Electronic Supplementary Material

Bifunctional Catalyst of Ultrathin Cobalt Selenide Nanosheets for Plastic-Electroreforming-Assisted Green Hydrogen Generation

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1. Experimental

1.1. Reagents and chemicals

Nickel foam (NF) was purchased from Guangzhou Muxi Biological Technology Co., Ltd., Isopropyl alcohol ($(CH_3)_2CHOH$), potassium hydroxide (KOH) and selenium (Se) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Ethanol (CH_3CH_2OH) was purchased from Tianjin Baishi Chemical Co., Ltd. Hydrochloric acid (HCl) was obtained from Guangzhou Rongman Biological Technology Co., Ltd. Cobaltous Chloride ($CoCl_2$) and ammonium hydroxide ($NH_3 \cdot H_2O$) were purchased from Sigma-Aldrich Co., Acetone (CH_3COCH_3) was obtained from Guangzhou Xinhong Trading Co., Ltd. Hydrazine hydrate (N_2H_4) was purchased from Guangzhou Yueyang Chemical Co., Ltd. The commercial 20% Pt on Vulcan XC-72 carbon (Pt/C) was obtained from Cabot Corp and the ruthenium (IV) oxide (RuO_2) was obtained from Shanghai Macklin Blochemical Co., Ltd. The polylactic acid (PLA, Mw=10, 000 g/mol) was purchased from Shanghai Yuanye Biotechnology Co., Ltd.

1.2. The synthesis of catalyst

1.2.1 Preparation of $Co(OH)_2$ nanosheet on Ni foam [$Co(OH)_2$/NF]

The $Co(OH)_2$ nanosheet was grown on 1 cm×1 cm nickel foam (NF) by a simple one-step hydrothermal treatment. In brief, NF was first washed sequentially with acetone, HCl and ethanol for 15 minutes to remove the organic substance and oxide layer on the surface. The cleaned NF was directly immersed into a solution containing 1 mL 0.1 M $CoCl_2$ and 0.3 mL $NH_3 \cdot H_2O$ for 30 min, allowing the mixed solution to penetrate the three-dimensional (3D) pores of the NF. Subsequently, 0.45 mL N_2H_4 was added to the above mixed solution and maintained at 40°C for 12 h. After reaction, $Co(OH)_2$/NF was washed with water, and dried at 75 °C for 10 h.

1.2.2 Preparation of $CoSe_2$ nanosheet on Ni foam ($CoSe_2$/NF) from $Co(OH)_2$/NF

In a typical procedure, different amounts of Se powder (such as 0.02 g, 0.1 g and 0.5 g), as a selenium source, was put into a porcelain boat and placed in upstream of a tube furnace. A piece of $Co(OH)_2$/NF was placed in another porcelain boat seated in the center of the heating area of the tube furnace. At the same time, the tube furnace was heated to 400 ℃ with a heating rate of 10 ℃ min^{-1} and kept for 2 h in Ar atmosphere, resulting in the conversion of $Co(OH)_2$/NF to $CoSe_2$/NF. The resultant samples were denoted as 0.02-$CoSe_2$/NF, 0.1-$CoSe_2$/NF and 0.5-$CoSe_2$/NF, respectively. Finally, the product was taken out after natural cooling to room temperature and cleaned repeatedly with water, and dried at 75 °C for 10 h.

For comparsion, we directly placed $Co(OH)_2$/NF in a porcelain boat seated in the center of the heating zone of the tube furnace. At the same time, the tube furnace was heated to 400 ℃

at rate of 10 ℃ min^{-1} and kept for 2 h in air, resulting in the conversion of $Co(OH)_2$/NF to Co_3O_4/NF.

1.3. Morphological, structural and compositional characterizations

Scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS) measurement were executed to access $Co(OH)_2$/NF and $CoSe_2$/NF with a SU-8010 instrument. X-ray diffraction (XRD) patterns were carried out with a PANalytical Empyrean X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) data was captured from an ESCALAB 250 spectrometer (Thermo-VG Scientific). The nanosheets were detached from the substrate by strong ultrasound sonication and drop casted on a TEM grid. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) of these nanosheets were captured on a FEI TECNAI G2F30 instrument. Atomic Force Microscope (AFM) measurement was conducted on dimension fastscan bio.

1.4. Electrochemical measurements

Electrochemical tests including linear sweep voltammetry (LSV), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronopotentiometry were performed by a CHI-760 electrochemical analyzer with a three-electrode cell consisting of a reference electrode [saturated calomel electrode (SCE)], an auxiliary electrode (carbon rod) and a working electrode (electrocatalyst-modified NF). According to the equation $E_{RHE} = E_{SCE} + 0.242\ V + 0.0591\ pH$, all electrode potentials were calibrated to the reversible hydrogen electrode (RHE). In LSV curves, iR-corrected was compensated at 85% through the positive feedback model using the CHI-760 electrochemical analyzer. And before the HER and PLA electrooxidation performance testing, repeated cyclic voltammetry scans were applied to stabilize the catalyst surface.

The $CoSe_2$/NF can directly act as the working electrode. Precise weighing revealed the loading mass of $CoSe_2$ nanosheet on NF substrate was about 1.5 mg cm^{-2}.

The specific preparation procedures of commercial Pt/C/NF and RuO_2/NF with a loading mass of 1.5 mg cm^{-2} are as follows. The Pt/C and RuO_2 suspensions were prepared by dispersing 2 mg Pt/C or RuO_2 into 200 μL isopropyl alcohol, 785 μL water and 15 μL Nafion, respectively. Then, 750 μL of the prepared suspension was carefully loaded onto the NF substrate and dried at 40 ℃.

1.5. Faradaic efficiency

The Faradaic efficiency PLA oxidation to acetic acid (FE) can be calculated by equation $FE_{(acetic\ acid)} = (4F \times n_{(acetic\ acid)})/Q$, where F is Faraday constant (96,485 C mol^{-1}), $n_{(acetic\ acid)}$ is the moles of the acetic acid produced, and Q is the total charge passed across the electrode.

2. Supplementary Figures

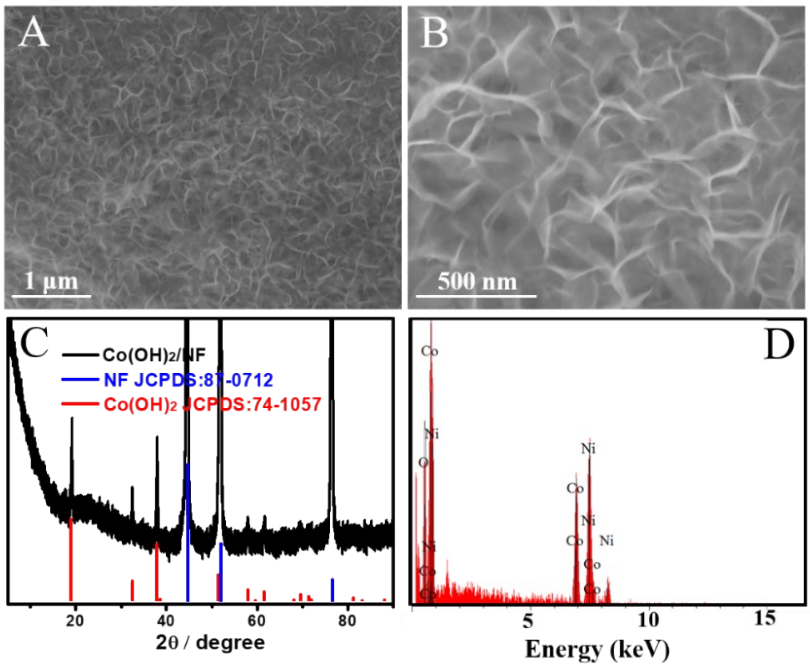

Fig. S1. Morphology characterization and composition analyses of $Co(OH)_2$/NF. (A, B) SEM images, (C) XRD pattern, and (D) EDX spectrum.

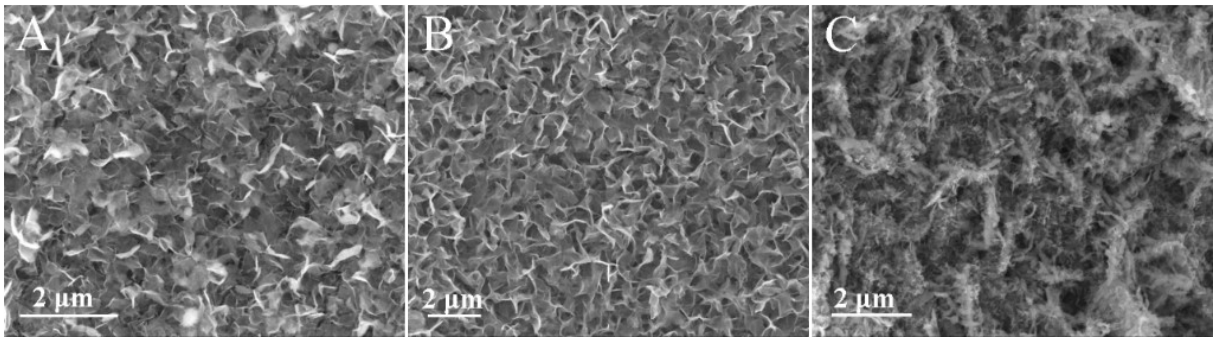

Fig. S2. SEM images of (A) 0.02-$CoSe_2$/NF, (C) 0.1-$CoSe_2$/NF and (D) 0.5-$CoSe_2$/NF.

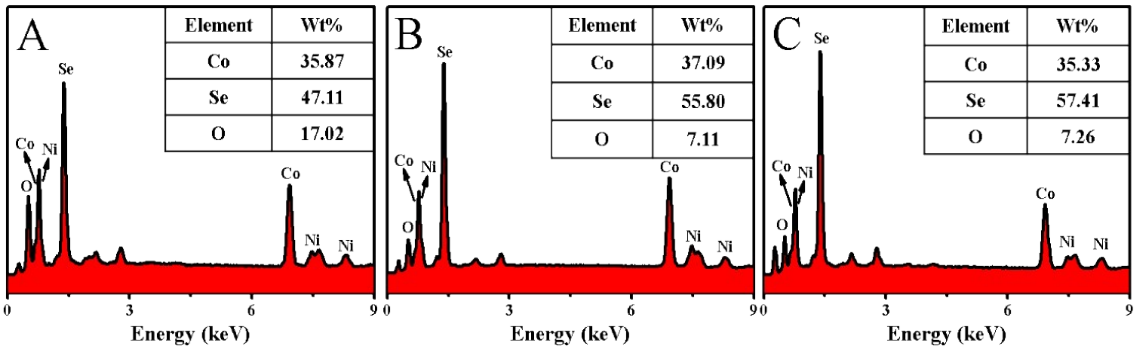

Fig. S3. SEM-EDS pattern of 0.02-$CoSe_2$/NF, 0.1-$CoSe_2$/NF and 0.5-$CoSe_2$/NF.

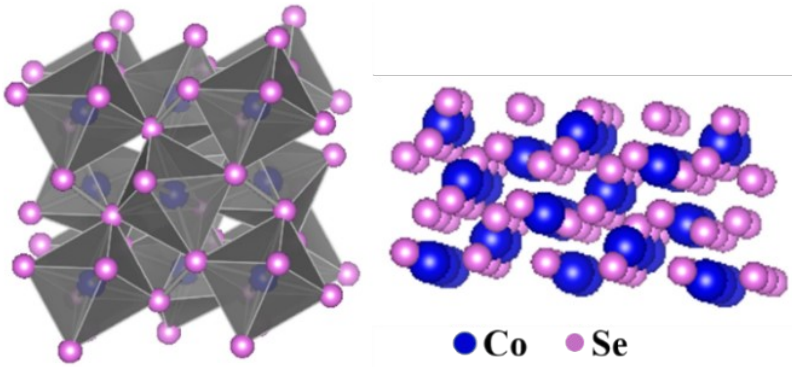

Fig. S4. The crystal structure of $CoSe_2$ (left) and the atomic model (right) of the $CoSe_2$ nanosheet (210) surface.

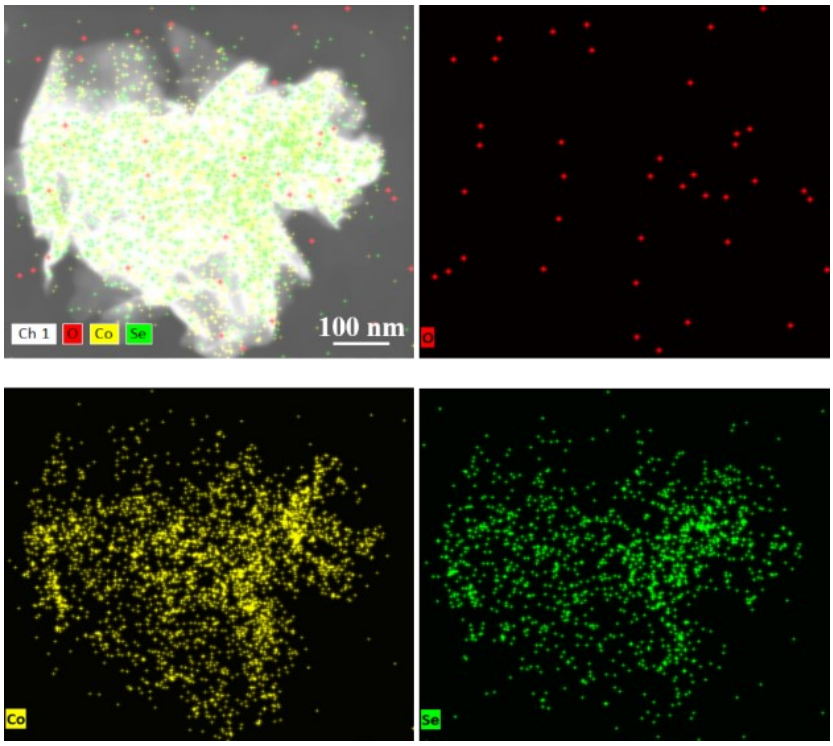

Fig. S5. TEM-EDX elemental maps of O, Ni, and Se of 0.1-$CoSe_2$ nanosheets.

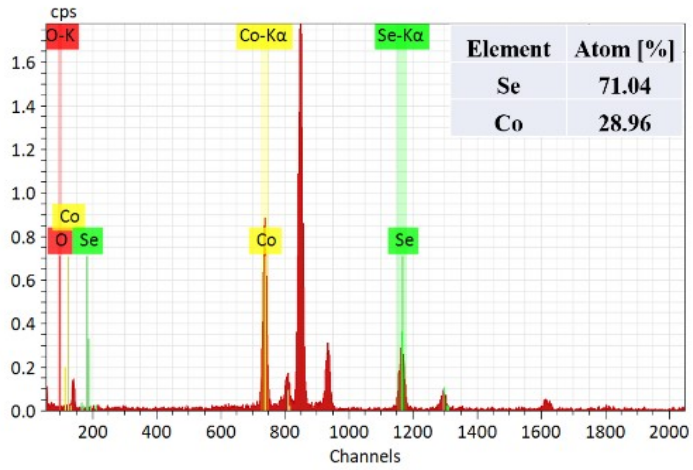

Fig. S6. EDX spectrum and quantification results of the nanosheets detached from 0.1-$CoSe_2$/NF.

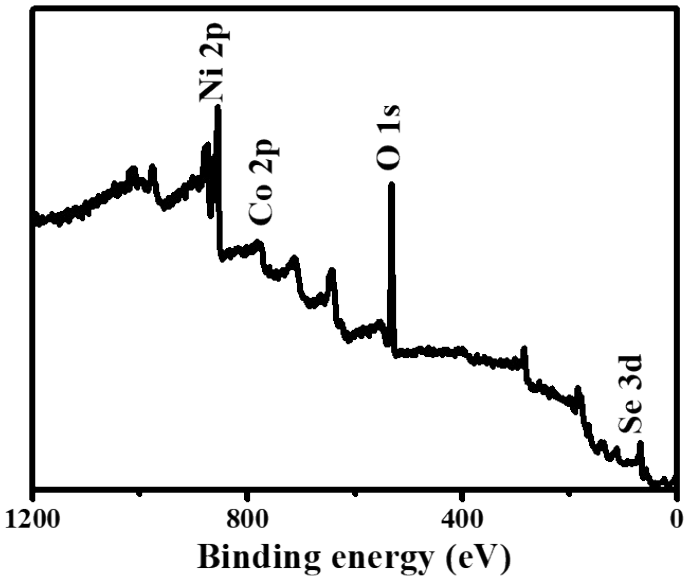

Fig. S7. XPS survey spectrum of 0.1-$CoSe_2$/NF.

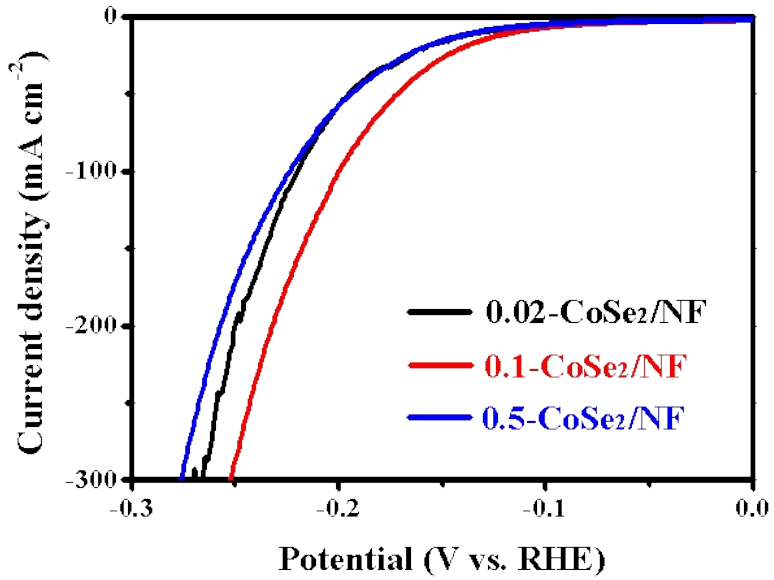

Fig. S8. iR-corrected LSV curves of 0.02-$CoSe_2$/NF, 0.1-$CoSe_2$/NF and 0.5-$CoSe_2$/NF in 1 M KOH solution.

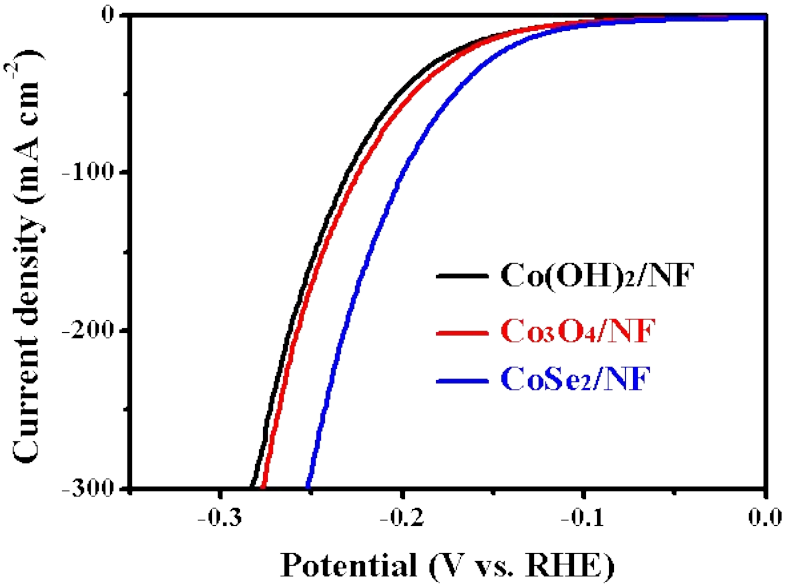

Fig. S9. iR-corrected LSV curves of the $CoSe_2$/NF, Co_3O_4/NF and $Co(OH)_2$/NF in 1 M KOH.

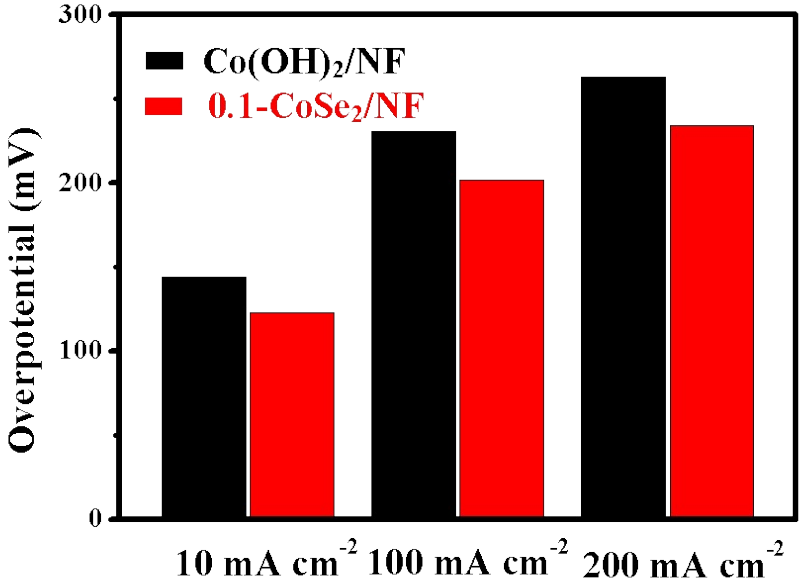

Fig. S10. Comparison of the overpotentials of $Co(OH)_2$/NF and 0.1-$CoSe_2$/NF at current densities of 10, 100 and 200 mA cm^{-2}.

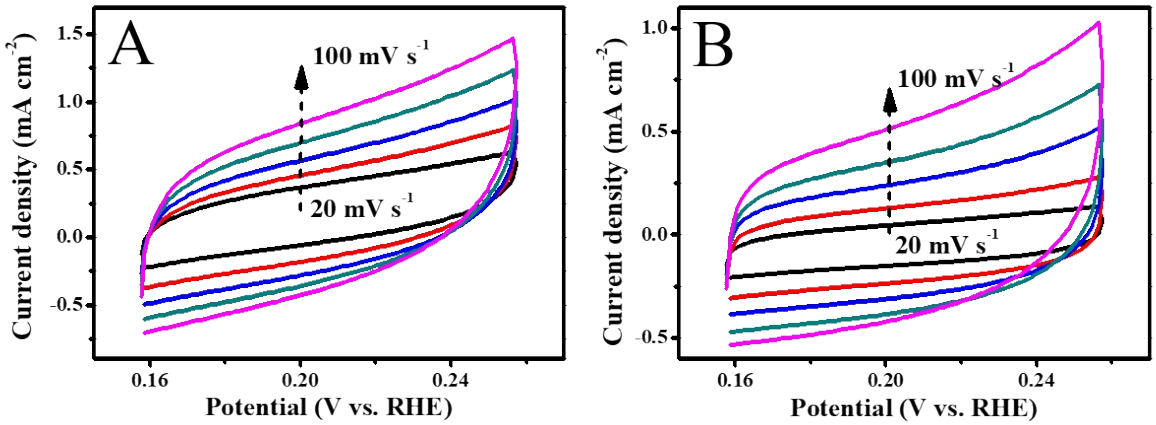

Fig. S11. CV curves and plots of the current density of (A) 0.1-$CoSe_2$/NF and (B) $Co(OH)_2$/NF.

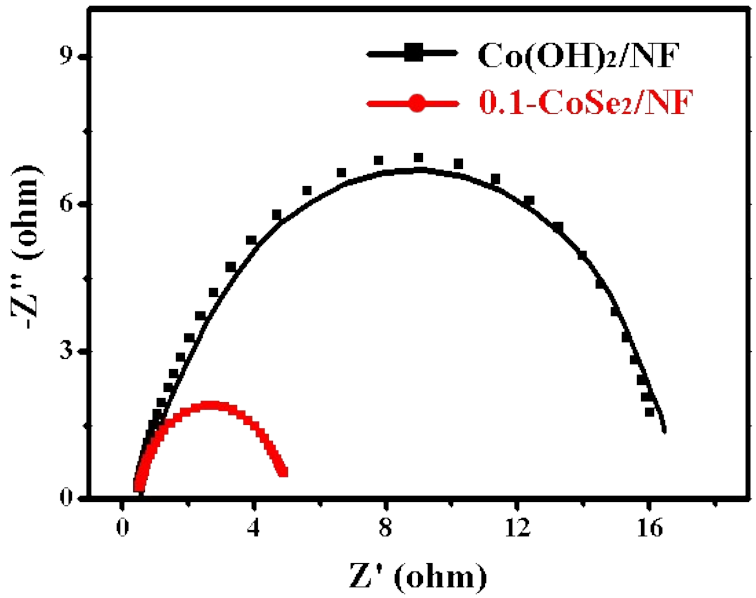

Fig. S12. Nyquist plots of 0.1-$CoSe_2$/NF and $Co(OH)_2$/NF in N_2-saturated 1 M KOH solution at -0.1 V vs. RHE.

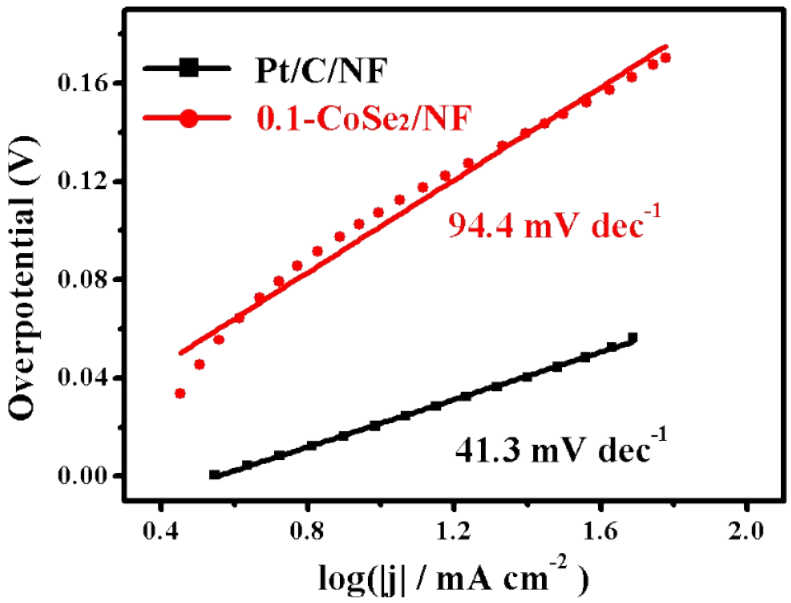

Fig. S13. Tafel plots of the 0.1-$CoSe_2$/NF and Pt/C/NF.

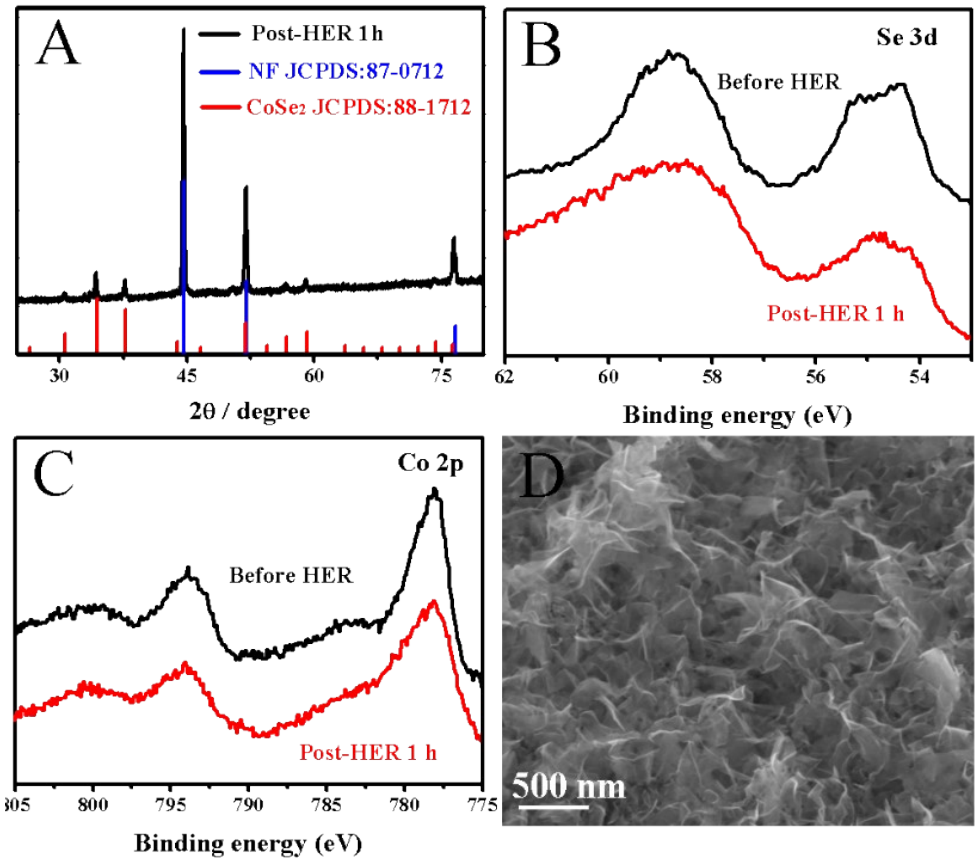

Fig. S14. Composition analyses and morphology characterization of 0.1-$CoSe_2$/NF after HER test. (A) XRD pattern, high-resolution XPS spectra of (B) Se 3d and (C) Co 2p peaks of the 0.1-$CoSe_2$/NF, (D) the SEM image of the 0.1-$CoSe_2$/NF.

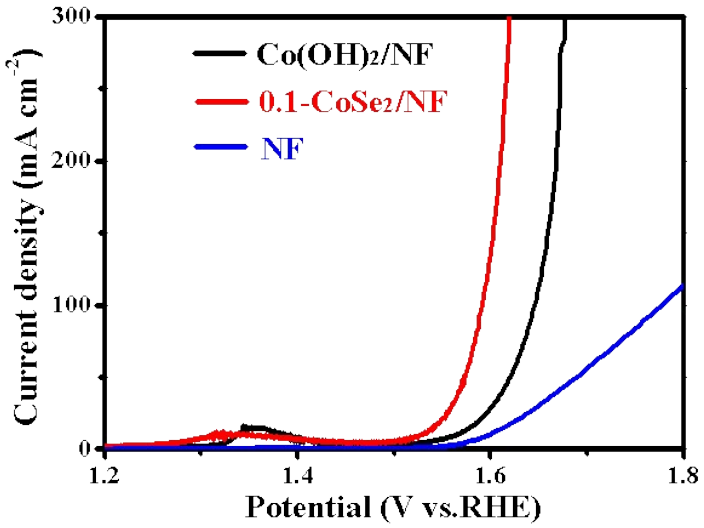

Fig. S15. LSV curves of 0.1-$CoSe_2$/NF, $Co(OH)_2$/NF, and bare NF in 1 M KOH electrolyte.

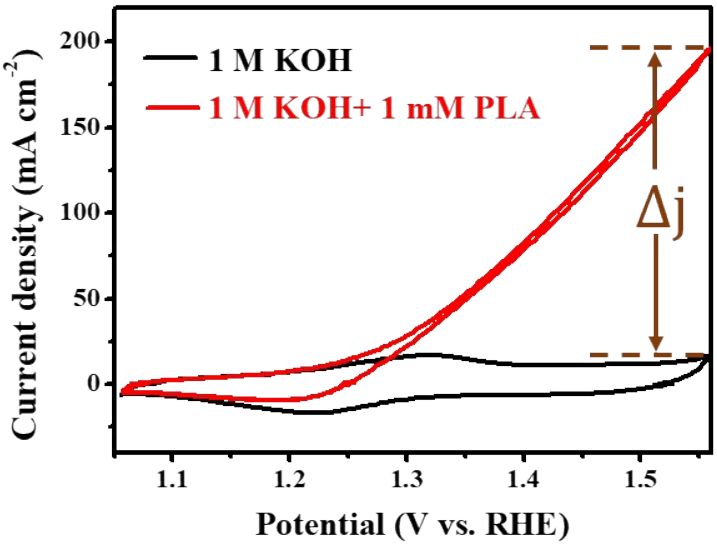

Fig. S16. CV curves of the 0.1-$CoSe_2$/NF in 1 M KOH + 1 mM PLA electrolyte.

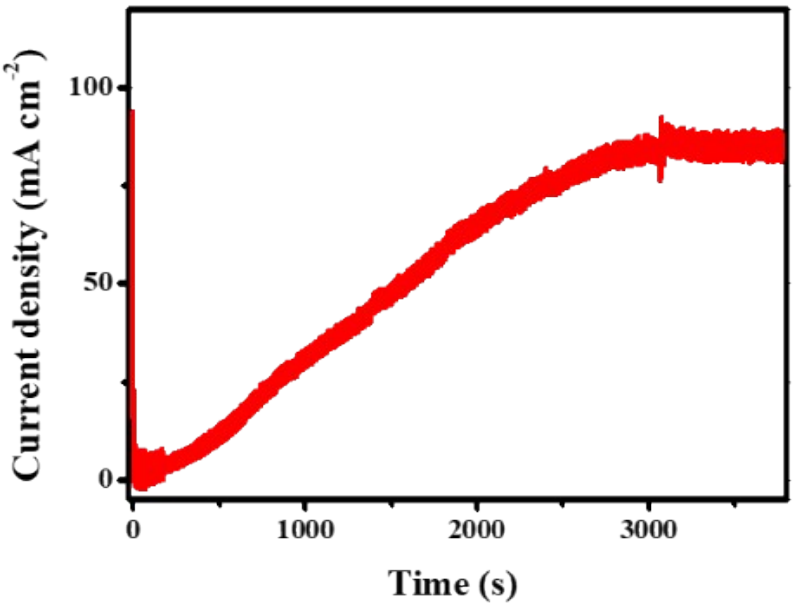

Fig. S17. Chronoamperometry curves of 0.1-$CoSe_2$/NF at 1.45 V vs. RHE after adding PLA into 1 M KOH solution.

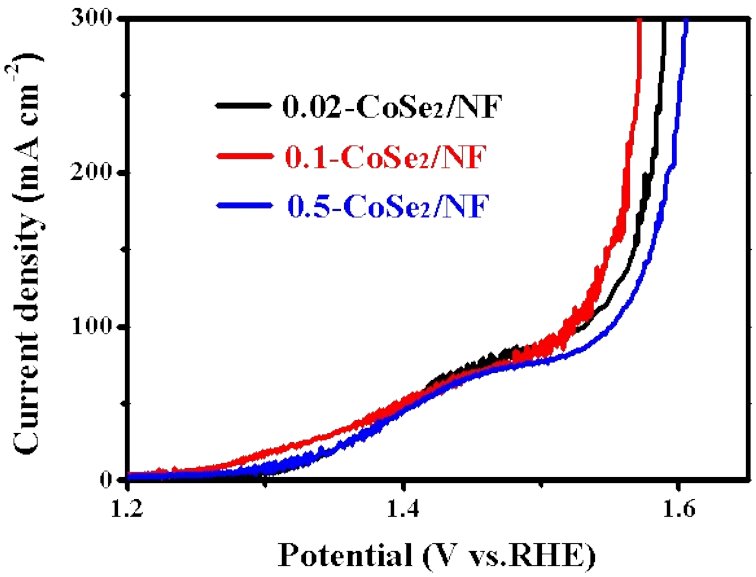

Fig. S18. LSV curves of 0.02-$CoSe_2$/NF, 0.1-$CoSe_2$/NF and 0.5-$CoSe_2$/NF in 1 M KOH with 1mM PLA.

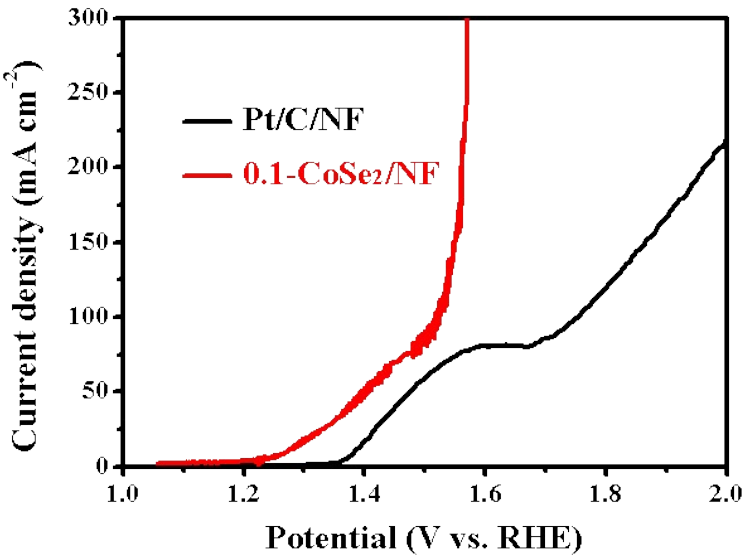

Fig. S19. LSV curves of 0.1-$CoSe_2$/NF and Pt/C/NF for PLA oxidation.

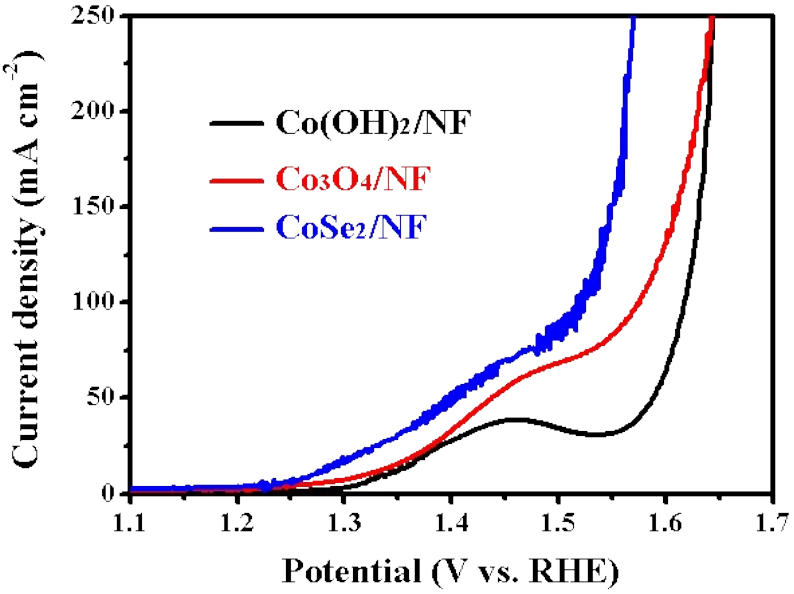

Fig. S20. LSV curves of the $CoSe_2$/NF, Co_3O_4/NF and $Co(OH)_2$/NF in 1 M KOH with 1 mM PLA.

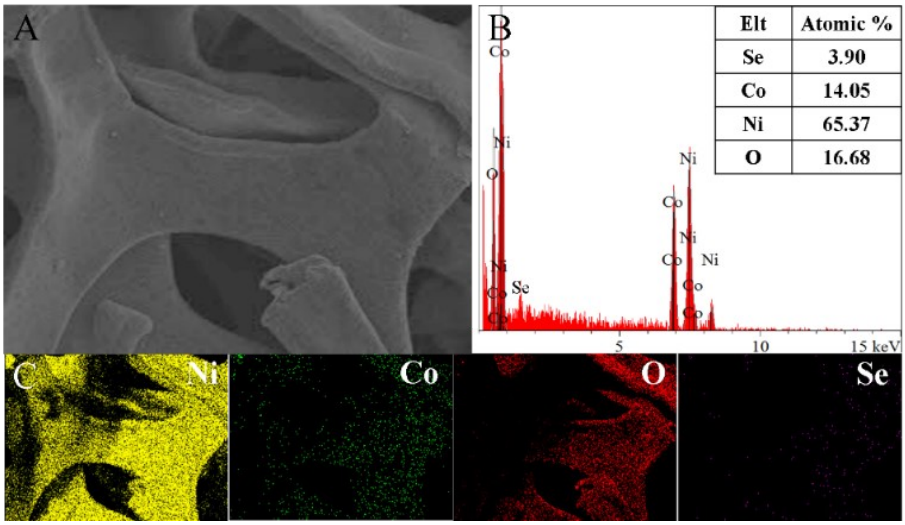

Fig. S21. Composition analyses of 0.1-$CoSe_2$/NF after PLA electrooxidation test. (A) SEM images, (B) EDS spectral and (C) EDS mapping of the 0.1-$CoSe_2$/NF.

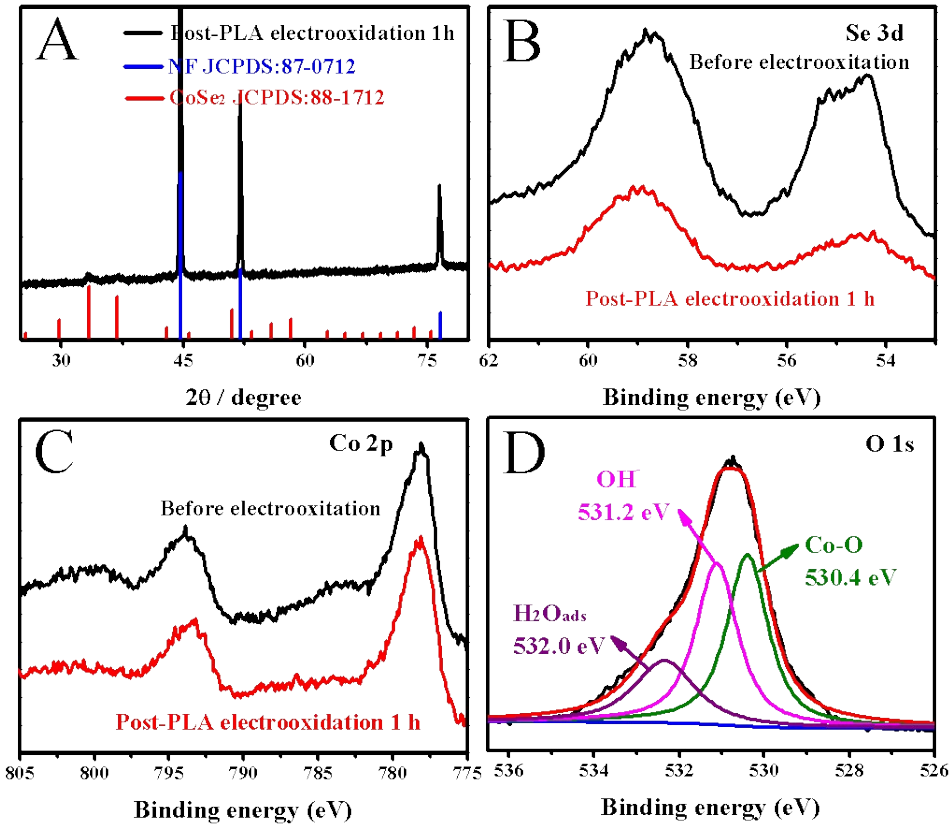

Fig. S22. Composition analyses of 0.1-$CoSe_2$/NF after prolonged PLA electrooxidation test. (A) XRD pattern, high-resolution XPS spectra of (B) Se 3d, (C) Co 2p and (D) O 1s peaks of the 0.1-$CoSe_2$/NF.

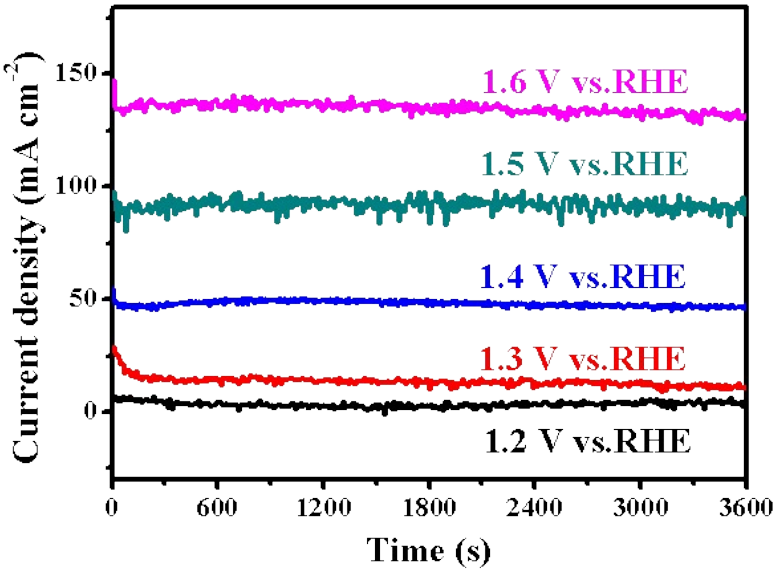

Fig. S23. Chronoamperometry results of 0.1-$CoSe_2$/NF at the corresponding potentials.

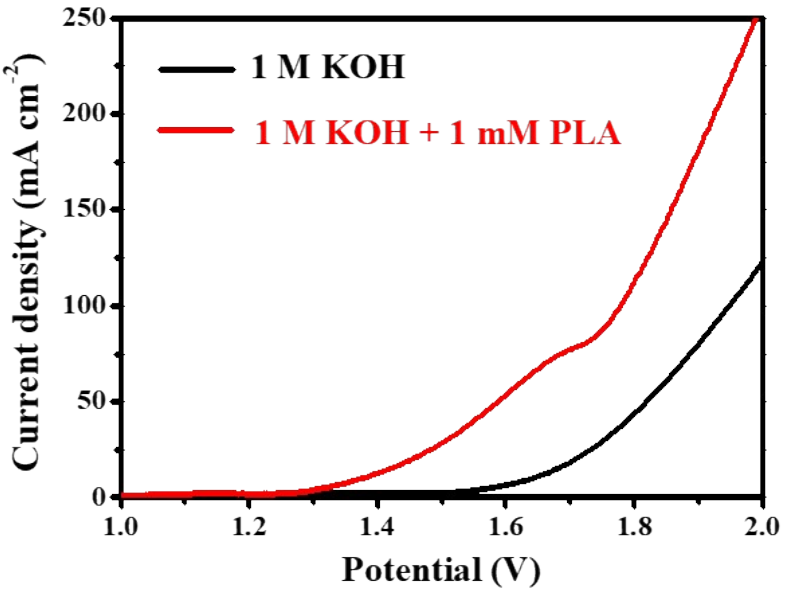

Fig. S24. Polarization curves of $CoSe_2$/NF||$CoSe_2$/NF in 1 M KOH with and without 1 mM PLA.