# Supporting Information

## Enhanced Charge Transport in $ReSe_2$-Based 2D/3D Electrode for Efficient Hydrogen Evolution Reaction

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## Experimental Section

### Material Preparation

Fabrication of PCC:

Carbon cloth (WOS1002) was cleaned by deionized water, acetone and ethyl alcohol in sequential 10 mins sonication, respectively. Then, it was dried at 90 °C. The preprocessed carbon cloth was placed in a ceramic boat and heated up to 600 °C at a speed of 5°C/min for 3h to form the porous surface structure.

CVD growth of $ReSe_2$@PCC:

2.5 mg $ReO_3$ (99.9%, Alfa Aesar) and 350 mg Se (99.9%, Alfa Aesar) were placed in the center of tube furnace, respectively. The PCC was put on the central of the Ceramic boat, which contains $ReO_3$. The reaction temperature was set to 500 °C. During the CVD process, a mixture of Ar (100 sccm) and $H_2$ (3 sccm) was used as the carrier gas. The growth time was 20 min.

### Characterization

Field emission scanning electron microscopy (FE-SEMC, ZEISS Ultra 55) was used to characterize the morphologies of $ReSe_2$ and PCC. The composition of $ReSe_2$ was characterized by energy-dispersive X-ray (EDX) mapping and X-ray photoelectron spectroscopy (XPS), using a Thermo Fisher Scientific K-Alpha+. Raman spectroscopy was conducted by a Renishaw 42K864 system with a 532 nm excitation laser. The crystal structure of $ReSe_2$ was investigated by transmission electron microscopy (TEM, JEM-2100 HR) and spherical aberration corrected transmission electron microscopy (ACTEM, Titan Themis G2 300).

### Electrochemical measurement

A three-electrode PEC was prepared in the measurements using 0.5M $H_2SO_4$ solution with an electrochemical workstation (CHI-660E, CHI Shanghai Inc). The working electrode was the prepared sample with an active area of 0.5 $cm^2$, the reference electrode was an Ag/AgCl (saturated KCl) electrode and the counter electrode was carbon rod. Linear sweep voltage was started from -0.6 to 0 V vs Ag Ag/AgCl electrode, with a scan rate of 5 $mVs^{-1}$. The potential shift of the reference electrode was calibrated to be −0.21 V vs. reversible hydrogen electrode (RHE). Current density-potential (J-E) curve was measured via a linear sweep voltammetry from 0 to -0.8 V vs. Ag/AgCl electrode, with a scan rate of 50 $mVs^{-1}$. Electrochemical impedance spectroscopy (EIS) was tested at 0.14 V vs. RHE, under the sweeping frequency range of 1-$10^5$ Hz with 10 steps per decade.

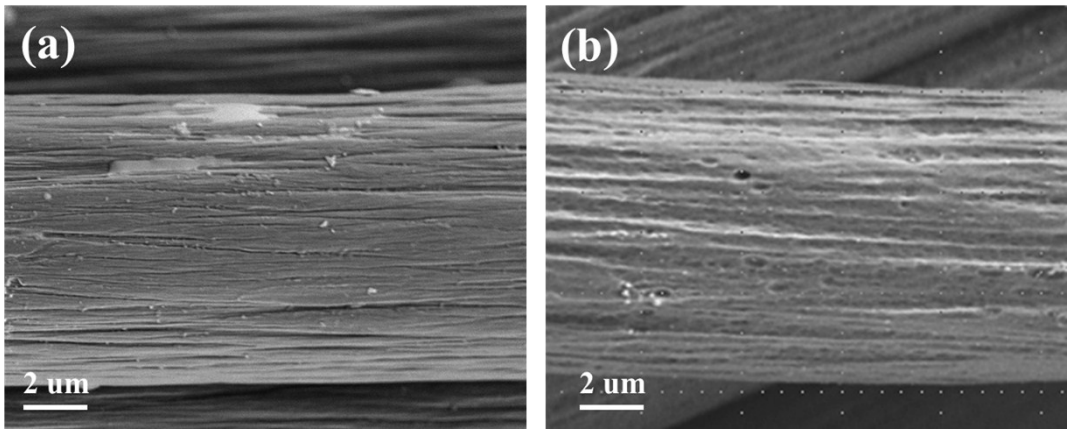


Figure S1. (a) and (b) SEM images of the original carbon fiber and the heat-treated one with porous surface structure, respectively.

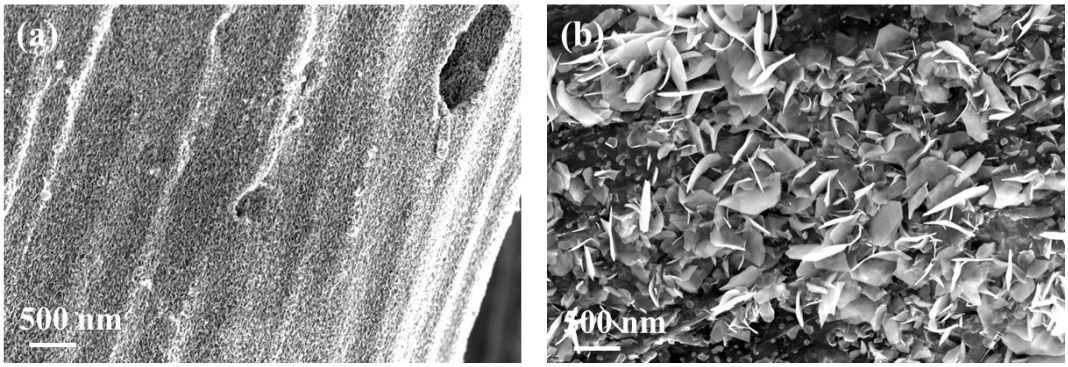


Figure S2. (a) and (b) $ReSe_2$ grown on PCC and CC with distinctively different 2D sizes and growth densities at the same CVD conditions, respectively.

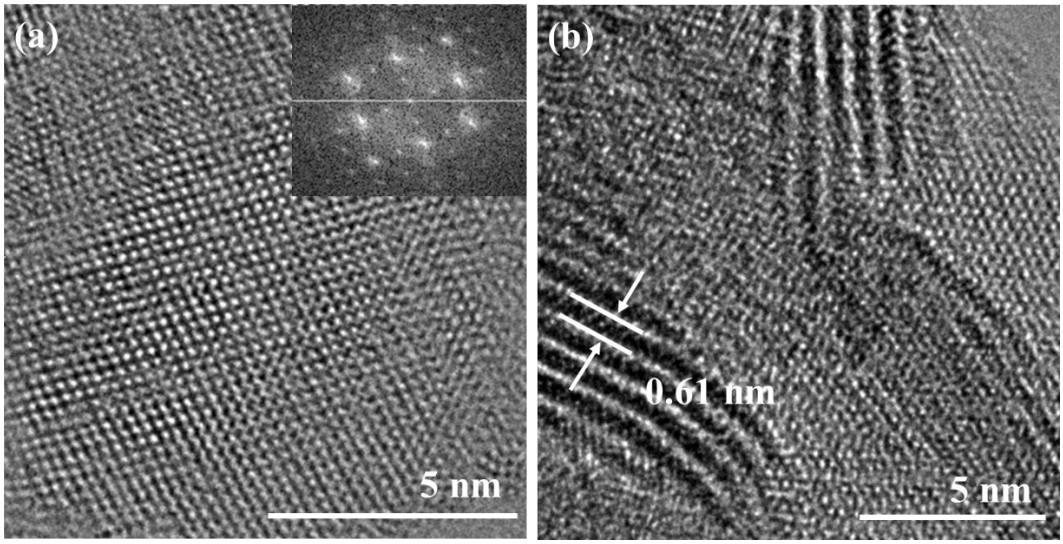


Figure S3 (a) and (b) HR-TEM image of $ReSe_2$ nanoflakes grown on PCC with different viewing directions, and inset of (a) is the corresponding SAED pattern.

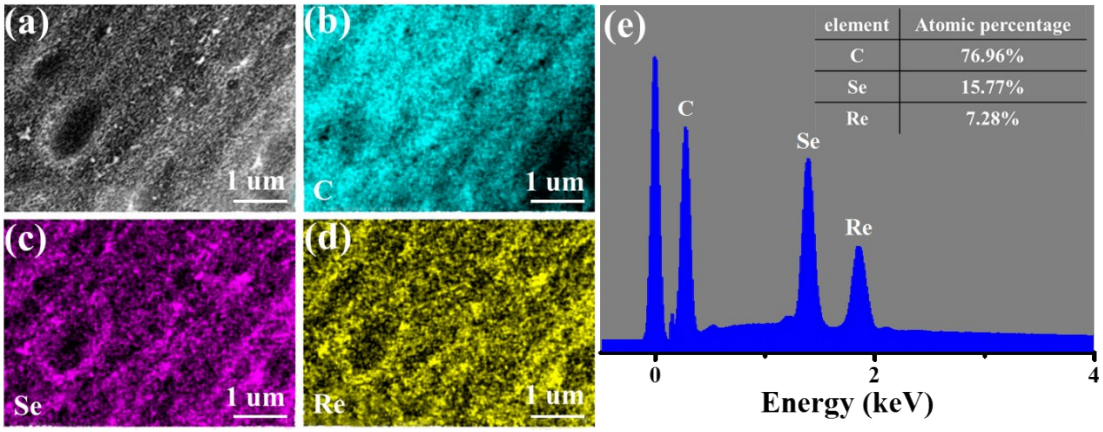


Figure S4. (a) SEM image of $ReSe_2$@PCC, and the corresponding EDX elemental mappings of (b) C, (c) Se, (d) Re. (e) The EDX spectrum with atomic percentages of Re, Se and C.

| | Re | Se | Stoichiometric ratio |
|---|---|---|---|
| As-prepared $ReSe_2$ nanosheets | 26.13% | 58.52% | 2.23 |
| Heat-treated $ReSe_2$ nanosheets | 10% | 22.22% | 2.22 |

**Table S1.** The contents of Re 4f and Se 3d from $ReSe_2$ nanoflakes grown on PCC before and after the post-heat treatment.

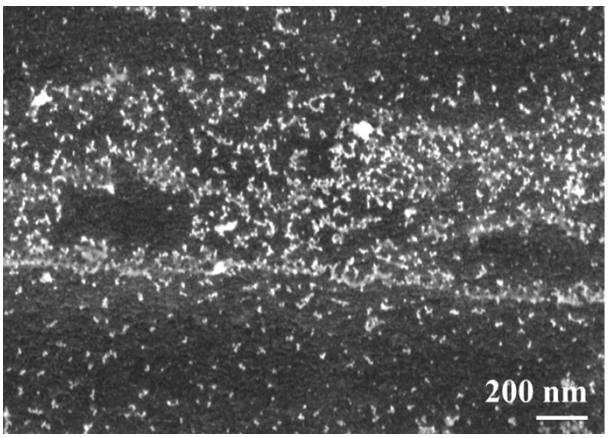


Figure S5 SEM image of $ReSe_2$ nanoflakes on PCC after a 240 °C post-heat treatment.

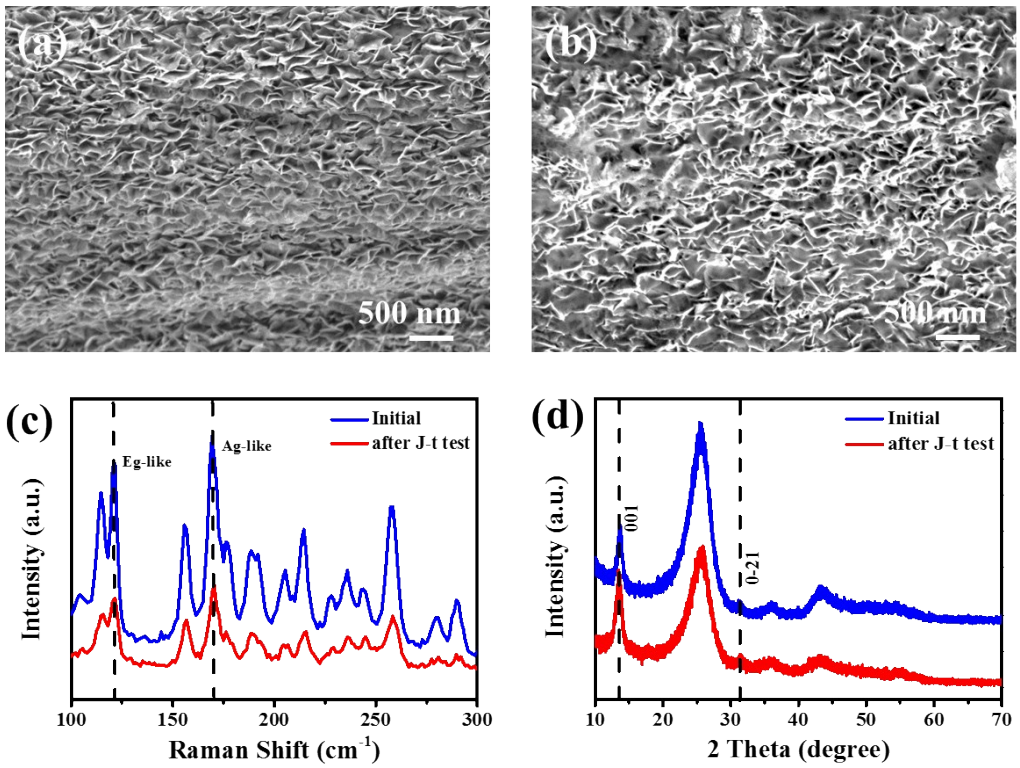


Figure S6 (a), (b) SEM images of $ReSe_2$@PCC before and after the J-t test. (c), (d) The Raman and XRD spectra of $ReSe_2$@PCC before and after the J-t test.