Supporting Information

Achieving Near-equilibrium H_{ad} Adsorption/Desorption by Introducing Asymmetric S-Re-Se modules in a-ReS_xSe_{2-x} Cocatalysts for Enhanced Photocatalytic H_2 Evolution

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EXPERIMENTAL SECTION

Preparation of TiO_2

600 mL of deionized water was added to a 1000 mL beaker. Under magnetic stirring, 50 mL of tetrabutyl titanate was added dropwise. The suspension was continuously stirred for 2 hours and aged at room temperature for 18 hours. The resulting amorphous TiO_2 was separated by centrifugation and washed three times with deionized water and ethanol. The white solid was dried in an oven at 60 °C for 24 h, then transferred to a crucible and calcined in a muffle furnace at 550 °C for 4 h with a heating rate of 5 °C/min. The product was thoroughly ground and stored in a sealed bottle for subsequent use, yielding anatase-phase TiO_2 material.

The cycling photocatalytic H_2-evolution experiment

In this study, four consecutive runs of the photocatalytic H_2 generation were performed to evaluate the stability and reusability of the synthesized a-$ReS_{1.2}Se_{0.8}/TiO_2$ photocatalysts. Typically, 50 mg of the a-$ReS_{1.2}Se_{0.8}/TiO_2$ photocatalysts was dispersed in a sacrificial reagent (80 mL, 30 vol% ethanol solution). The above suspension was firstly degassed with pure N_2 for 15 min, and then irradiated by a xenon lamp (PLS-SXE300) to trigger the photocatalytic H_2 evolution reaction. During light irradiation, continuous stirring was applied. Finally, gas (0.4 mL) was intermittently sampled every 30 min through a septum, and the generated hydrogen was analyzed by a gas chromatograph (SP-6801A, Lunan Ruihong Co., Ltd., China, nitrogen as a carrier gas) equipped with a 5 Å molecular sieve column and a thermal conductivity detector. After analyzed for 2 h, the first

recycle test has been recorded. The above a-$ReS_{1.2}Se_{0.8}/TiO_2$ suspension was re-degassed with pure N_2 for 15 min to drive away the producted H_2 in the system, and then applied for the next photocatalytic H_2 generation test. After performed for four consecutive runs, the recycling performance of the photocatalytic H_2 evolution for the a-$ReS_{1.2}Se_{0.8}/TiO_2$ photocatalysts was obtained.

Density functional theory (DFT) calculations

Vienna *ab* initio simulation package (VASP) was utilized for the following computational calculations. Typically, the generalized gradient approximation (GGA) with PBE (Perdew-Burke-Ernzerhof) functional was used to reveal the exchange and correlation effects. The (001) surface of the typical ReS_2 models was chosen as a typical calculation surface. The convergence threshold for total energy converged within 10^{-5} eV/atom and average force was 0.01 eV/Å. For the grid integration, a cutoff energy of 450 eV was applied and projector augmented wave PAW potentials were selected for describing ion cores. Moreover, (2 × 2 × 1) Monkhorst-Pack grids were applied for typical calculations.

The Gibbs free energies (ΔG) of adsorbed intermediates are calculated as:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

where ΔE, ΔZPE, T and ΔS are the calculated total energy of intermediates on catalysts surface, the zero-point energy, temperature, and entropy.

The AQE calculation

The apparent quantum efficiency (AQE) of the prepared photocatalysts was calculated using the following formula The formula is as follows：

$$AQE(\%) = \frac{number\ of\ reacted\ electrons}{number\ of\ incident\ photons} \times 100\%$$

$$= \frac{number\ of\ evolved\ H_2\ molecules \times 2}{number\ of\ incident\ photons} \times 100\%$$

$$= \frac{2R_{H_2}t_1N_A}{EAt_2\lambda/\mathrm{hc}} \times 100\% = 6.6482 \times 10^{-5} \times R_{H_2}/(E \times A \times \lambda) \times 100\%$$

In this context, the term R_{H_2} (mol h^{-1} g^{-1}) represents the rate of H_2 evolution, E (W cm^{-2}) represents the intensity of monochromatic light, A (cm^2) represents the area of light radiation for the reaction system, and λ (m) represents the monochromatic wavelength. The constants t_1 (h), t_2 (s), h (J·s), and c (m s^{-1}) have values of 1, 3600, 6.626×10^{-34}, and 3×10^8, respectively.

In this work, we used four 365 nm LED lamps as light source. The dimensions of the light radiation area (A) and the average light intensity (E) of the reaction system are 1×4 cm^2 and 1540.38 mW cm^{-2}, respectively. Consequently, the AQE of the a-$ReS_{1.2}Se_{0.8}$/TiO_2 photocatalyst can be calculated as follows:

$$\mathrm{AQE}=(6.6482\times 10^{-5} \times 1588 \times 10^{-6})/(1540.38\times 10^{-3} \times 4 \times 365 \times 10^{-9})$$

$$\times 100\% = 4.69\%$$

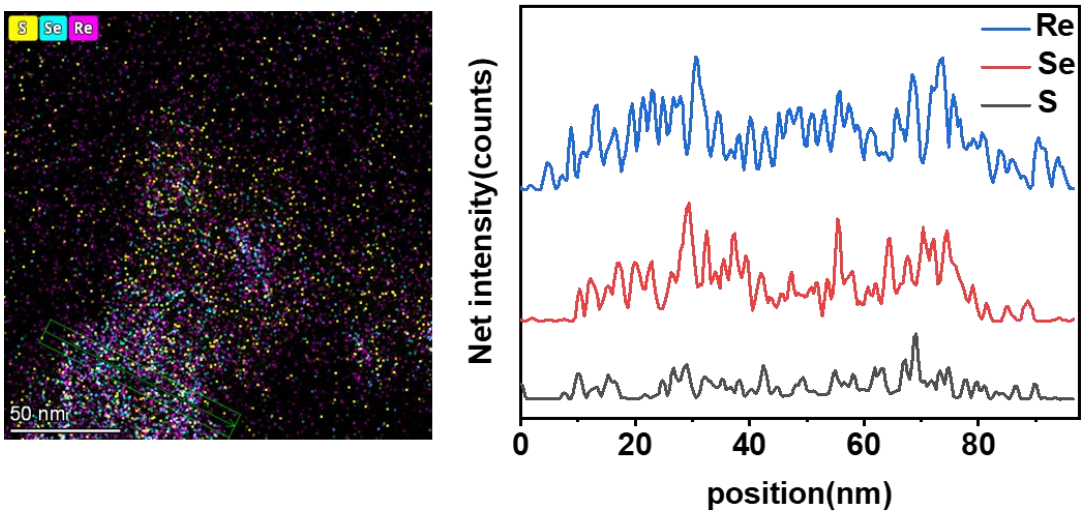

Fig. S1. The elemental-mapping image and line-scan electron energy loss spectroscopy data of the a-$ReS_{1.2}Se_{0.8}$ cocatalysts.

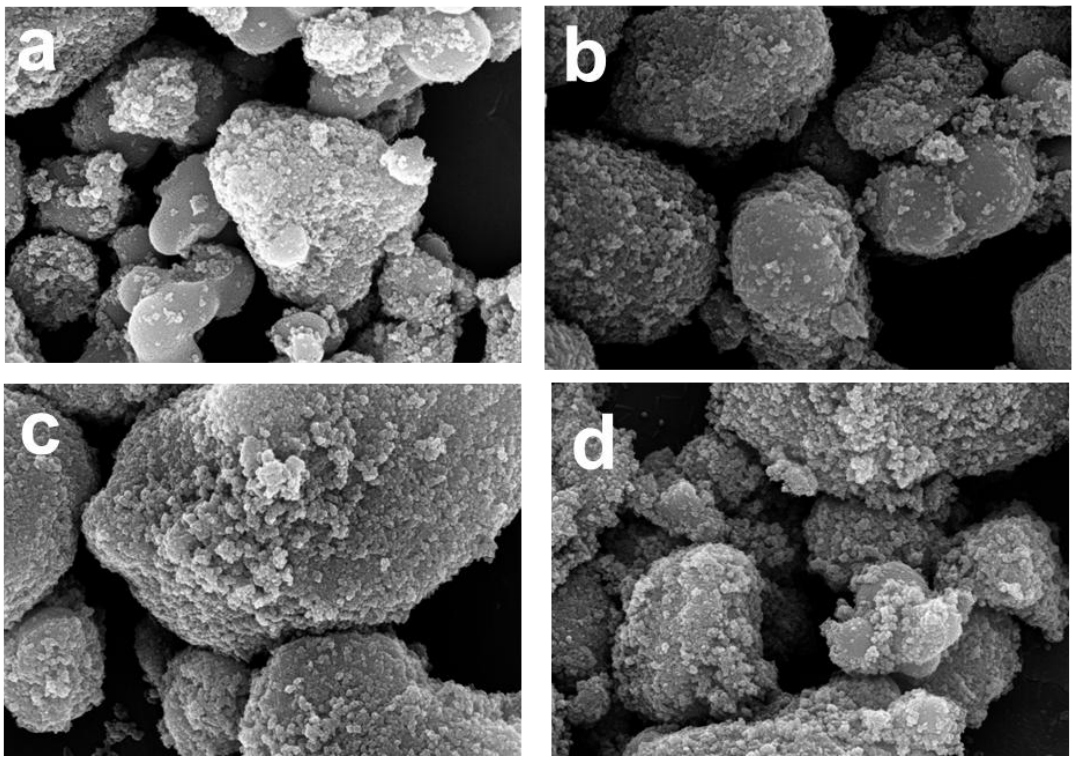

Fig. S2. SEM images of (a) TiO_2, (b) a-ReS_2/TiO_2, (c) a-$ReS_{1.2}Se_{0.8}/TiO_2$ and (d) a-$ReSe_2/TiO_2$ photocatalysts.

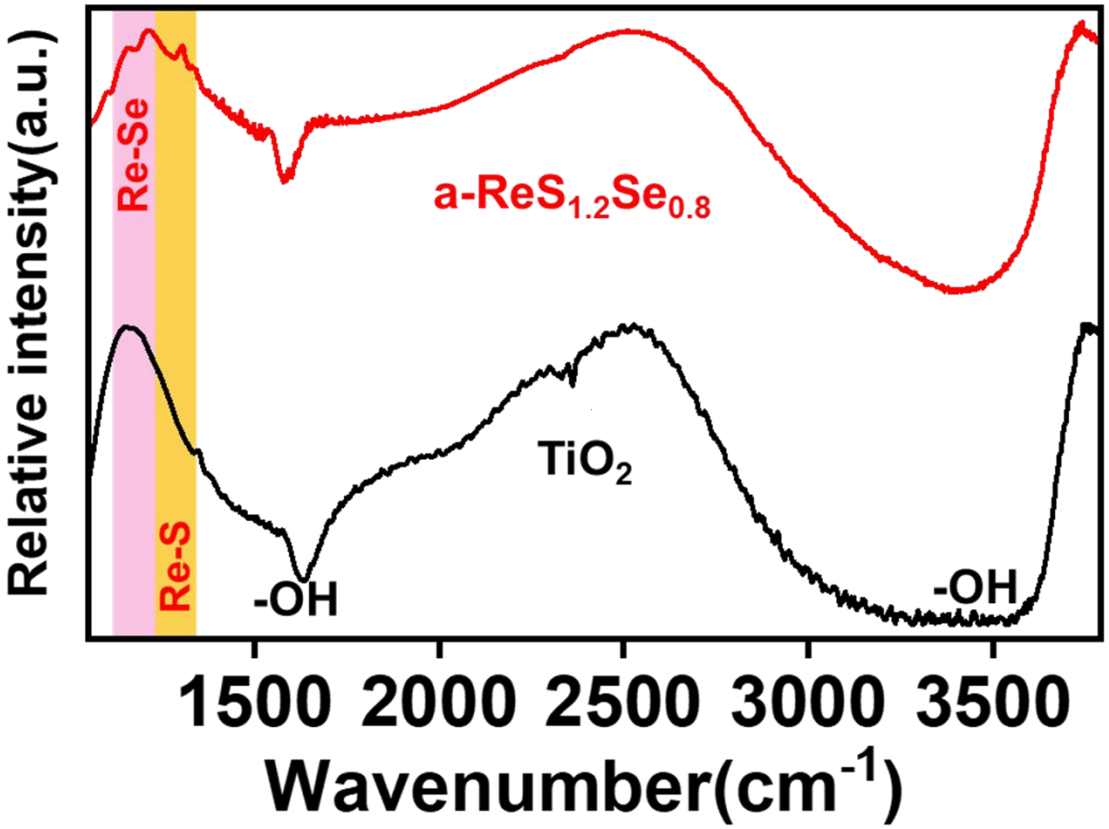

Fig. S3. FT-IR spectra of a-$ReS_{1.2}Se_{0.8}$/TiO_2 and TiO_2 photocatalysts.

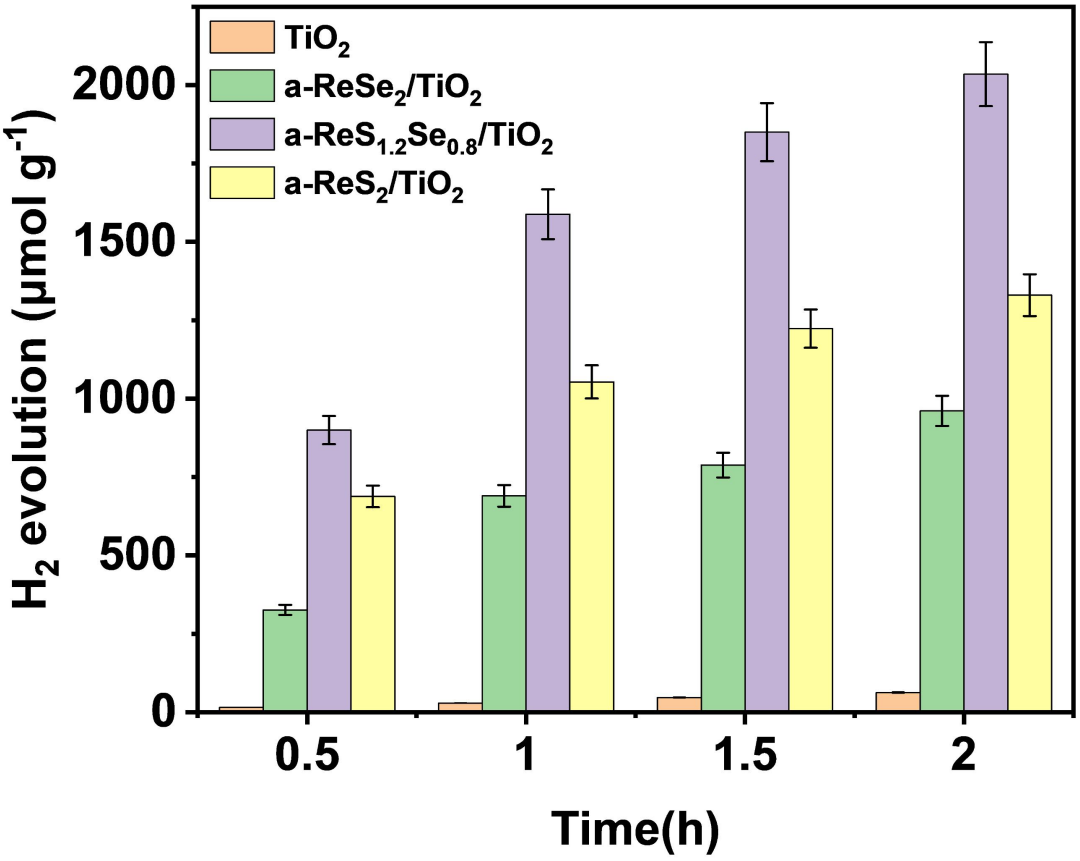

Fig. S4. The photocatalytic H_2 generation rates for various samples.

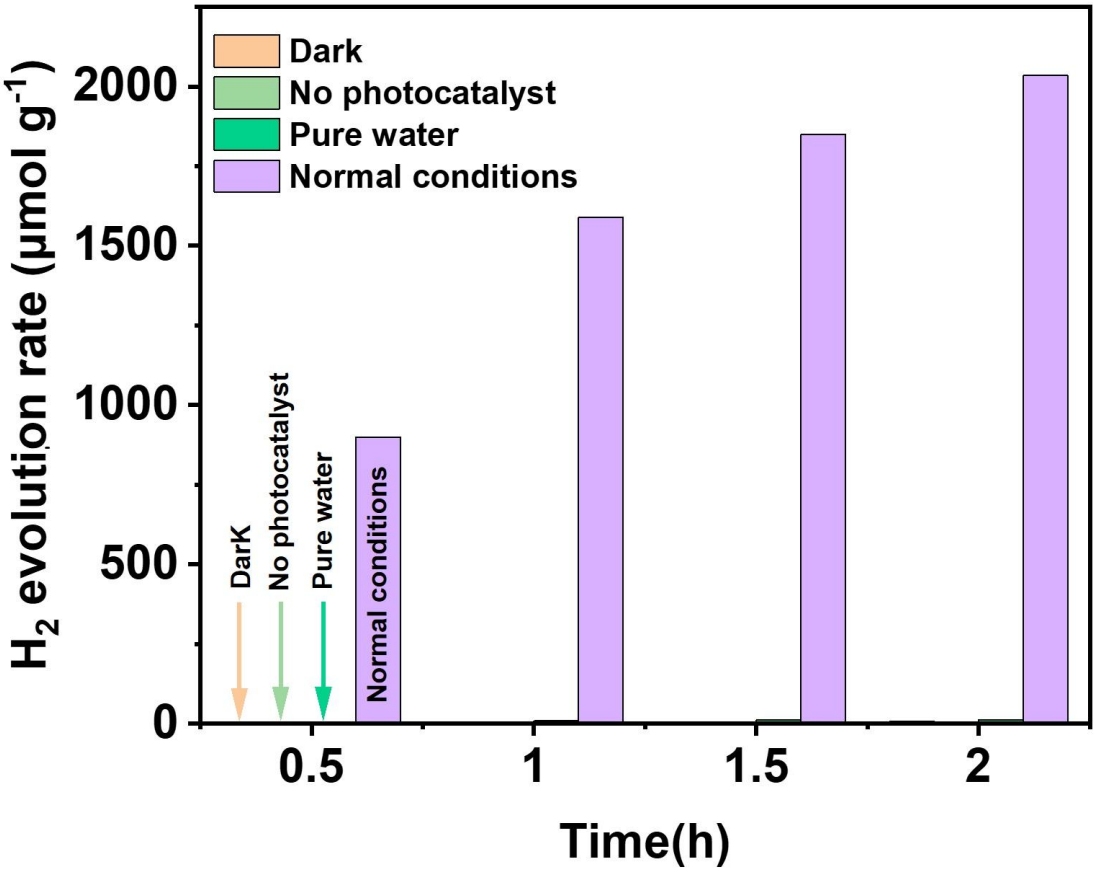

Fig. S5. The photocatalytic H_2 evolution rates of the a-$ReS_{1.2}Se_{0.8}/TiO_2$ photocatalysts under different conditions (e.g., without light irradiation, without photocatalyst, without organic substance).

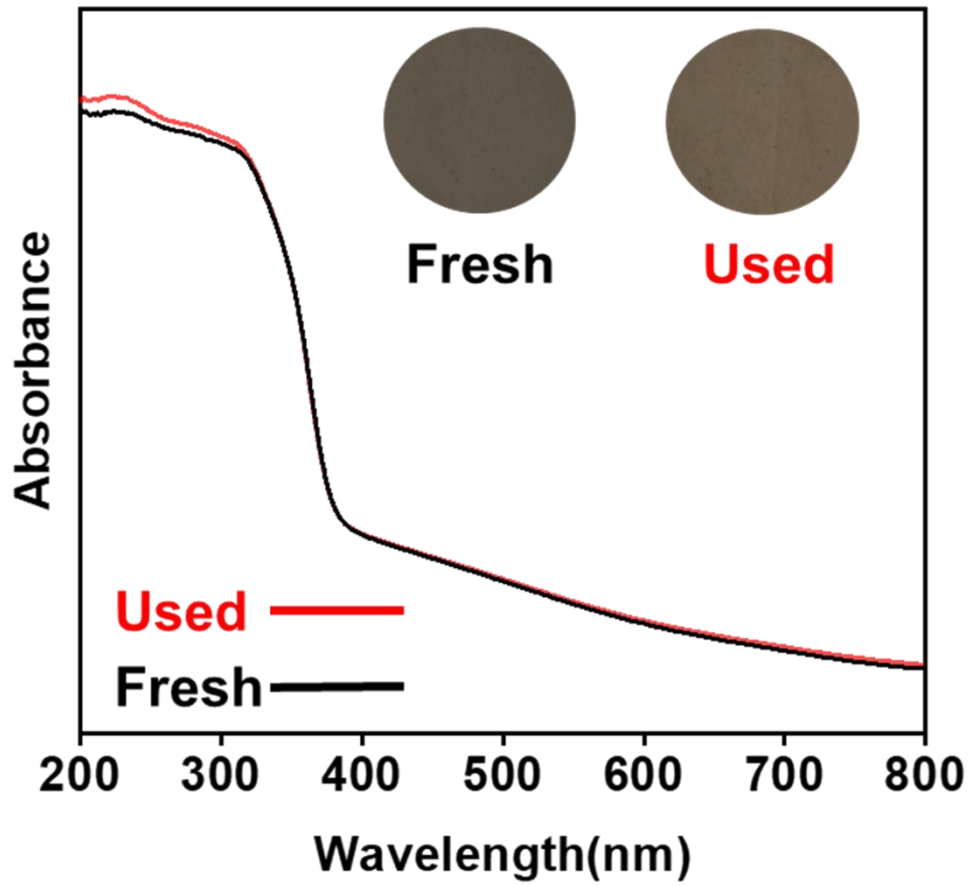

Fig. S6. UV-vis DRS spectra of a-$ReS_{1.2}Se_{0.8}/TiO_2$ photocatalysts before and after the photocatalytic H_2 production.

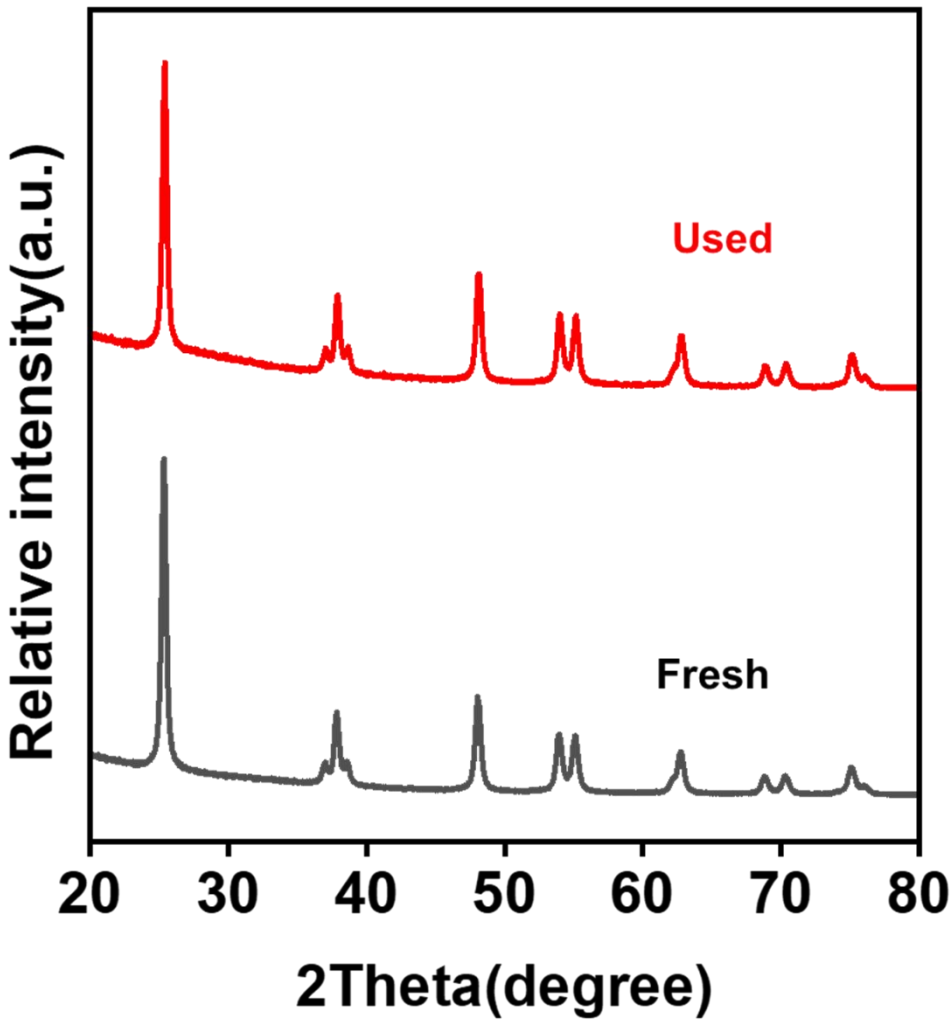

Fig. S7. XRD patterns for a-$ReS_{1.2}Se_{0.8}/TiO_2$ photocatalyst before and after the photocatalytic H_2 production.

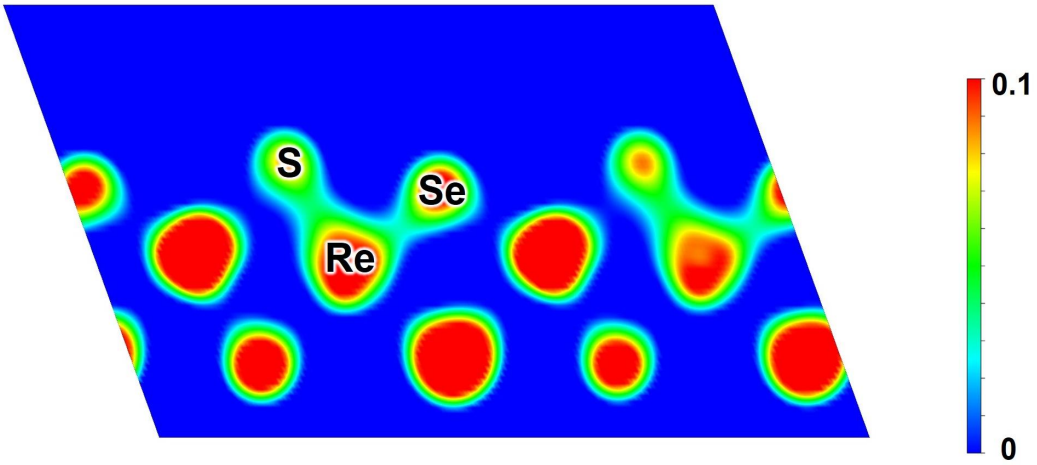

Fig. S8. Calculated electron localization function of typical $ReS_{1.2}Se_{0.8}$ structure.