Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Band Structure Engineering of the W Replacement in $ReSe_2$ Nanosheets for Enhancing Hydrogen Evolution

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Experimental Section

Material Preparation

The bulk $Re_{1-x}W_xSe_2$ ($0 \leq x \leq 0.3$) crystals were synthesized via high temperature solid-state reaction. Re powder, W powder and Se powder were mixed according to stoichiometric ratio and pressed into a pellet. It was transferred into muffle furnace and annealed at 1323 K for 24 hours with the heating rate of 5 $K \cdot min^{-1}$. Afterwards, the samples were cooled down to room temperature naturally. Ultimately, the samples were dispersed in deionized water and dried in a vacuum oven at room temperature. $Re_{1-x}W_xSe_2$ nanosheets were obtained from an ultrasonication-assisted exfoliation process. In a typical procedure, 0.5 g of bulk $Re_{1-x}W_xSe_2$ powder was added to 30 mL of N,N-dimethylformamide (DMF) in a 50 mL glass vial and this mixture was subjected to ultrasonication for 24 h to get the exfoliated $Re_{1-x}W_xSe_2$ NSs.

Materials characterization

X-ray diffraction (XRD) characterization was carried out by Bruker D8 advance. Raman spectra were obtained using a thermal dispersive spectrometer with laser excitation at 635nm. Material microstructure was observed by a Hitachi S-4800 field emission scanning electron microscope (SEM). Transmission Electron Microscopy (TEM) images were obtained by JEOL JEM-2100F. X-ray Photoelectron Spectroscopy (XPS) measurements were run on a Thermo VG Scientific with Al Kα radiation (λ = 1486.6 eV). The images were imaged in high Angle annular dark field (HAADF) and bright field (BF), obtaining the mass-thickness and diffraction contrast information, respectively. The internal and external receiving angles of HAADF imaging were 68 and 280 m rad, respectively, and the receiving angles of BF imaging were 17 m rad.

Electrochemical measurements

The electrochemical experiment was carried out using a CHI-760E electrochemical workstation at ambient temperature. The measurements were performed in 0.5 M H_2SO_4 solution (deaerated by Ar) using a three-electrode setup, with a saturated calomel electrode (in saturated KCl solution) reference electrode, a graphite rod counter electrode and the glassy carbon working electrode. The catalyst was treated by ultrasonically dispersing in

Nafion/alcohol solution (0.5 wt.%, Alfa Aesar) to obtain 5.0 mg mL^{-1} slurry. The catalyst was dispersed in Nafion/alcohol solution (0.5 wt.%, Alfa Aesar) by sonication for 60 min. Then, 10 μL of the mixed solution was drop-casted onto a glassy carbon rotating disk working electrode (5 mm diameter) and dried with N_2. Initially, cyclic voltammogram (CV) was operated at least 20 cycles to guarantee the activation of the catalyst. LSV scan rate was 0.01 $V \cdot s^{-1}$. The electrochemical active surface area (ECSA) of the catalyst was tested in this way, that double-layer capacitance (C_{dl}) was tested in the potential window of -0.25 ~ -0.15 V (*vs*. RHE) at the scan rates of 20, 40, 60, 80, 100 and 120 $mV \cdot s^{-1}$ in the CV model.

Theoretical calculation

The calculations were based on the density functional theory (DFT) using Vienna Ab-initio Simulation Package (VASP). Ultra-soft (US) pseudopotentials and Perdew-Burke-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) are applied for the core-valence electron interaction and exchange-correlation functional, respectively. The cutoff energy was set as 600 eV. The total energy convergence was less than 10^{-4} eV per atom. The force-on-atom was converged below a threshold of 0.02. For WS_2 or $ReSe_2$, a 12 × 12 × 3 or 6 × 6 × 6 Monkhorst-Pack K-point grid was applied based on single cell unit for density of states (DOS). For $Re_{0.7}W_{0.3}Se_2$, one Re atom was substituted by W in $ReSe_2$.

Supporting Figures

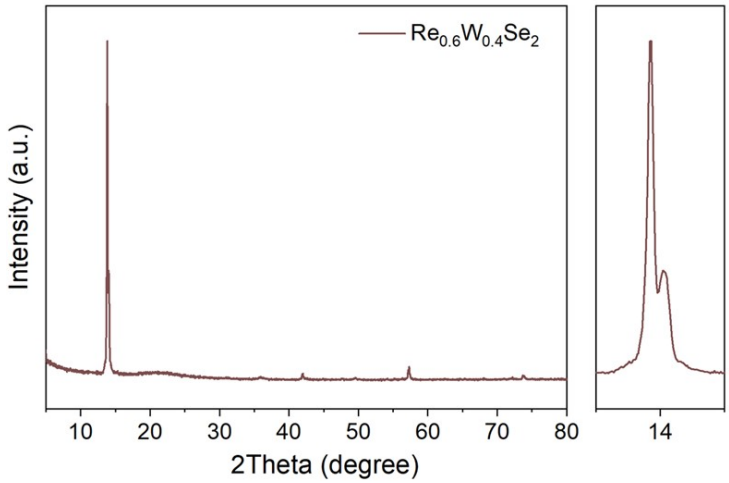

Figure S1. Powder X-ray diffraction pattern of $Re_{0.6}W_{0.4}Se_2$ is calculated by stoichiometry.

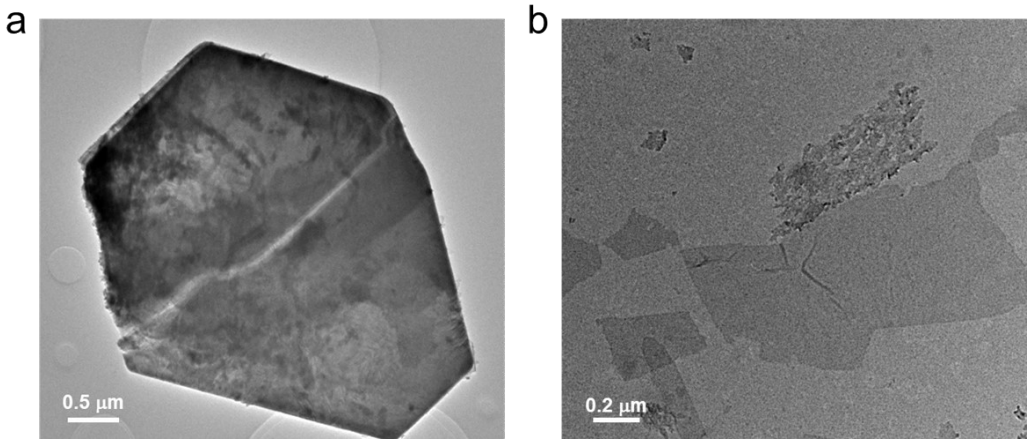

Figure S2. SEM images of (a) bulk $Re_{0.7}W_{0.3}Se_2$ and (b) $Re_{0.7}W_{0.3}Se_2$ nanosheets.

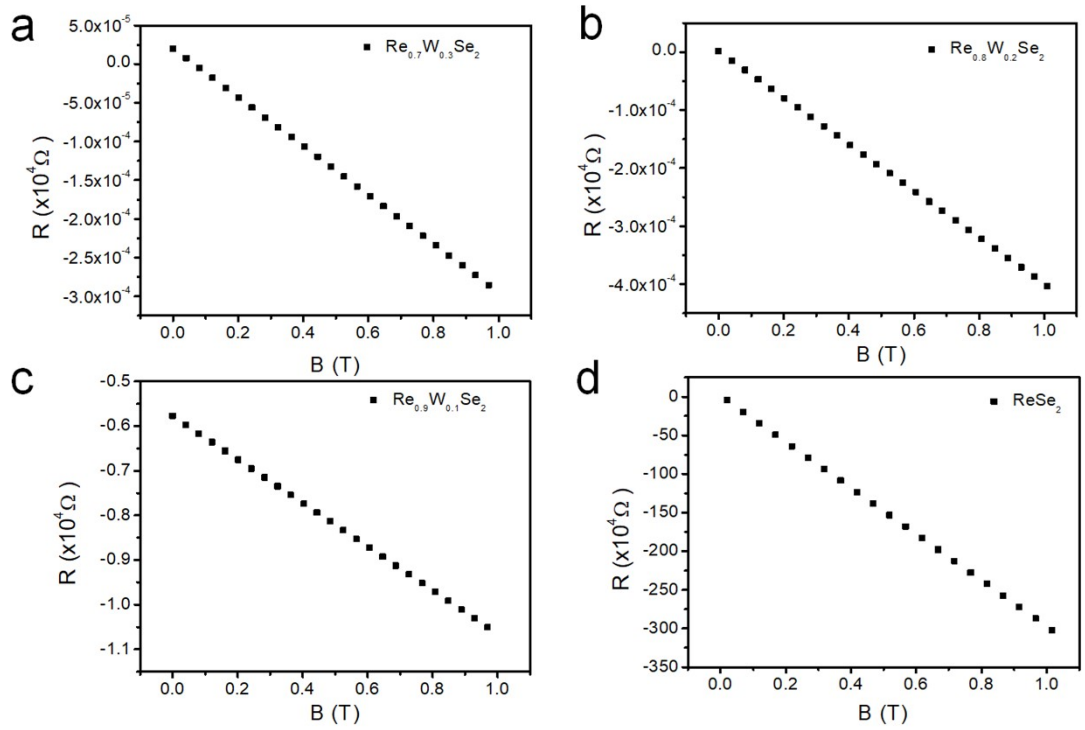

Figure S3. Room-temperature Hall measurements based on $Re_{1-x}W_xSe_2$ crystals. Typical plot of the transverse Hall resistance R versus an external magnetic field (B) for the $Re_{1-x}W_xSe_2$ (x = 0.3, 0.2, 0.1 and 0) crystals.

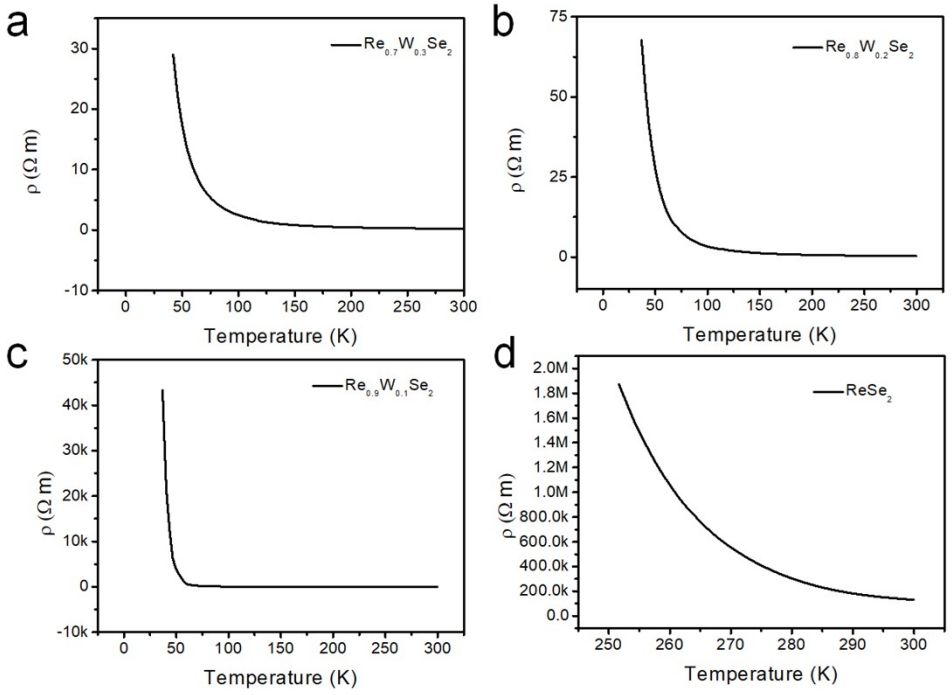

Figure S4. The temperature-dependent resistivity (R-T) curves of $Re_{0.7}W_{0.3}Se_2$, $Re_{0.8}W_{0.2}Se_2$, $Re_{0.9}W_{0.1}Se_2$ and $ReSe_2$.

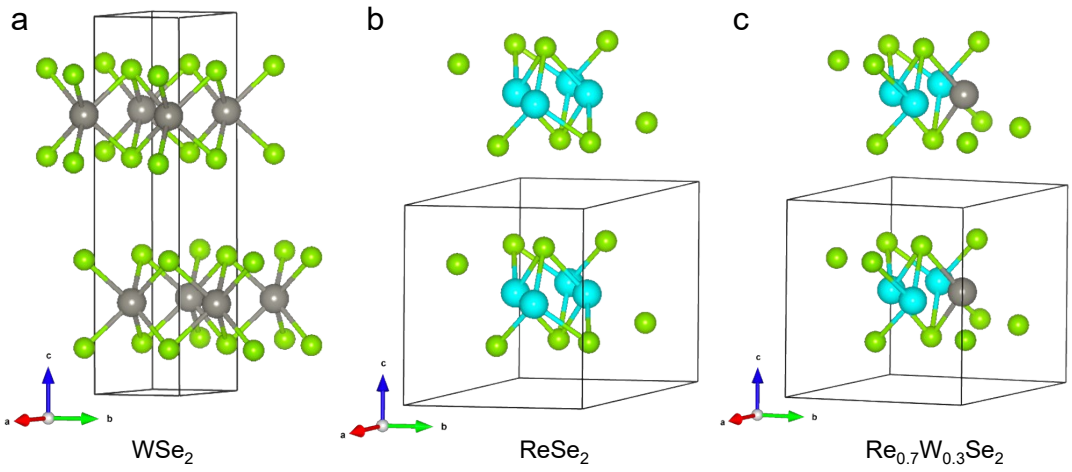

Figure S5. Geometrically optimized cells of WSe_2 (a), $ReSe_2$ (b) and W-doped $ReSe_2$ (c).

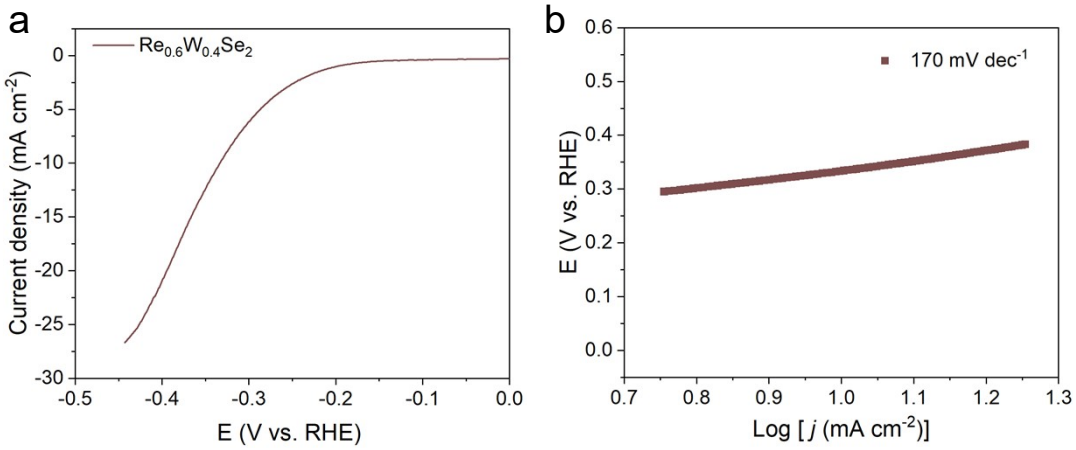

Figure S6. (a) Linear sweep voltammetry (LSV) curves of $Re_{0.6}W_{0.4}Se_2$. (b) Tafel plots derived from the LSV curves.

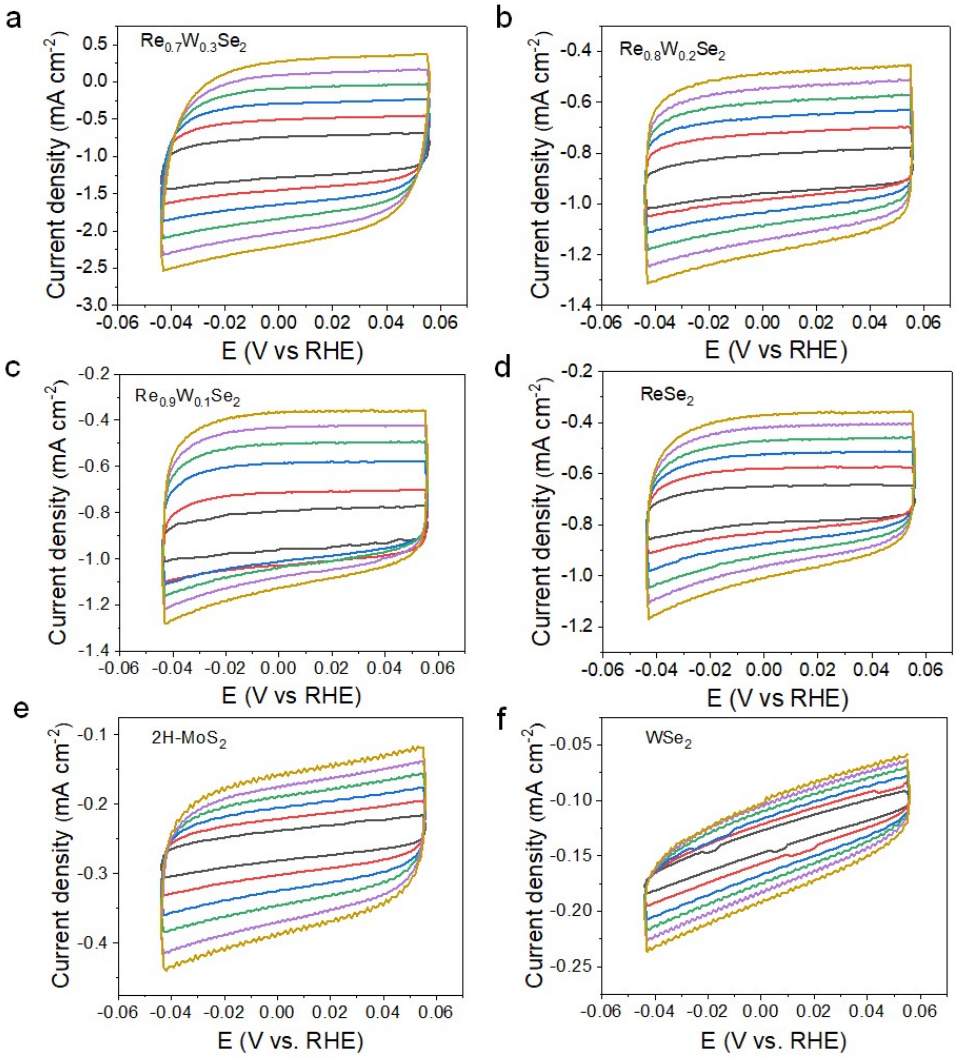

Figure S7. Cyclic voltammograms (CVs) of as-prepared samples: (a) $Re_{0.7}W_{0.3}Se_2$, (b) $Re_{0.8}W_{0.2}Se_2$, (c) $Re_{0.9}W_{0.1}Se_2$, (d) $ReSe_2$, (e) 2H-MoS_2 and (f) WSe_2. Current density is the difference between anodic and cathodic current densities at 0.06 V (*vs* RHE). In the plot, the capacitance was normalized by the geometric surface area of electrodes.

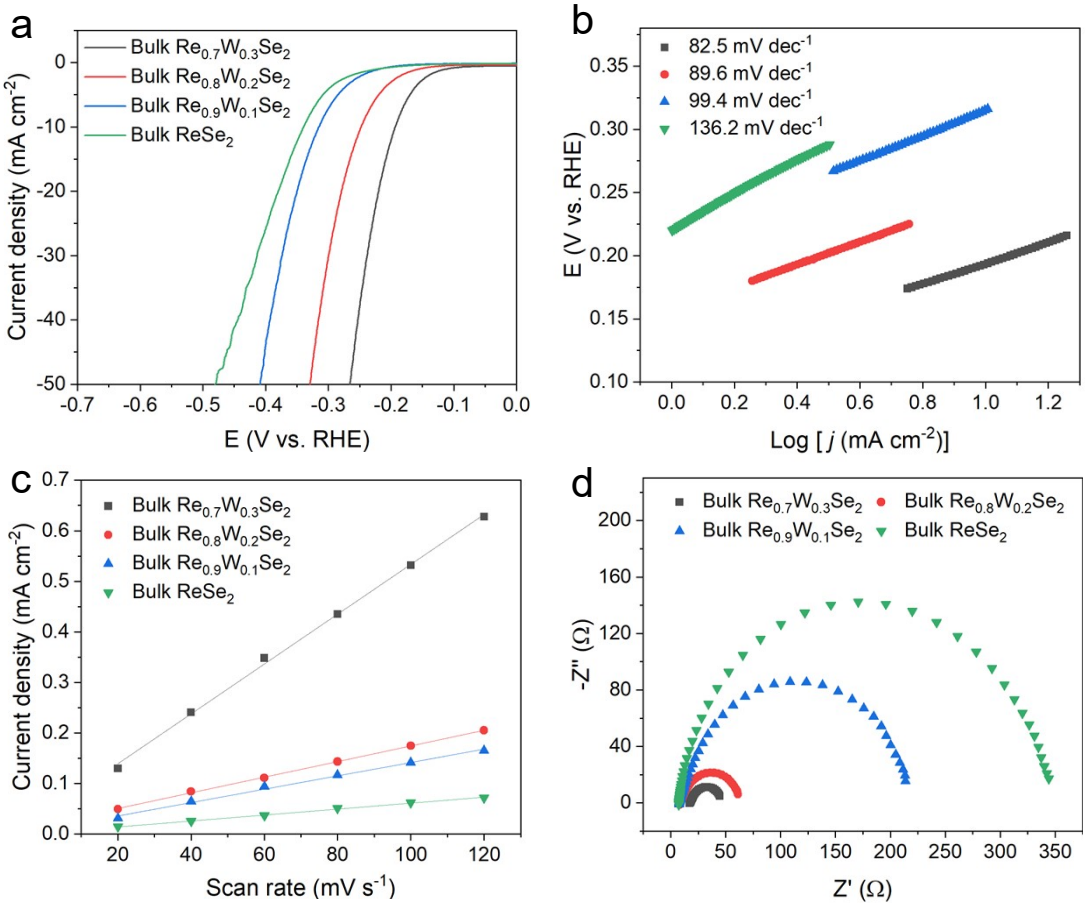

Figure S8. HER performance in 0.5M H_2SO_4. (a) Linear sweep voltammetry (LSV) curves of bulk $Re_{1-x}W_xSe_2$. (b) Tafel plots derived from the LSV curves. (c) ECSA at E=0.06 V versus RHE (reversible hydrogen electrode) for $Re_{1-x}W_xSe_2$. (d) Electrochemical impedance spectroscopy Nyquist plots of $Re_{1-x}W_xSe_2$ samples.

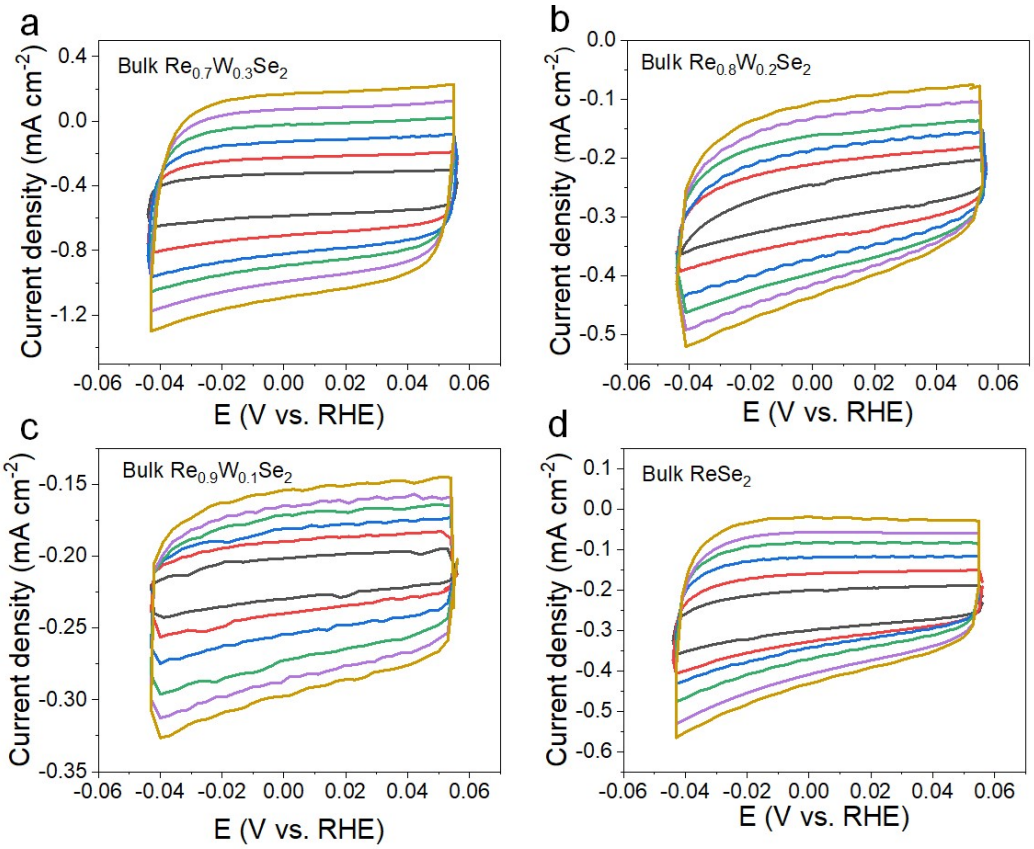

Figure S9. Cyclic voltammograms (CVs) of as-prepared samples: (a) bulk $Re_{0.7}W_{0.3}Se_2$, (b) bulk $Re_{0.8}W_{0.2}Se_2$, (c) bulk $Re_{0.9}W_{0.1}Se_2$ and (d) bulk $ReSe_2$. Current density is the difference between anodic and cathodic current densities at 0.06 V (*vs* RHE). In the plot, the capacitance was normalized by the geometric surface area of electrodes.

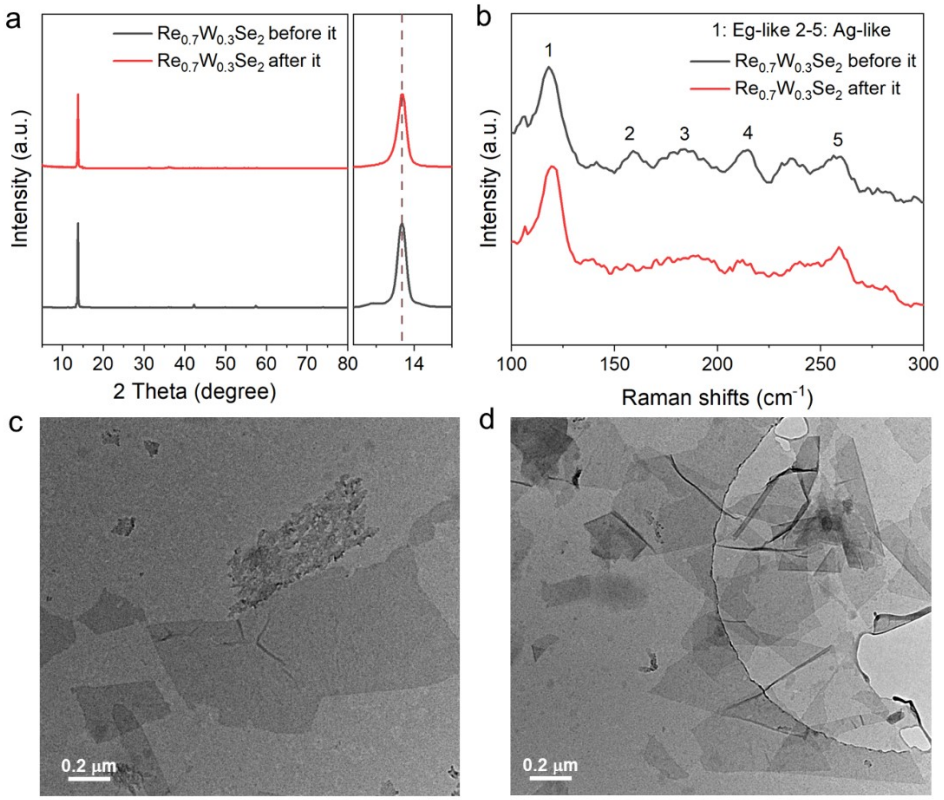

Figure S10. (a) XRD patterns and (b) Raman spectra of $Re_{0.7}W_{0.3}Se_2$ before and after long-term HER test. (c-d) Comparison of morphology before and after long-term HER test.

Cell parameter

Table S1. Comparison of cell parameters between calculated WSe_2, $ReSe_2$ and W-doped $ReSe_2$.

Parameters	WSe_2	$ReSe_2$	$Re_{0.7}W_{0.3}Se_2$
a (Å)	3.30694	6.65953	6.53146
b (Å)	3.30694	6.78769	6.81014
c (Å)	14.47976	7.51733	7.59956
α (°)	90.0000	91.9787	93.0375
β (°)	90.0000	103.6890	102.9353
γ (°)	120.0000	118.8190	118.4648