

*Supporting Information for*

# One-step synthesis of cubic pyrite-type $\text{CoSe}_2$ at low temperature for efficient hydrogen evolution reaction

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## **I. Experimental**

### **1. Chemicals and Materials**

Selenium powder (99.9%), cobalt(II) chloride hexahydrate (99%), ethanol, graphite (99.9%), hydrochloric acid, nitric acid, sulfuric acid, acetone, ultrapure water (18 M $\Omega$  cm) are all analytical grade and were used as received without further purification. The gases with high purity were received from Hangzhou Jingong Co. Ltd.

### **2. Preparation of Graphite Disk Supports**

The fresh graphite rods are cut into thin disks with a diameter of 6 mm and a thickness of ~0.4 mm. Such graphite disks have a geometric area of 0.2826 cm<sup>2</sup>. They are sonicated subsequently in deionized water for 20 min, then were dried in an oven at 105 °C for 10 min before use.

### **3. Synthesis of $\text{CoSe}_2$ particles on Graphite Substrates**

Firstly,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (31 mg) was dissolved in 2.5 ml ethanol.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  coated graphite disk (GD) was prepared by drop casting a mixture solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and

ethanol. The CoSe<sub>2</sub> loading in CoSe<sub>2</sub>/graphite was controlled by varying the amount of the mixture solution of CoCl<sub>2</sub>•6H<sub>2</sub>O/ethanol, for example, 70 µl of the mixture solution of CoCl<sub>2</sub>•6H<sub>2</sub>O/ethanol resulted in a loading of CoSe<sub>2</sub> of 2.8 mg/cm<sup>2</sup> on graphite. The CoSe<sub>2</sub> particles were synthesized through the reaction between CoCl<sub>2</sub> and Se vapor in a quartz tube (1 inch I.D), which was connected to an Argon gas inlet and a vacuum pump and placed in a tube furnace (Thermal Fisher, Linderberg Blue). Typically, the graphite substrates coated with CoCl<sub>2</sub>•6H<sub>2</sub>O was placed at center of the tube furnace, and an alumina boat containing 0.2 g selenium powder was placed at the upstream side of the quartz tube which is far away from heating zone. Before heating up, the tube is evacuated to a bass pressure of 0.5 Pa and flushed with Ar. After 3 times, the center of the furnace is quickly elevated to the reaction temperature of 350 °C in 5 minutes, then the selenium powder is pushed into the heating zone, where the temperature is about 250 °C. During the synthesis, the selenium vapor is carried down to CoSe<sub>2</sub>/graphite substrates by an Ar flow of 150 sccm. The synthetic process continues 30 minutes. The temperature was then decreased to 200 °C while maintaining the Ar flow at 50 sccm under a pressure of 10 Pa for another 10 min to remove the possible residual selenium on the surface of samples. Finally the tube was cooled naturally to room temperature. Using the same procedures, we also synthesized other samples at 300, 400 and 500 °C.

#### **4. Structural Characterization**

X-ray diffraction was carried out on a Shimadzu XRD-6000 X-ray diffractometer using Cu K $\alpha$  radiation. The samples were step-scanned in steps of 0.02 ° in the range of 10-90 ° using a counter time of 24 s per step. X-ray photoelectron spectra (XPS) were obtained on a Escalab 250Xi (Thermo Fisher Scientific) X-ray photoelectron spectrometer. Calibration of binding energy was carried out by setting binding energy of C1s peak to 284.4 eV. Scanning electron microscopy (SEM) was performed on a SIRON-100(FEI America) field emission

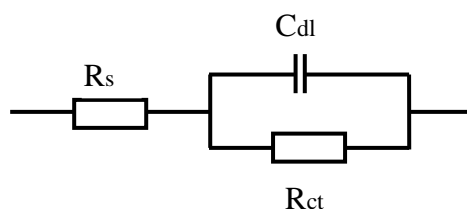
scanning electron microscopy. The samples were pretreated by spraying gold for 30 s. Thermogravimetric analysis (TGA) were recorded on a SDT Q600 thermogravimetric analyzer using N<sub>2</sub> flow of 100 sccm and a heating rate of 10 °C per minutes from room temperature to 800 °C. To prepare the specimen for transmission electron microscope (TEM), the as-grown substrates were immersed in 2 mL of ethanol and sonicated for 1 min. The TEM images was gained by field emission transmission electron microscope (2100F Japan) coupled with energy-dispersive X-ray spectrometer at an accelerating voltage of 200 kV. The resulting suspension was drop casted onto a piece of a TEM grid. Raman spectra were carried out using UV laser Raman spectrometer (LabRaman HRUV France) with a 514 nm laser.

## 5. Electrochemical Characterization

Electrochemical measurements were performed in a three-electrode electrochemical cell using a Bio-Logic VSP potentiostat. All measurements were performed in 100 mL of 0.5 M H<sub>2</sub>SO<sub>4</sub>(aq) electrolyte and constantly purged with H<sub>2</sub> gas with high purity, CoSe<sub>2</sub>/graphite as the working electrode, a graphite rod as a counter electrode, and a saturated calomel (SCE) reference electrode (CH Instruments).

To allow potentials to be referenced against the reversible hydrogen electrode (RHE), the SCE was calibrated against the reversible hydrogen potential using platinum wire as both the working and counter electrodes after each measurement. Linear sweep or cyclic voltammograms of samples were measured from +0.25 V to -0.45 V vs. RHE at a scan rate of 3 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was performed in potentiostatic mode at -0.24 V vs. RHE from 200 kHz to 50 mHz. The main arc in each EIS spectrum was modeled using a simplified Randles equivalent circuit as shown below. R<sub>s</sub> is the series resistance of the system, including R<sub>solution</sub>, R<sub>wire</sub> and R<sub>GD</sub>. C<sub>dl</sub> and R<sub>ct</sub> are the double layer capacitance and charge transfer resistance of the electrocatalyst-electrolyte interface,

respectively.  $R_s$  can be obtained from the impedance at the high frequencies of AC impedance spectroscopy.



In order to accurately investigate the apparent catalytic activity of the various samples, it is necessary correct the measurements of current density ( $J$ ) vs. applied voltage ( $E$ ) for all ohmic losses throughout the system. Then, for each measured value of current, the potential loss can be calculated using  $R_s$  and Ohm's Law and subtracted from the raw data to give the  $iR$ -corrected data. Cyclic voltammograms taken with various scan rates (4-128 mV/s) were collected to estimate the double-layer capacitance.

## II. TGA and XRD of the original $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

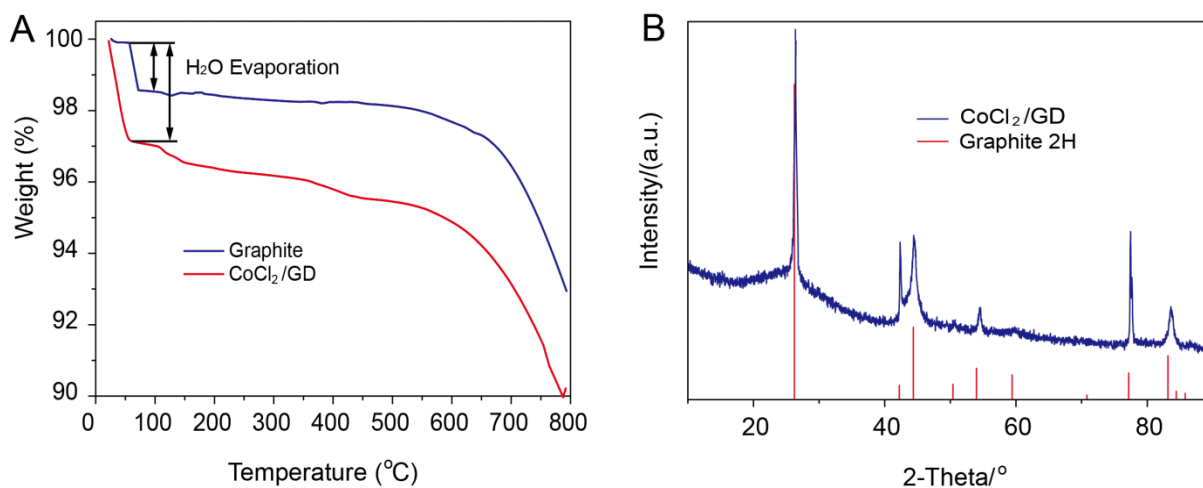


Figure S1. (A) TGA of graphite and  $\text{CoCl}_2/\text{GD}$ . (B) XRD of the original  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  on GD showing that  $\text{CoCl}_2$  existed in amorphous.

### III. SEM Images of CoSe<sub>2</sub>/GD Grown at 300 and 400 °C

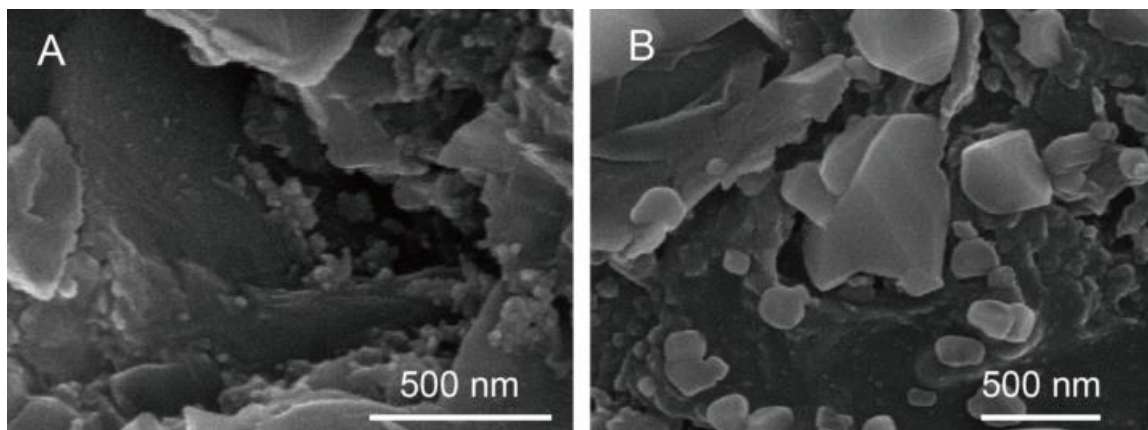


Figure S2. Typical SEM images of CoSe<sub>2</sub>/GD at 300 °C (A) and 400 °C (B). The CoSe<sub>2</sub> loading was 2.8 mg/cm<sup>2</sup>.

### IV. EDS of CoSe<sub>2</sub>/GD Grown at 350 °C

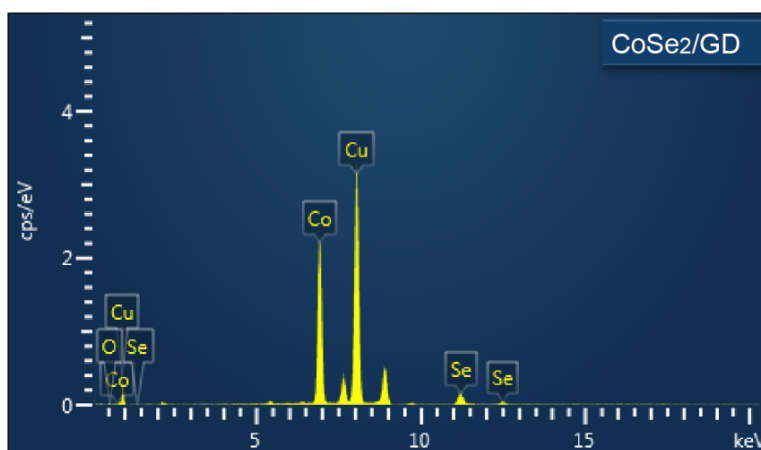
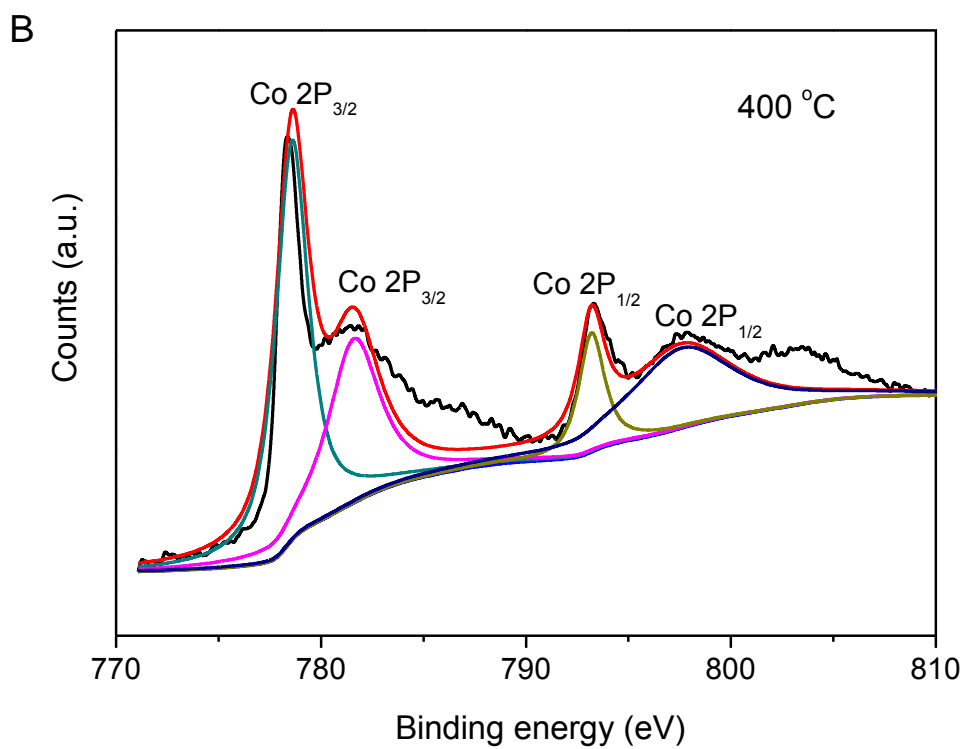
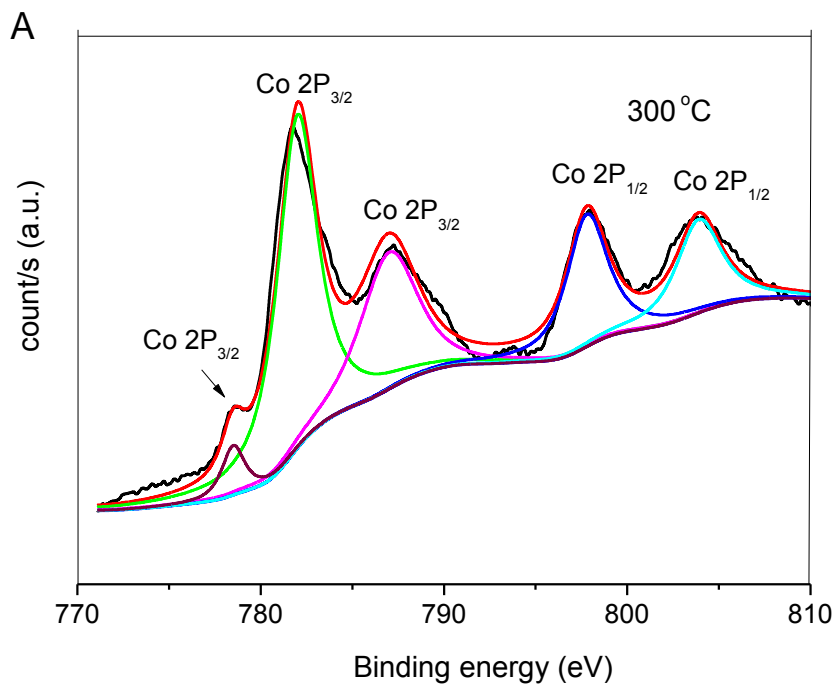


Figure S3. EDS of CoSe<sub>2</sub>/GD grown at 350 °C showing the existence of Se and Co. The CoSe<sub>2</sub> loading was 2.8 mg/cm<sup>2</sup>.

## V. XPS of CoSe<sub>2</sub>/GD Grown at 300 and 400 °C



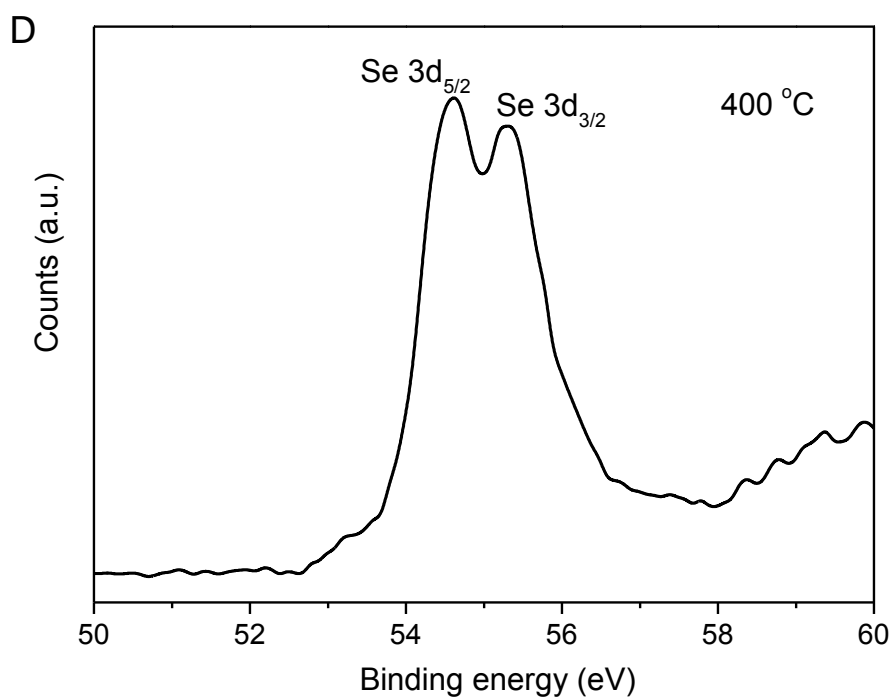
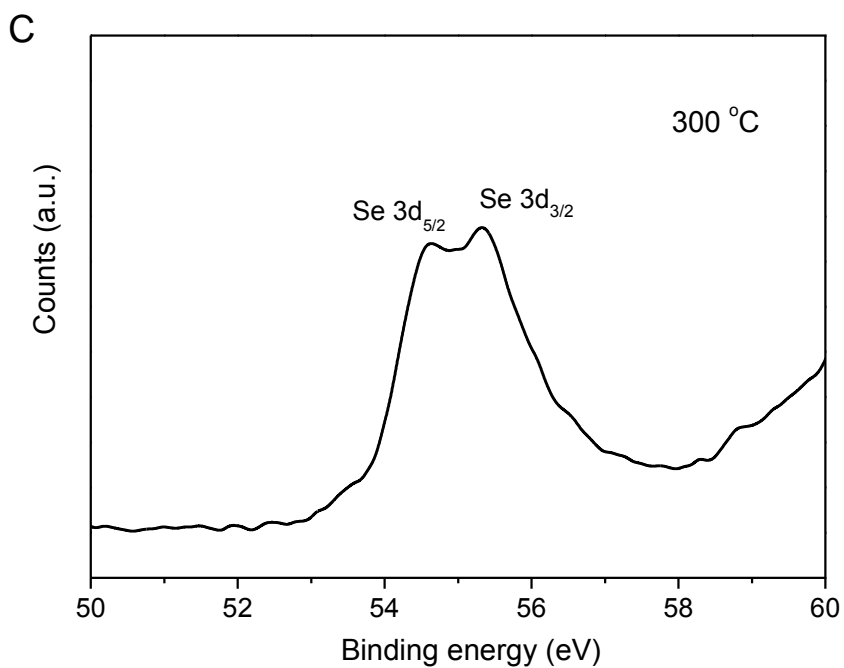


Figure S4. XPS of Co 2p in CoSe<sub>2</sub>/GD grown at 300 °C (A) and 400 °C (B). Se 3d in CoSe<sub>2</sub>/GD grown at 300 °C (C) and 400 °C (D). The CoSe<sub>2</sub> loading was 2.8 mg/cm<sup>2</sup>.

## VI. XRD of CoSe<sub>2</sub>/GD Grown at 500 °C

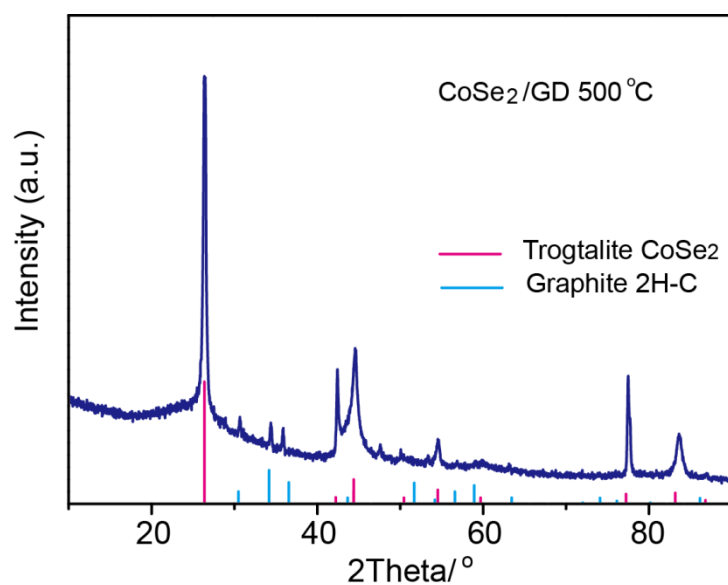


Figure S5. XRD of CoSe<sub>2</sub>/GD Grown at 500 °C. The CoSe<sub>2</sub> loading was 2.8 mg/cm<sup>2</sup>.

## VII. Polarization Curves of Other CoSe<sub>2</sub>/GD Samples with Different CoSe<sub>2</sub> Loadings and Temperature (500 °C)

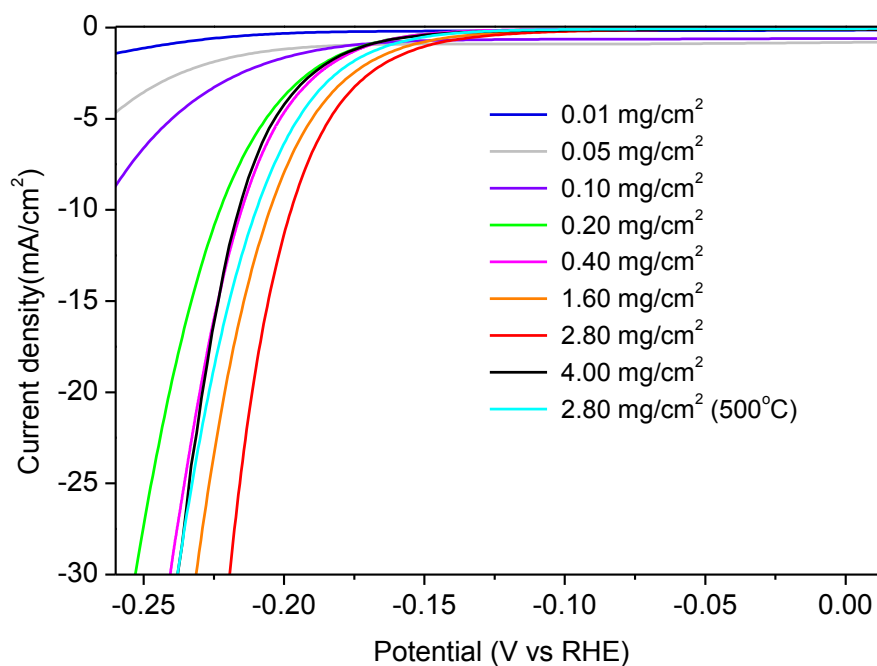


Figure S6. Polarization curves of CoSe<sub>2</sub>/GD at 350 °C with different CoSe<sub>2</sub> loadings and CoSe<sub>2</sub>/GD at 500 °C with a CoSe<sub>2</sub> loading of 2.8 mg/cm<sup>2</sup>.



### VIII. Cyclic Voltammograms Recorded for CoSe<sub>2</sub>/GD Grown at 300 and 400 °C

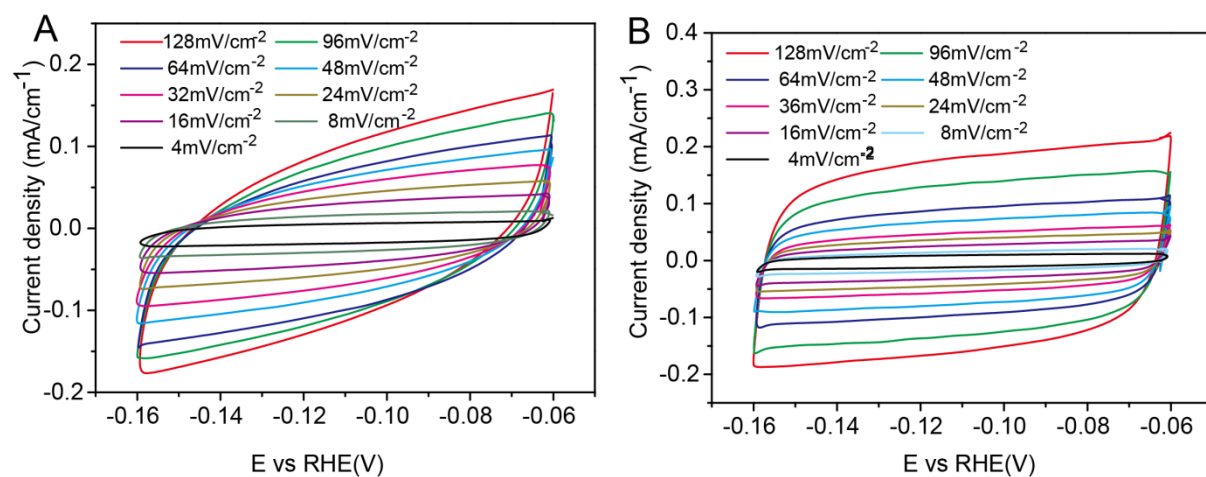


Figure S7. Cyclic voltammograms recorded for a CoSe<sub>2</sub>/GD electrode grown at 300 °C (A) and 400 °C (B) at various scan rates to determine the double layer capacitance ( $C_{dl}$ ).