemically accessible $\text{Co}^{2+}$ sites before activation	$= 7.99 \times 10^{16}$
Utilization of $\text{Co}^{2+}$ site in $\text{CoSe}_2$ before activation	$= 1.40\%$
Electrochemically accessible $\text{Co}^{2+}$ sites after activation	$= 8.36 \times 10^{16}$
Utilization of $\text{Co}^{2+}$ site in $\text{CoSe}_2$ after activation	$= 1.47\%$

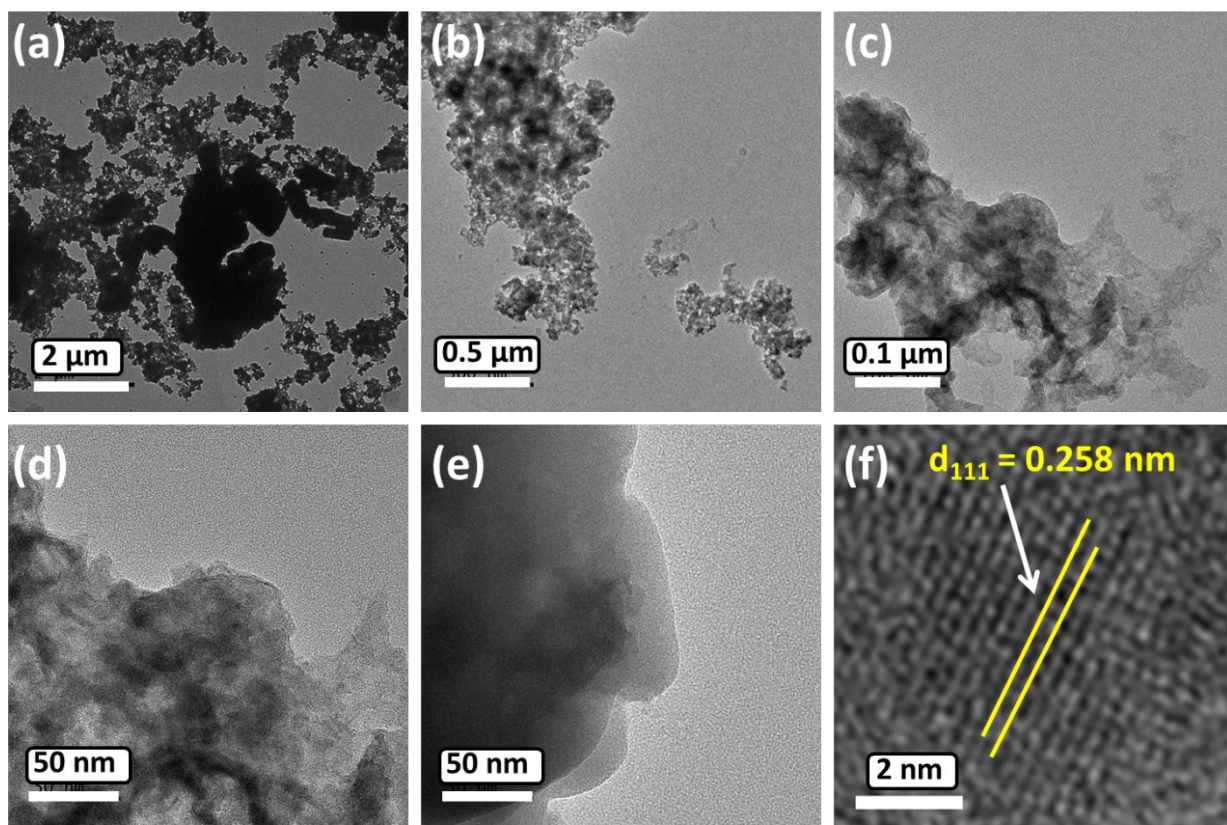


**Figure S1.** p-XRD patterns of as synthesized  $\text{CoSe}_2$  and  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$  catalyst powders.

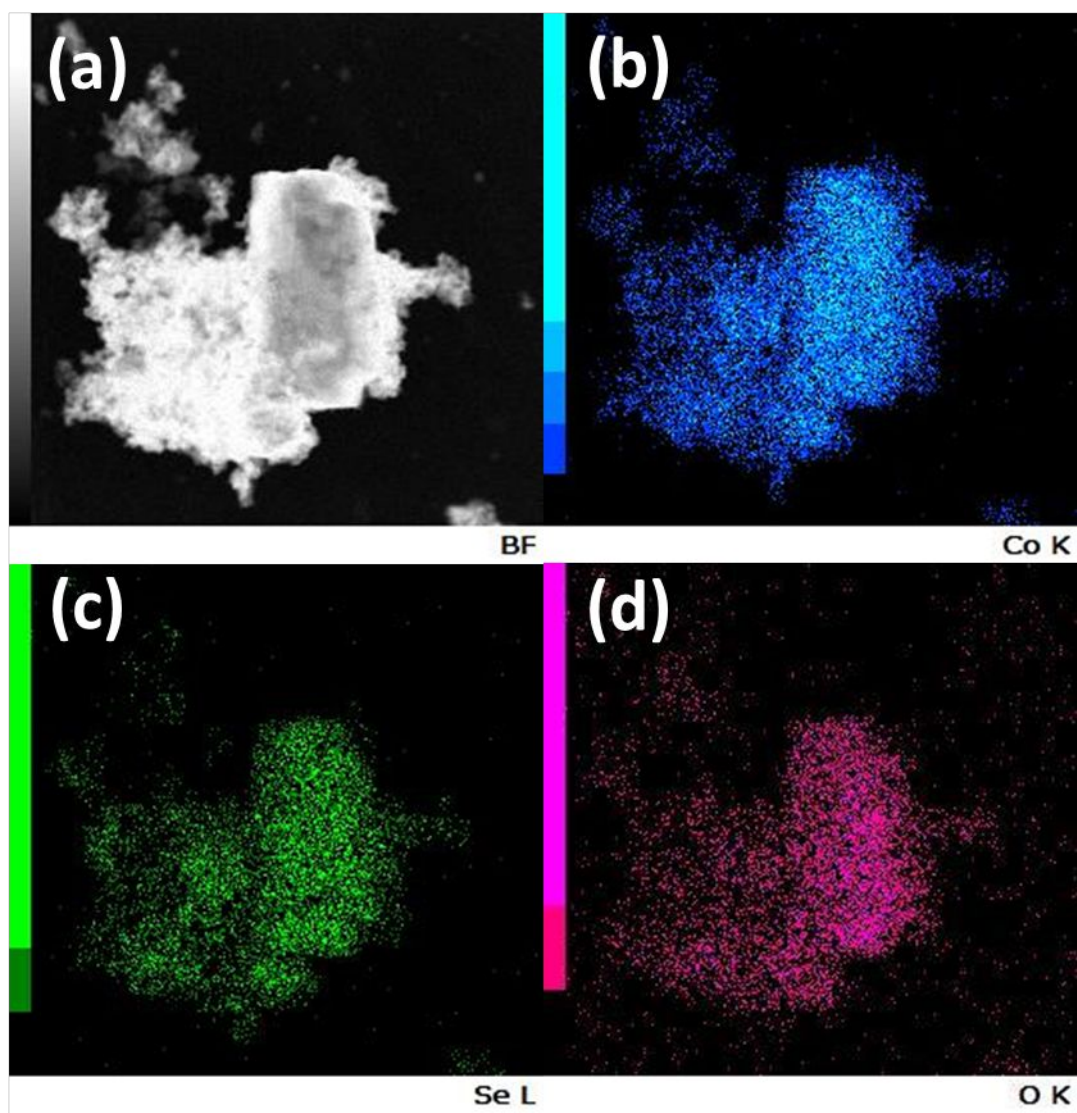


**Figure S2.** SAED pattern of  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ .

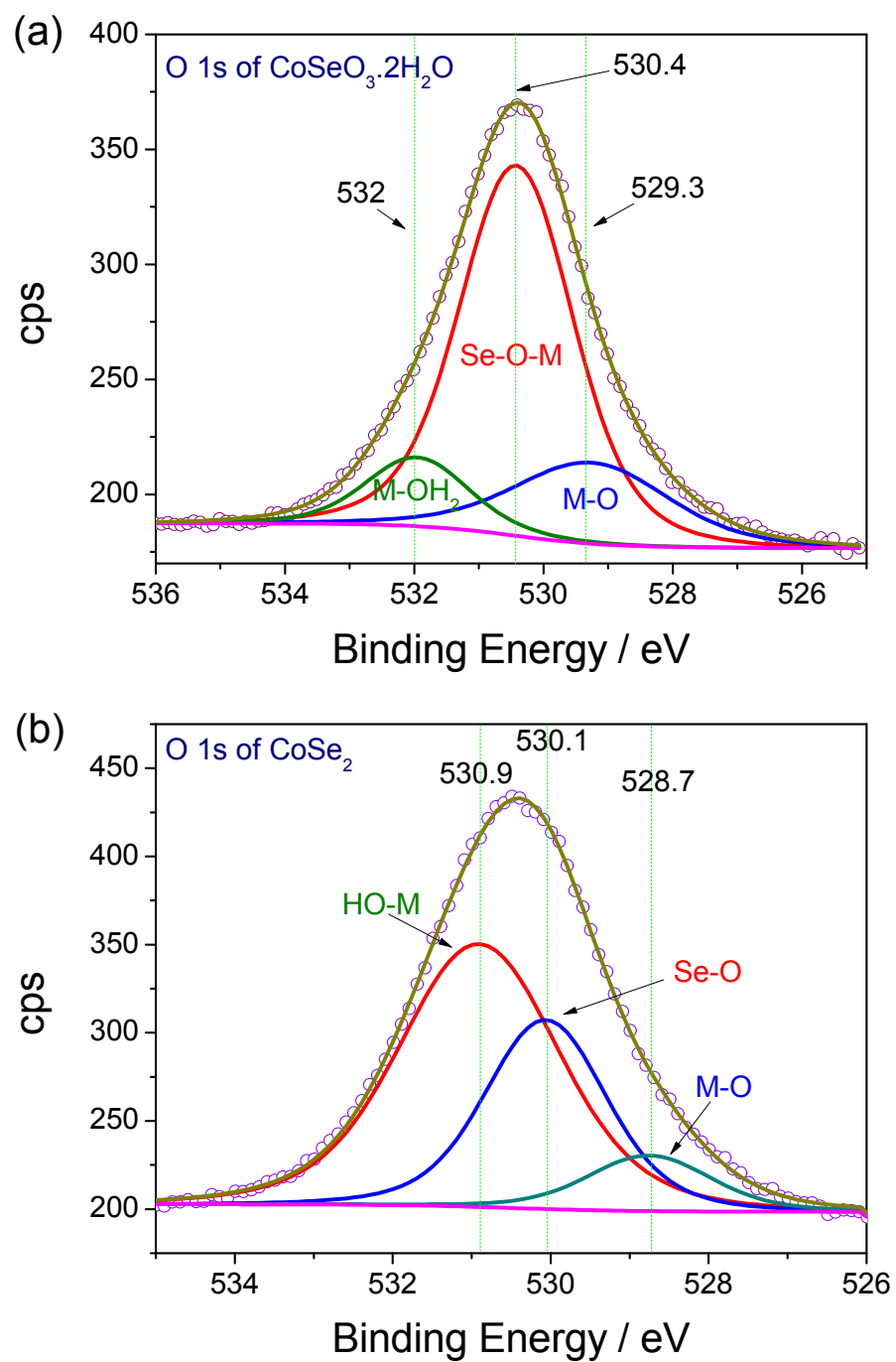




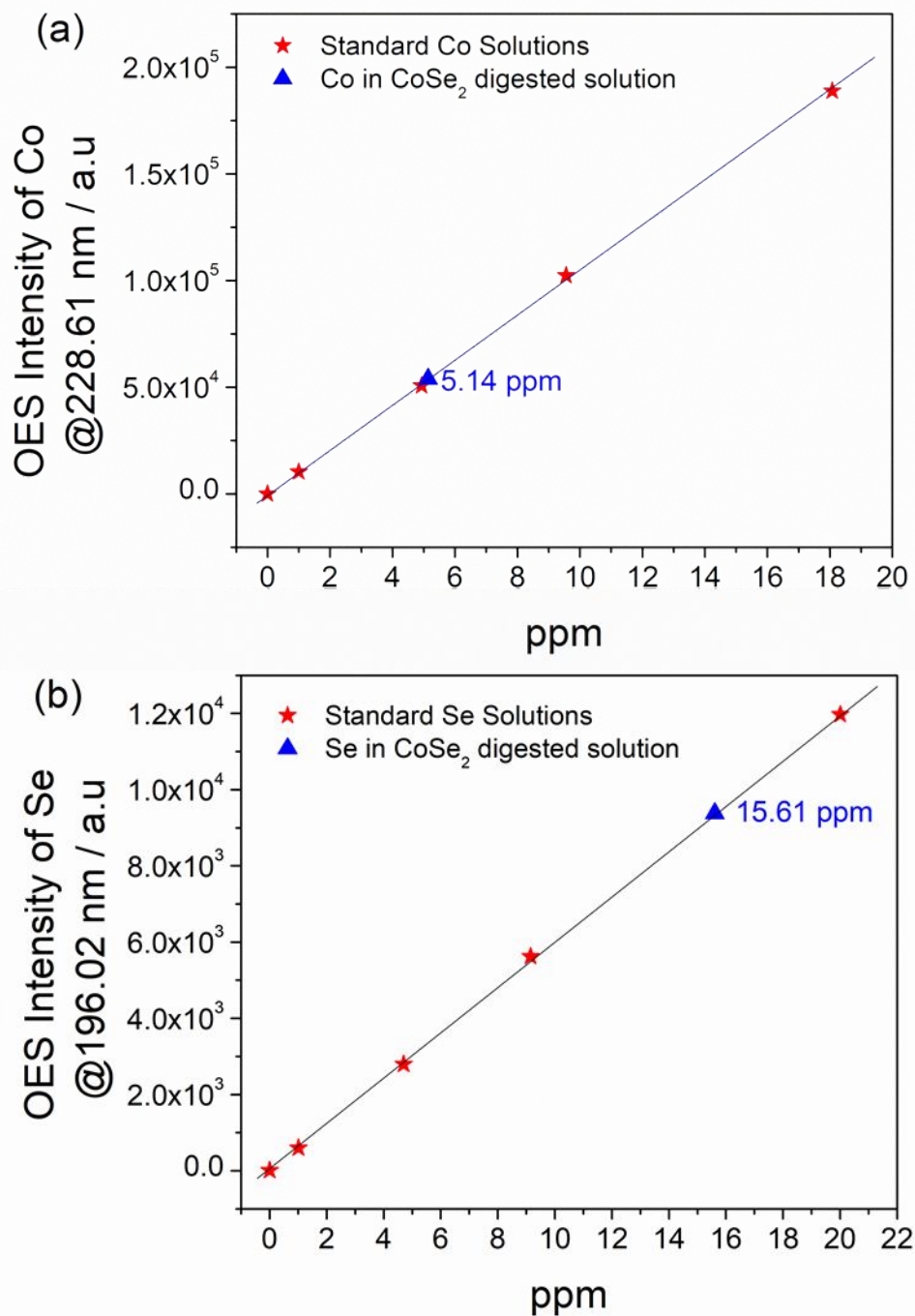
**Figure S3.** (a-e) TEM micrographs of CoSe<sub>2</sub> with increasing magnifications. (f) TEM micrograph of CoSe<sub>2</sub> at higher magnification showing lattice fringes.



**Figure S4.** (a) HAADF image of CoSe<sub>2</sub>. (b-d) Electronic smart maps of Co, Se and O of CoSe<sub>2</sub>.

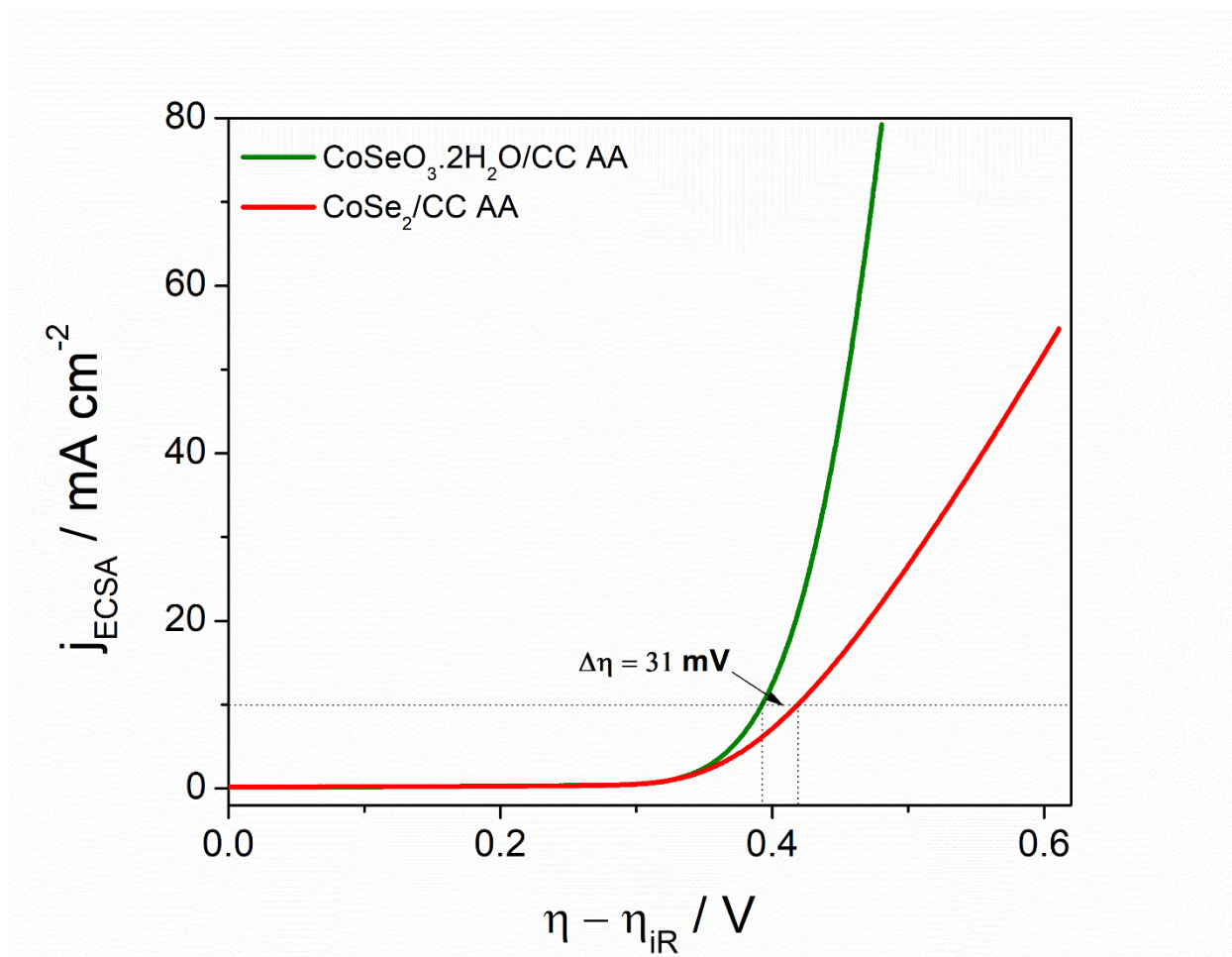


**Figure S5.** XPS O 1s spectra of  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$  and  $\text{CoSe}_2$  powders.

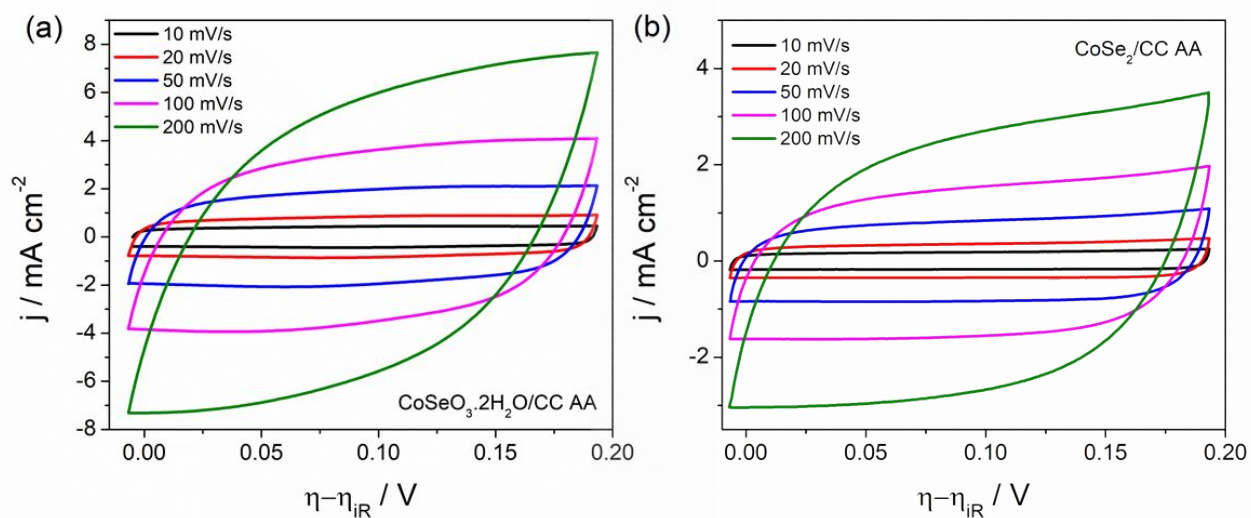


**Figure S6.** ICP-OES calibration curves constructed with the standard solutions indicating the concentrations of Co and Se in the digested CoSe<sub>2</sub> solution.

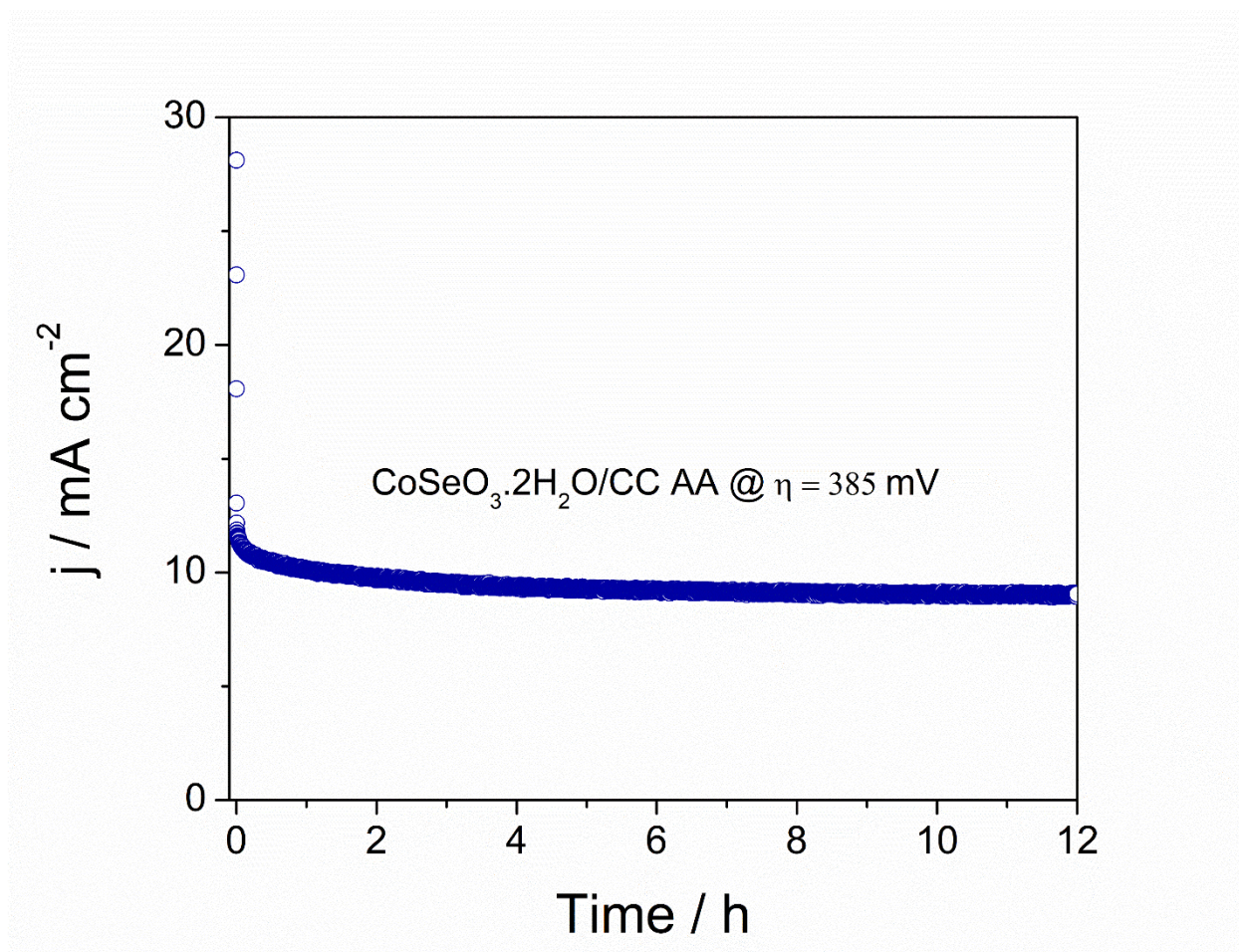




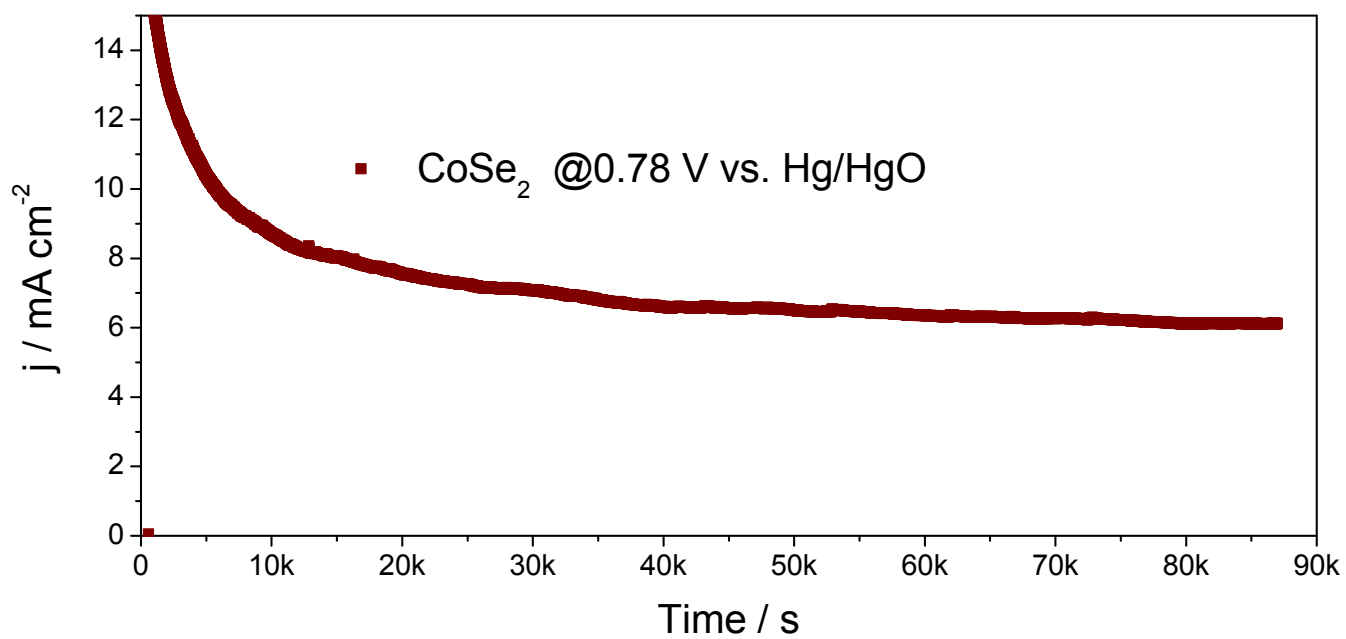
**Figure S7.** ECSA normalized OER activities of CoSeO<sub>3</sub>.2H<sub>2</sub>O and CoSe<sub>2</sub> after activation acquired at 5 mV s<sup>-1</sup>.



**Figure S8.** (a) Scan-rate dependent CVs of  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$  and  $\text{CoSe}_2$  after activation in the non-Faradaic region acquired with the scan rates of 10, 20, 50, 100, and 200  $\text{mV s}^{-1}$  in 1 M KOH.

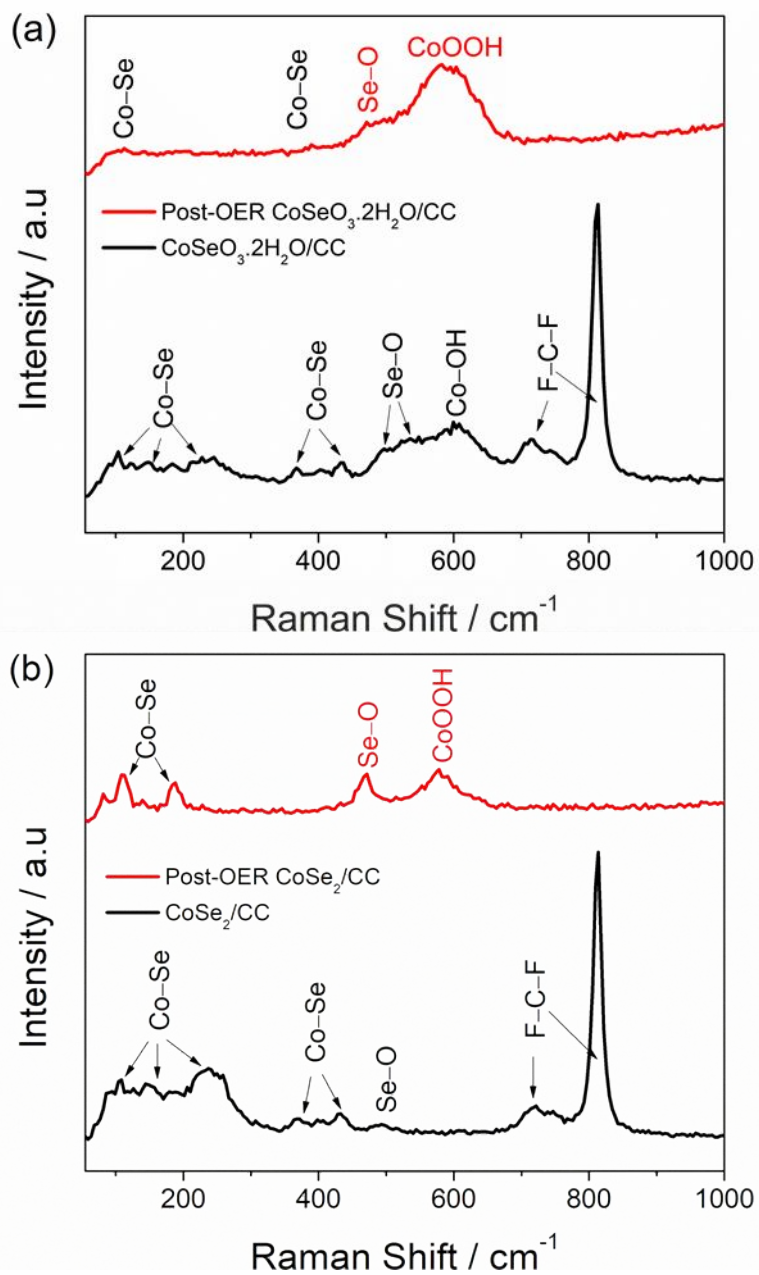


**Figure S9.** Chronoamperometric  $j - t$  response of  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$  after activation at  $\eta = 385 \text{ mV}$  in 1 M KOH.

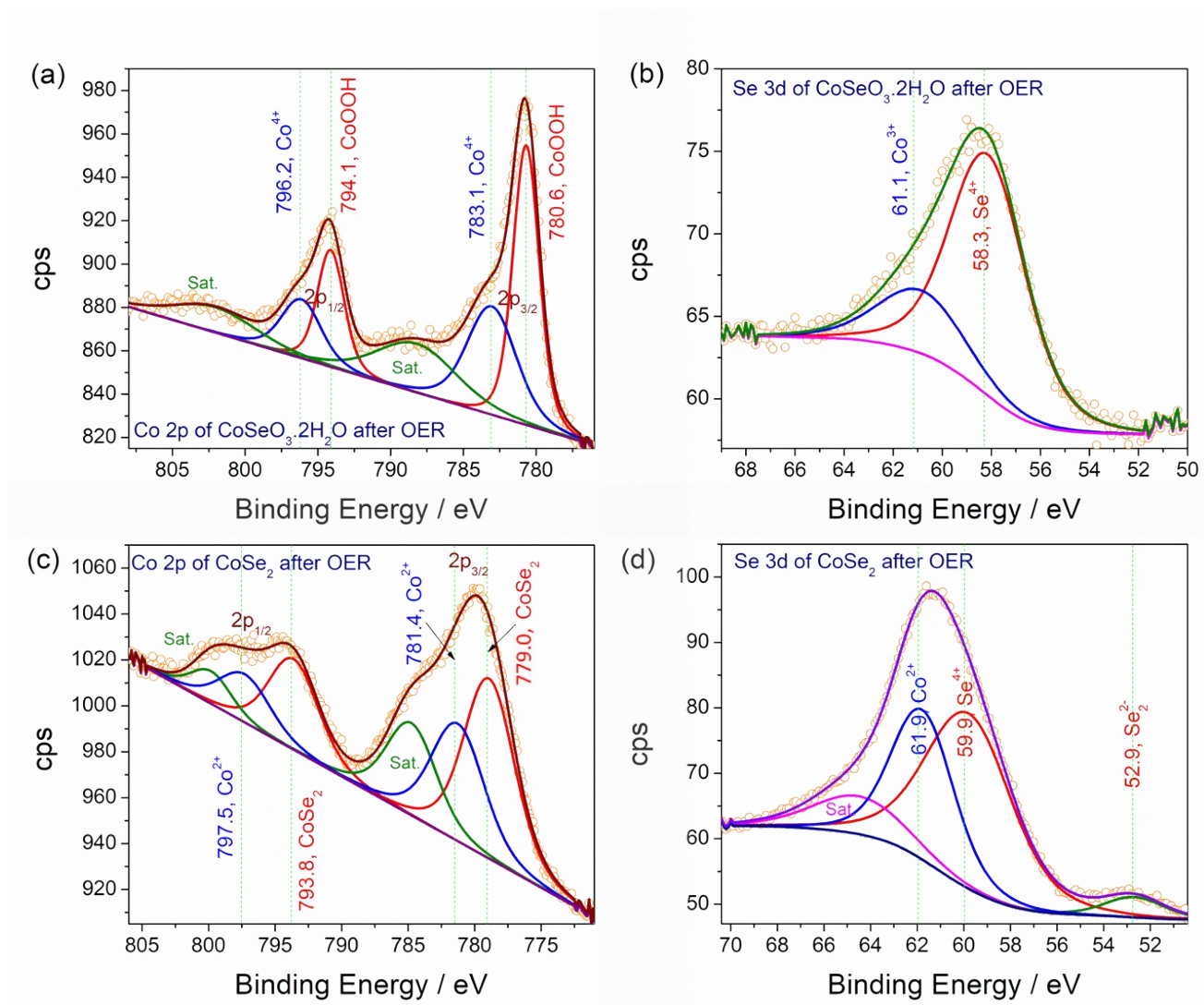


**Figure S10.** CA Response of  $\text{CoSe}_2$  at 0.78 V vs. Hg/Hg in 1 M KOH.





**Figure S11.** Raman spectra of  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}/\text{CC}$  (a) and  $\text{CoSe}_2/\text{CC}$  (b) before and after OER studies in 1 M KOH.



**Figure S12.** XPS spectra of  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}/\text{CC}$  (a – Co 2p and b- Se 3d) and  $\text{CoSe}_2/\text{CC}$  (c – Co 2p and d – Se 3d) acquired after OER in alkali.