Supporting Information for

Polymorphic $CoSe_2$ with Mixed Orthorhombic and Cubic phases for Highly Efficient Hydrogen Evolution Reaction

*Hongxiu Zhang, Bin Yang, Xiaolin Wu, Zhongjian Li, Lecheng Lei, Xingwang Zhang**

Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, Zhejiang Province 310027, China

* E-mail: xwzhang@zju.edu.cn

I. Experimental

1. Materials

Cobalt chloride hexahydrate, selenium dioxide, disodium hydrogen phosphate, ethanol, graphite (99.999%), hydrochloric acid, nitric acid, sulfuric acid, acetone, deionized water was used to prepare all solutions. All chemical compounds were in analytical grade and used as received without further purification. Ultra-high purity nitrogen (99.999%) and gas mixture (10% H_2 and 90% N_2) were supplied by Hangzhou Jingong Co. Ltd.

2. Preparation of $CoSe_x$ films on graphite disk (GD)

A standard three-electrode, single-compartment configuration was used in electrochemical deposition experiment. The electrolyte was bubbled with ultra-high purity nitrogen (99.999%) under stirring for 20 min prior to deposition to achieve an oxygen-free solution. The working electrode was a graphite disk fixed on the bottom of an electrode bar by conductive carbon adhesives. Such graphite disks have a geometric area of 0.2826 cm^2. The counter electrode was a platinum electrode of high purity with a large-area (1 cm * 1 cm). The reference electrode was a commercially available saturated calomel electrode (SCE).

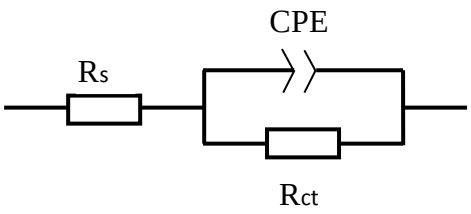
Electrolyte solution were prepared by adding 10 mmol cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and 10 mmol selenium dioxide (SeO_2) to 50 mmol potassium chloride solution (pH=3.4). Cyclic voltammograms recorded an oxidation peak at E_{pa}= 0.75 V vs. Hg/Hg_2Cl_2. The amorphous $CoSe_x$ films were obtained by chronoamperometry at -0.7 V vs Hg/Hg_2Cl_2 for 10-60 min. After the formation of

metallic $CoSe_x$ films, the electrode surface was carefully rinsed with large amounts of ultrapure water in order to remove any residues of bath chemicals.

Then the graphite supported $CoSe_x$ were dried under vacuum at 40 ℃, followed by calcination at different temperatures (250, 300, 450, 600 ℃) under Argon (100 sccm) for 40 min in a home-made tube reactor.

3. Electrochemical Characterization

Electrochemical measurements of current-potential polarization curve (*i*-V plot) were conducted with a scan rate of 3 mV/s. Electrochemical impedance spectroscopy (EIS) was performed in potentiostatic mode at −0.5 V *vs.* SCE from 200 kHz to 50 mHz. Signal semi-circles can be observed, and we choose the simplified Randles equivalent circuit to fit the experimental results. The equivalent circuit was shown below. Here R_s is the series resistance including the solution resistance etc., R_{ct} represents the charge transfer resistance. The value of R_s is readily obtained from the Nyquist plots. A constant phase element (CPE) was used in place of a double layer capacitance (C_{dl}) in order to give a more accurate fit to the experimental results. We used cyclic voltammetry method to determine C_{dl}. The potential was swept from -0.06 V to -0.16 V (*vs* SCE) three times at each of 9 different scan rates (4, 8, 16, 24, 32, 48, 64, 96, 128 mV/s).



II. SEM and EDX analysis of the as-deposited CoSex and $CoSe_x$ calcined at different temperatures

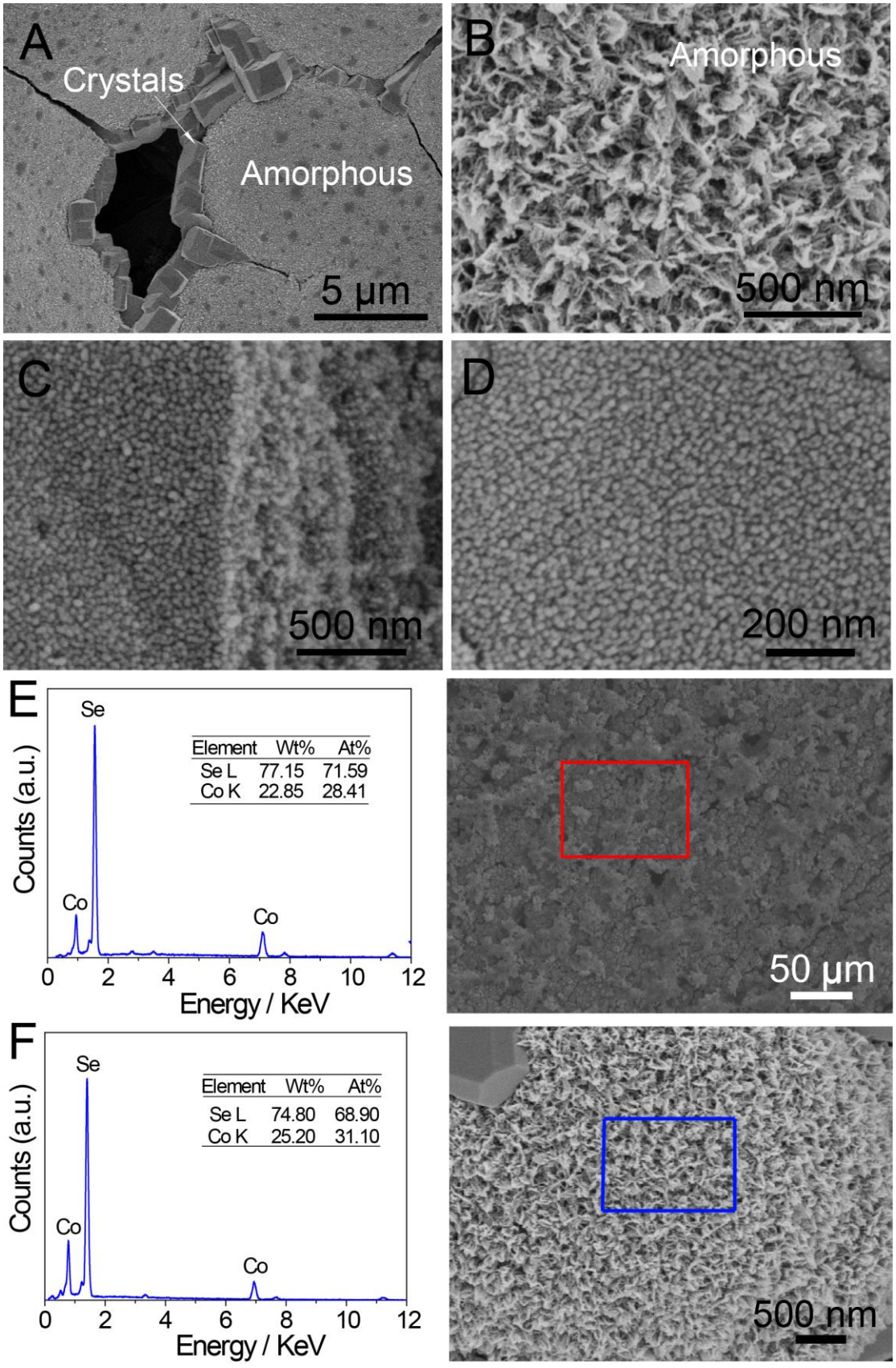


Figure S1. SEM Images of $CoSe_x$ calcined at different calcination temperature: (A, B) 250 ℃, (C) 450 ℃, and (D) 600 ℃. SEM-EDX analysis: (E) as-deposited $CoSe_x$ and (F) the amorphous regions of $CoSe_x$ calcined at 250 ℃, where left were the EDX spectra and right were the corresponding SEM images.

III. TEM images of $CoSe_x$ calcined at 450 and 600 ℃

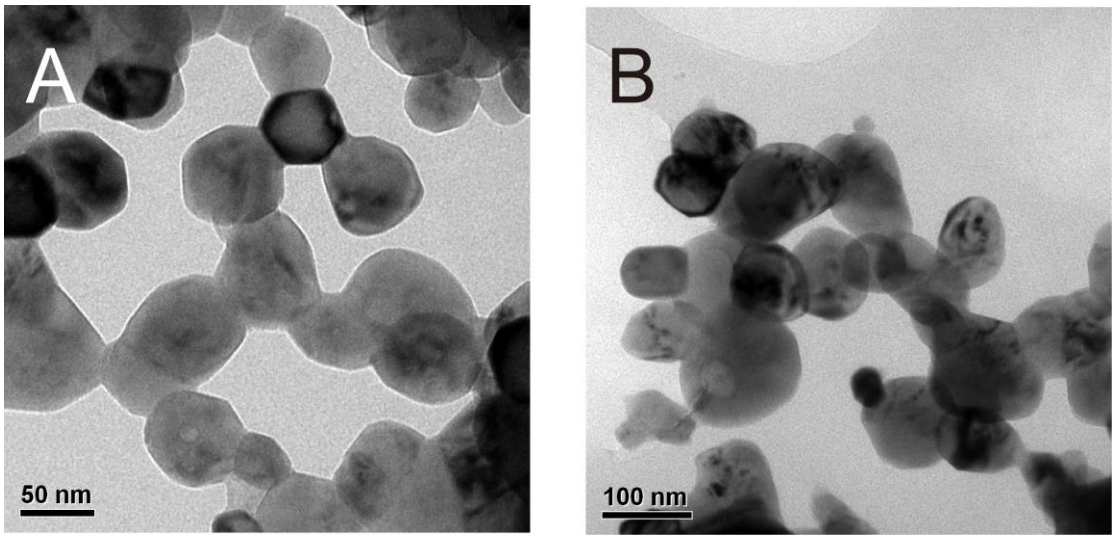
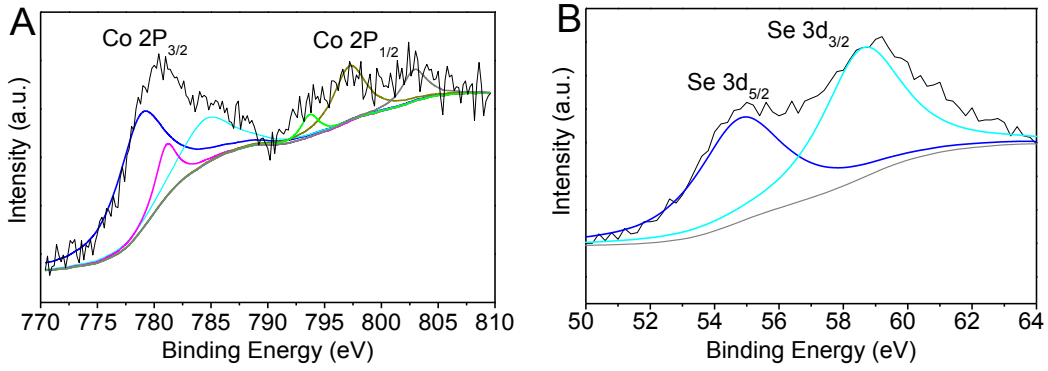


Figure S2. TEM images of the as-prepared $CoSe_x$ samples calcined at different temperatures. (A) 450 ℃ and (B) 600 ℃.

IV. XPS spectra of Co 2p and Se 3d of $CoSe_x$ calcined at 250 and 450 ℃



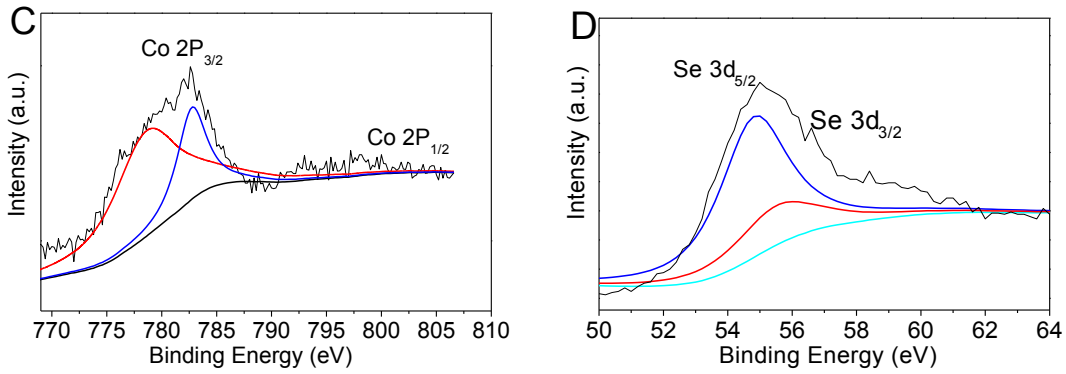
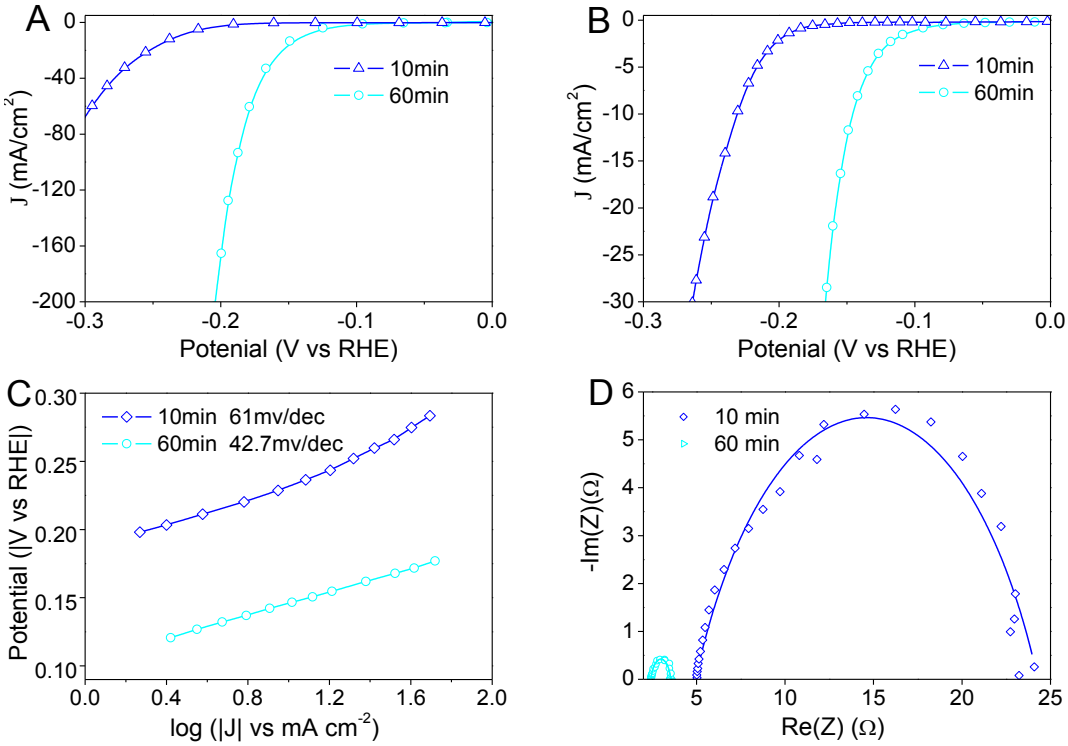


Figure S3. XPS of the Co 2p and Se 3d regions for $CoSe_x$ calcined at 250 ℃ (A, B) and (C, D) 450 ℃.

V. The electrochemical test data of *p*-$CoSe_2$ with different electrodepostion time calcined at 300 ℃



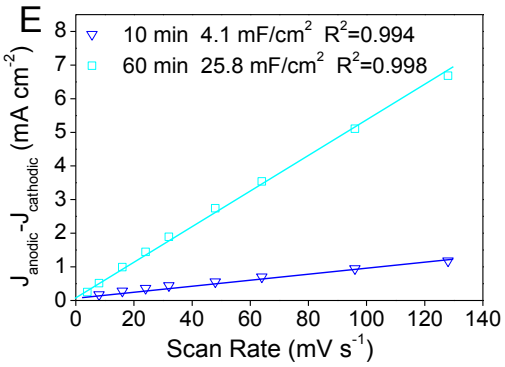


Figure S4. Electrochemical characterization of *p*-$CoSe_2$ sample with different electrodepostion time calcined at 300 ℃. Polarization curves at (A) higher and (B) lower applied overpotentials. (C) Tafel analysis derived from data in (A). (D) Electrochemical impedance spectroscopy (EIS) Nyquist plots. The data was fit to the simplified Randles equivalent circuit, and the fitting results are shown as solid traces. (E) Plots showing the extraction of the double layer capacitance (C_{dl}) for different electrodes.

VI. The double layer capacitance (C_{dl}) of samples calcined at different temperatures

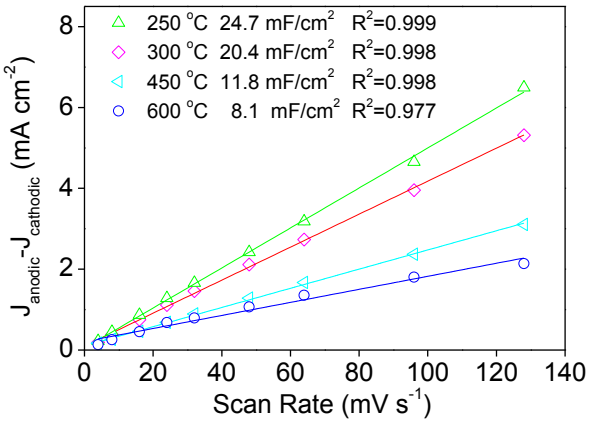


Figure S5. Plot showing the extraction of the double layer capacitance (C_{dl}) for electrodes of $CoSe_x$ (250 ℃), *p*-$CoSe_2$ (300 ℃), c-$CoSe_2$ (450 ℃), and CoSe

(600 ℃). The electrodeposition time of $CoSe_x$ was 40 min for all samples.

VII. Crystal structure diagrams

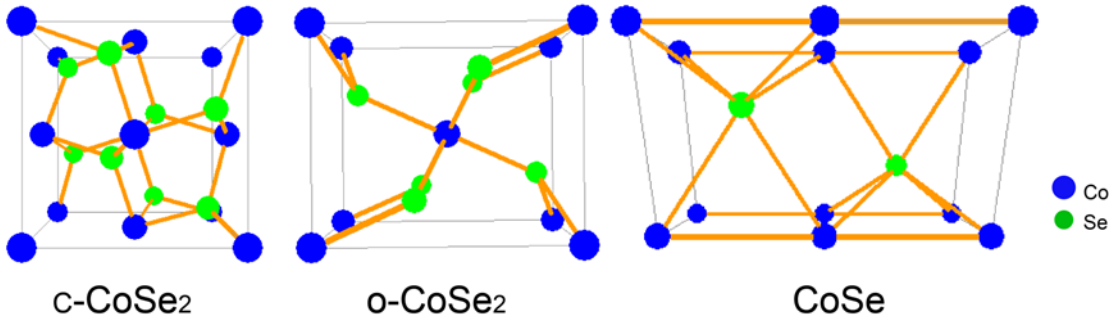


Figure S6. Crystal structure of $CoSe_2$ in cubic phase (c-$CoSe_2$), orthorhombic phase (o-$CoSe_2$), and the crystal structure of CoSe. Co and Se are displayed in blue and green, respectively.

VIII. Summary of the Electrochemical Properties of samples

Table S1. Summary of the Electrochemical Properties of Samples with Different Deposition Time and Calcination Temperatures for HER

Calcination temperature (℃)	*Deposition time (min)*	*Onset overpotential (mV)*	*Potential for (J=10mA/cm^2) (V)*[a]	*Tafel slope (mV/decade)*[b]	*R_{ct} (Ω)*[c]	*C_{dl} (mF/cm^2)*[d]
250	40	95	0.18	38.3	1.8	24.7
300	10	170	0.23	61.1	1.4	4.1
300	40	70	0.15	31.2	2.0	20.4
300	60	70	0.14	42.7	1.2	25.8
450	40	150	0.20	38.8	4.1	11.8
600	40	210	0.27	55.4	88.7	9.1

[a]the potential defined at 10 mA cm^{-2} of cathodic current density; [b]Tafel slopes obtained from current-potential polarization curve; [c]charge-transfer resistance; [d]the double layer capacitance.