

*Supplementary Information for:*

# ELECTROCATALYSIS OF THE HYDROGEN-EVOLUTION REACTION BY ELECTRODEPOSITED AMORPHOUS COBALT SELENIDE FILMS

AZHAR I. CARIM<sup>1</sup>, FADL H. SAADI<sup>2, 3</sup>, MANUEL P. SORIAGA<sup>3,6</sup> AND NATHAN S. LEWIS<sup>1,3-5</sup>

<sup>1</sup>Division of Chemistry and Chemical Engineering

<sup>2</sup>Division of Engineering and Applied Sciences

<sup>3</sup>The Joint Center for Artificial Photosynthesis

<sup>4</sup>Beckman Institute

<sup>5</sup>Kavli Nanoscience Institute

California Institute of Technology

Pasadena, CA 91125

<sup>6</sup>Department of Chemistry

Texas A&M University

College Station, TX 77843

\*Corresponding Author: [nslewis@caltech.edu](mailto:nslewis@caltech.edu)

## **S1. Contents**

This document contains detailed descriptions of the experimental procedures used in this work (Section S2), X-ray diffraction data (Section S3) and X-ray photoelectron spectra (Section S4) for electrochemically prepared cobalt selenide films, calculations of the turnover frequencies of such films for the electrochemical hydrogen-evolution reaction (Section S5) and a list of associated references (Section S6).

## S2. Experimental Methods

*Materials and Chemicals:* H<sub>2</sub>(g) (99.999%, Air Liquide), H<sub>2</sub>SO<sub>4</sub> (J.T. Baker, A.C.S. Reagent), Ti foil (99.7+%, 0.127 mm thick, Sigma-Aldrich), SeO<sub>2</sub> (99.999%, Acros Organics), Co(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O (98%, Strem Chemicals) and LiCl (≥ 99.0%, Sigma-Aldrich) were used as received. H<sub>2</sub>O with a resistivity ≥ 18.2 MΩ cm<sup>-1</sup> (Barnsted Nanopure System) was used throughout.

*Cobalt Selenide Electrodeposition:* Cobalt selenide films were prepared on Ti substrates via electrodeposition. The sealed, single-compartment electrochemical cell equipped was with a graphite-rod counter electrode (Alfa Aesar, 99%) and a Ag/AgCl reference electrode (3 M KCl; Bioanalytical Systems) that were collectively controlled by a Bio-Logic SP-200 potentiostat. Squares ~ 2 cm x 2 cm in dimension were cut from the Ti foil and were then sealed into an O-ring compression cell that confined the contact region between the electrolyte, an aqueous solution of 0.065 M Co(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>, 0.035 M SeO<sub>2</sub> and 0.200 M LiCl (pH = 4.7), and the Ti foil, to a circular area of 0.1 cm<sup>2</sup>. An external electrical contact to the Ti foil was made using an alligator clip. Electrodeposition was effected by potentiostatically biasing the Ti at a potential of -0.45 V vs. the Ag/AgCl reference electrode for 8 h at room temperature. After deposition, the Ti foil pieces were removed from the compression cell and rinsed first with 0.500 M H<sub>2</sub>SO<sub>4</sub> and then with H<sub>2</sub>O. The area of the Ti substrate that had not been covered by the electrodeposited cobalt selenide was then covered with nitrocellulose-based nail polish, to provide electrical insulation.

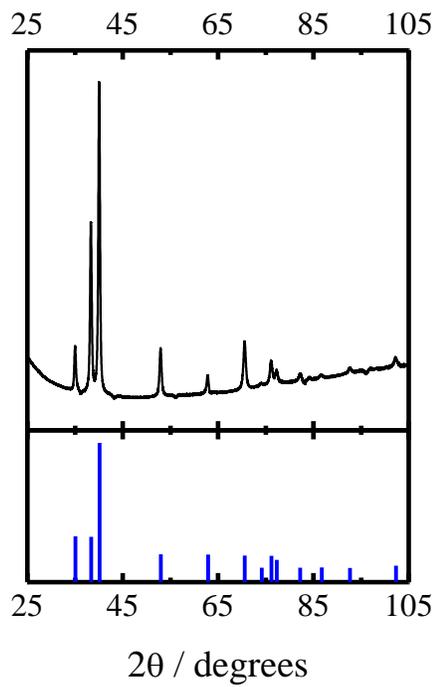
*Electrochemical Conditioning and Analysis:* A single-compartment cell equipped with a graphite-rod counter electrode and a saturated calomel electrode (SCE; CH Instruments) and controlled by a Bio-Logic SP-200 potentiostat was used for conditioning and analysis of the

electrodeposited material. An O-ring compression seal was used to mount the Ti substrate that supported the electrodeposited material in the cell. All experiments were performed using an aqueous solution of 0.500 M H<sub>2</sub>SO<sub>4</sub> that was continuously sparged with H<sub>2</sub>(g) and stirred using a magnetic stir bar. The potential of a reversible hydrogen electrode (RHE) relative to the SCE was determined by measuring the potential of a Pt foil (which was annealed in a H<sub>2</sub>-air flame immediately prior to use) in the H<sub>2</sub>(g)-saturated 0.500 M H<sub>2</sub>SO<sub>4</sub> electrolyte. All quoted potentials are referenced against RHE unless otherwise noted. Prior to voltammetric experiments and physical characterization, electrodes were preconditioned by galvanostatic electrolysis at a current density of -10 mA cm<sup>-2</sup> for 1 h. The CoSe mass loading was determined to be 3 mg cm<sup>-2</sup>. The uncompensated cell resistance ( $R_u$ ) was determined from a single-point electrochemical impedance measurement obtained by applying a sine-wave modulated potential with amplitude of 20 mV at a modulation frequency of 100 kHz centered at the open-circuit potential of the cell. All subsequent measurements were corrected for an uncompensated resistance of 85% of the value of  $R_u$ . Voltammetric data were recorded at a scan rate of 1 mV s<sup>-1</sup>. The electrochemical stability of the cobalt selenide films was assessed using both galvanostatic and accelerated degradation techniques. First, a current density of -10 mA cm<sup>-2</sup> was maintained galvanostatically and the electrode potential was monitored over the course of 16 h. Separately, the cobalt selenide films were subjected to 1000 full potential cycles between -0.175 V and 0.1 V vs. RHE at a sweep rate of 50 mV s<sup>-1</sup>. Voltammograms at a sweep rate of 1 mV s<sup>-1</sup> were recorded before cycling and after completion of the 1000 full potential cycles.

*Physical Characterization:* Scanning electron microscopy (SEM) was conducted using a FEI Nova NanoSEM 450 at an accelerating voltage of 15 kV with a working distance of 5 mm and an in-lens secondary electron detector. Energy-dispersive X-ray spectroscopy was performed

in the SEM at a working distance of 12 mm, using an accelerating voltage of 15 kV and an Oxford Instruments silicon drift detector. Raman spectra were obtained with a Renishaw inVia spectrometer equipped with a Leica DM 2500M microscope, a Leica N Plan 50x objective (numerical aperture = 0.75), an 1800 lines mm<sup>-1</sup> grating, and a CCD detector in a 180° backscatter geometry. A 532 nm diode-pumped solid state (DPSS) laser (Renishaw RL532C50) was used as the excitation source and a radiant flux of 20 μW was incident on the sample. X-ray diffraction (XRD) powder patterns were acquired with a Bruker D8 Discover diffractometer equipped with a Cu Kα source and a 2-dimensional Vantec detector. X-ray photoelectron spectra (XPS) were acquired with a Kratos Axis Nova spectrometer at a base pressure of 10<sup>-9</sup> torr with monochromatic Al Kα excitation at 1486.7 eV. High-resolution spectra were obtained using a pass energy of 40 eV. CasaXPS software (CASA Ltd) was used to fit peaks in the XP spectra, and peak fitting was performed assuming a Shirley background and symmetric Voigt line-shapes comprised of Gaussian (70%) and Lorentzian (30%) functions. The peak fitting was constrained to maintain both a 2:3 ratio between the areas of the Se 3d<sub>3/2</sub> and Se 3d<sub>5/2</sub> lines and to maintain a 0.85 eV separation between the binding energies of these two lines.

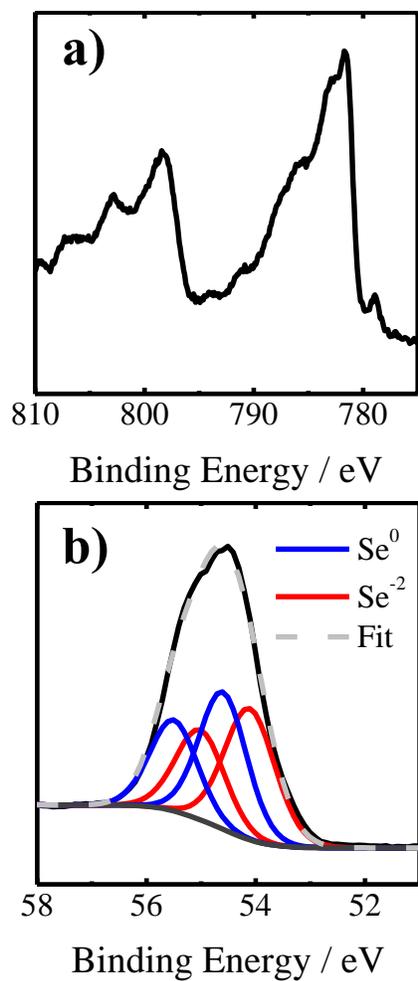
### S3. X-ray Diffraction



**Figure S1.** Top: Representative X-ray diffraction pattern collected from a cobalt selenide film. Bottom: Standard lines for polycrystalline Ti (JCPDS 65-9622).

#### **S4. X-ray Photoelectron Spectroscopy**

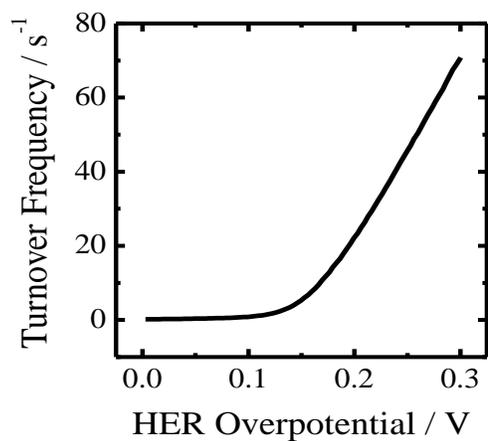
Figure S2 shows high resolution X-ray photoelectron spectra of an electrochemically prepared cobalt selenide film in the Co 2p (a) and Se 3d (b) regions. The presence of multiple intensity maxima in the region between  $\sim 790$  and  $780$  eV in Figure S2a may be due to the presence of oxidized cobalt species that formed due to air oxidation of the cobalt selenide film surface prior to loading into the spectrometer. XPS interrogates only the first several nanometers of the material surface. However, the Raman spectrum (Figure 1b), representative of a much larger depth, did not indicate the presence of any oxygenated cobalt species.



**Figure S2.** Representative high resolution X-ray photoelectron spectra of an electrochemically prepared cobalt selenide film in the (a) Co 2p and (b) Se 3d regions.

## S5. Calculation of Turnover Frequencies

Turnover frequencies of the cobalt selenide films for the hydrogen-evolution reaction were calculated the method previously reported for an amorphous molybdenum sulfide catalyst film.<sup>1</sup> The number of surface sites per unit area was estimated by calculating the area occupied by a CoSe unit in freboldite to determine the number of surface sites for a planar material and then scaling this value by the roughness factor of the cobalt selenide film (13, determined via electrochemical capacitance measurements). The selenium-selenium distance in frebdolite is 0.361 nm. Based on the arrangement of selenium atoms in the frebdolite basal plane, each Se atom, and thus each CoSe unit, occupies 0.13 nm<sup>2</sup>. Thus, freboldite has approximately  $8 \times 10^{14}$  surface sites per cm<sup>2</sup> in the basal plane. From this, it is estimated that the cobalt selenide films had approximately  $1 \times 10^{16}$  surface sites per cm<sup>2</sup>. The total number of hydrogen evolution turnovers was analytically derived from the current density via the conversion factor  $3.1 \times 10^{15}$  H<sub>2</sub> s<sup>-1</sup> mA<sup>-1</sup>. The turnover frequency is then the total number of turnovers divided by the number of active sites. Figure S3 presents a plot of turnover frequency as function of hydrogen-evolution reaction overpotential derived from the data in Figure 2a.



**Figure S3.** Turnover frequency of cobalt selenide films as function of overpotential for the hydrogen-evolution reaction in 0.500 M H<sub>2</sub>SO<sub>4</sub> saturated with H<sub>2</sub>(g) derived from the voltammetric data in Figure 2a.

## S6. References

1. J. D. Benck, Z. Chen, L. Y. Kuritzky, A. J. Forman and T. F. Jaramillo, *ACS Catal.*, 2012, 2, 1916-1923.