Supporting Information

Multi-Hydrogen Adsorption of Amorphous ReS$_x$ Cocatalysts for Boosting Photocatalytic Hydrogen Evolution

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Supporting Information Content

EXPERIMENTAL SECTION

SI-1 Synthesis of TiO_2 photocatalysts

TiO_2 was synthesized by a typical hydrolysis-calcination method 70 mL of Tetrabtyl titanate ($Ti(OC_4H_9)_4$) was gradually added into 1000 mL of deionized water and vigorously stirred at 60 °C for 2 hours. After filtration, washing, and drying, the resulting powder was calcined at 550 °C for 2 hours to obtain the crystalline TiO_2 photocatalyst.

SI-2 Synthesis of sulfur-rich ReS_x/TiO_2 photocatalysts

The sulfur-rich ReS_x/TiO_2 photocatalyst was synthesized by a one-step strategy in a water bath. Initially, 50 mg of TiO_2 photocatalyst powder was dispersed in 10 mL of deionized water and subsequently subjected to continuous magnetic stirring. Subsequently, 80 μL of ReO_4^- (0.1 mol/L) and 800 μL of thioacetamide (TAA, 0.1 mol/L) was added to the suspension, where the molar ratio of Re to S is controlled to be 1:10. Thereafter, 5 mL of HCl solution (1 mol/L) was introduced into the system. After continuous stirring for 30 minutes, the mixture was heated in a water bath at 90 °C for 3 hours. Following natural cooling, the product was collected by centrifugal filtration and dried under vacuum at 60 °C, and the resulting sample was denoted as ReS_x/TiO_2 (1:10). In this study, the mass ratio of Re to TiO_2 was set at 3 wt%. To investigate the influence of the Re/S molar ratio on the catalytic performance of ReS_x/TiO_2 photocatalysts, the Re/S molar ratios were controlled at 1:2, 1:5, 1:7, 1:10, 1:15, 1:20, and 1:30, respectively, and the corresponding sample was denoted as ReS_x/TiO_2 (1:x). For comparison, the crystalline ReS_2/TiO_2 sample was also achieved via high-temperature calcination of amorphous sulfur-rich ReS_x/TiO_2 (1:10) under N_2 atmosphere at 550 °C for 4 h.

SI-3 Characterization

The X-ray diffraction (XRD) patterns were obtained on a D/Max-RB X-ray diffractometer (Rigaku, Japan) with Cu Kα radiation. The morphology of samples was observed using field-emission scanning electron microscopy (FESEM, JSM 7500F, JEOL, Japan). Transmission electron microscopy (TEM, JEM 2100F, JEOL, USA) images were recorded on a Thermal Fisher Talos F200X electron microscope equipped with an energy-dispersive X-ray spectroscopy (EDX) spectrometer. The light absorption spectra were performed using a UV-visible spectrophotometer (UV-2600, Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCALAB 250Xi instrument with Al Kα X-ray radiation, and all the XPS binding energies of various elements were calibrated through the adventitious carbon C 1s peak at 284.8 eV. In-situ XPS was conducted under the same condition, except that UV light irradiation was introduced. The time-resolved photoluminescence (TRPL) spectra were acquired using a fluorescence lifetime spectrophotometer (FLS 1000, Edinburgh, UK). The elemental content analysis was implemented using an inductively coupled plasma optical emission spectroscopy (ICP-OES, Prodigy 7, USA).

SI-4 Photocatalytic H_2-generation test

The above photocatalyst (30 mg) was dispersed into 80 mL 10 vol% lactic acid (pH = 2) in a 100 mL three-necked Pyrex flask and subsequently purged with nitrogen for 20 minutes, and then irradiated with 4 LED lights (365 nm, 3 W) under continuous agitation to trigger the photocatalytic H_2-evolution reaction. Finally, gas (0.4 mL) was sampled intermittently every 0.5 h and the resulting hydrogen was analyzed with an equipped gas chromatograph. To further investigate the effect of pH on the ReS_x/TiO_2(1:10) H_2-

evolution activity, the pH of the solution was adjusted to 5, 7, 9, and 12 by adding varying amounts of NaOH solution (3 mol L^{-1}).

SI-5 The detailed procedures of cycling test

In this study, the stability and reusability of the ReS_x/TiO_2 (1:10) photocatalyst were evaluated by photocatalytic hydrogen production for 6 consecutive times. Specifically, the ReS_x/TiO_2 (1:10) photocatalyst (30 mg) was dispersed in a sacrifice reagent (80 mL 10 vol% lactic acid solution). To remove O_2 in the solution, the suspension was initially degassed with pure N_2 for 20 min and then irradiated with 4 LED lights (365 nm, 3 W) under continuous agitation to trigger the photocatalytic H_2-evolution reaction. Finally, gas (0.4 mL) was sampled intermittently every 0.5 h and the resulting hydrogen was analyzed with an equipped gas chromatograph. After analyzing for 2 h, the first recycle test was recorded. The above ReS_x/TiO_2(1:10) suspension was re-degassed with pure N_2 for 20 min to drive out the productd H_2 from the system before the next photocatalytic H_2-producted test. After 6 consecutive experiments, the recycling performance of the photocatalytic H_2-evolution for the ReS_x/TiO_2(1:10) photocatalyst was obtained.

SI-5 Photoelectrochemical performance

The photoelectrochemical properties were conducted on a CHI760E electrochemical workstation in a standard three-electrode system by using Na_2SO_4 (0.5 mol L^{-1}) as the electrolyte solution and a 300 W Xenon lamp as the light source, where the photocatalyst-coated FTO, Ag/AgCl and platinum wire acted as the working electrode, reference electrode, and counter electrode, respectively.

The working electrodes were prepared on FTO substrate with an active area of about 1.0 cm^2, where the side of FTO glass was protected by Scotch tape. 20 mg as-prepared photocatalyst was uniformly dispersed in 0.5 mL ethanol containing 20 μL Nafion, and subsequently ultrasonicated for 30 min to obtain a suspension solution. Finally, the above suspension was coated on the FTO surface (conductive side) to form a uniform film (with a thickness of 5-10 μm) and then dried at room temperature.

The linear sweep voltammetry (LSV) curves were measured at the potential ranging from 0 to −1.6 (vs Ag/AgCl) with a scan rate of 10 mV s^{-1}. The transient photocurrent responses with time (*i-t* curve) could be achieved at a bias potential of +0.164 V during repeated ON/OFF illumination cycles. The electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 0.1 Hz - 10^5 Hz with an ac amplitude of 5 mV at the open circuit voltage.

Table S1. TRPL and relevant percentage data

Samples	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{ave} (ns)
TiO_2	0.3	60.69	2.5	39.31	2.1
ReS_x/TiO_2(1:2)	1.4	47.45	6.0	52.55	5.9
ReS_x/TiO_2(1:10)	1.8	48.30	7.0	51.70	7.2
c-ReS_2/TiO_2	1.2	48.72	4.5	51.28	3.9

The decay curves of as-prepared samples from the TRPL can be effectively fitted using the following biexponential Eq. (1), and the fluorescent lifetime is calculated by Eq. (2).

$$A_{(t)} = A_{(0)} + A_1\, exp(-t/\tau_1) + A_2\, exp(-t/\tau_2) \qquad (1)$$

$$\tau_{ave} = ({A_1\tau_1}^2 + {A_2\tau_2}^2)/(A_1\tau_1 + A_2\tau_2) \qquad (2)$$

where A_1 and A_2 represent the weight factors, while τ_1 and τ_2 are the short and long fluorescent lifetimes, respectively.

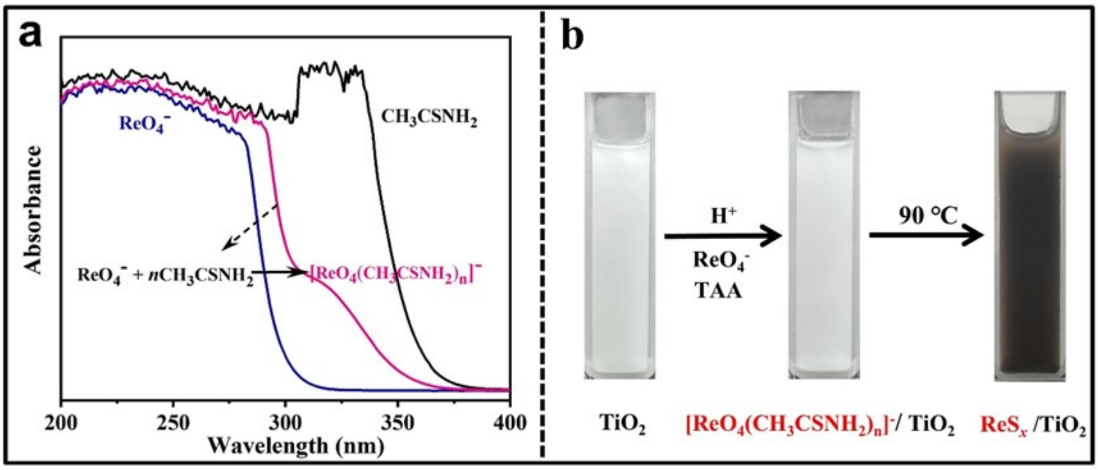

Fig. S1. (a) UV−visible absorption spectra of ReO_4^-, CH_3CSNH_2 and $[ReO_4(CH_3CSNH_2)_n]^-$. (b) The recorded photographs during the synthesis of ReS_x/TiO_2 photocatalyst: TiO_2, $[ReO_4(CH_3CSNH_2)_n]^-/TiO_2$ and ReS_x/TiO_2.

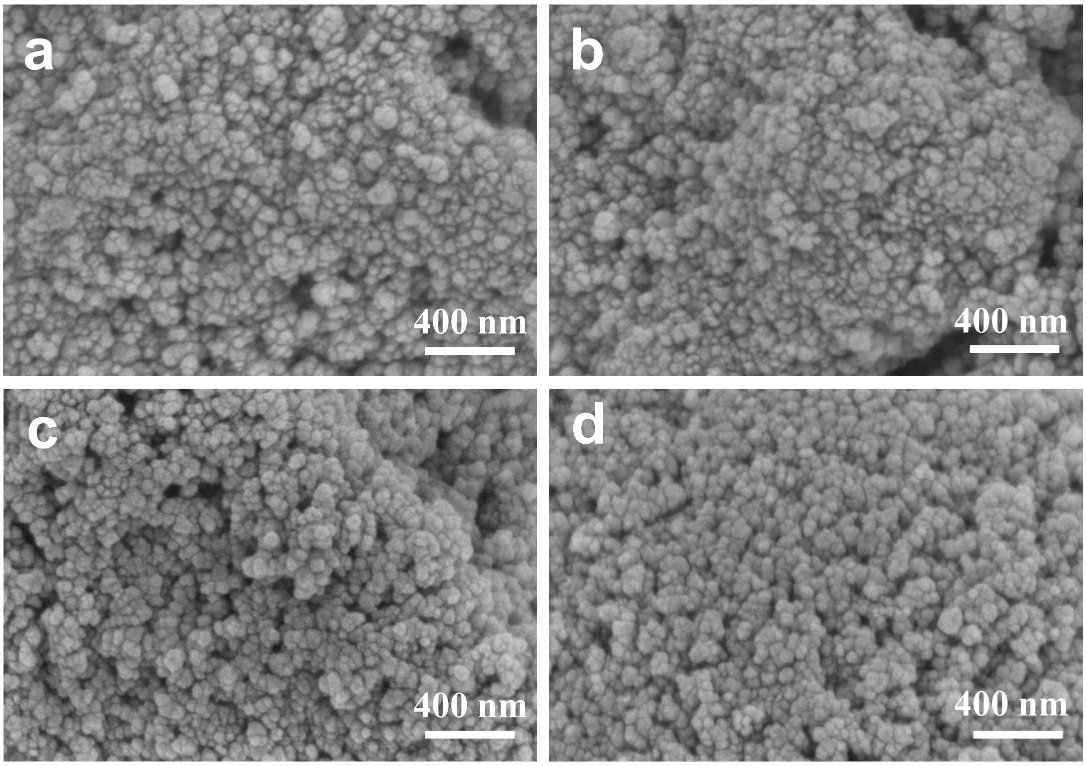

Fig. S2. FESEM images of (a) TiO_2, (b) ReS_x/TiO_2(1:2), (c) ReS_x/TiO_2(1:10), and (d) c-ReS_2/TiO_2.

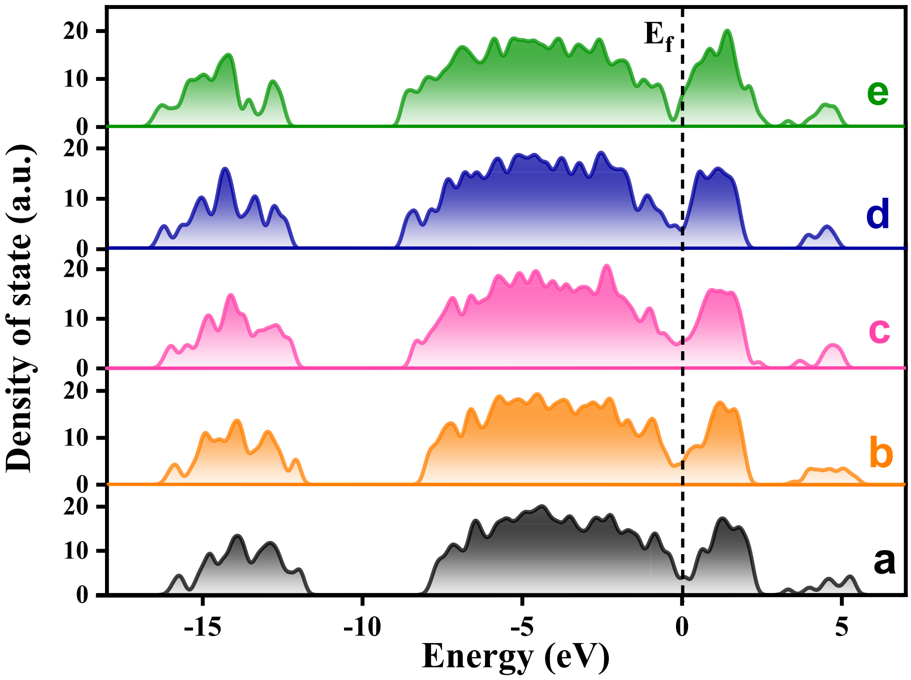

Fig. S3. The total density of states (TDOS) of (a) ReS$_x$, (b) ReS$_x$-H, (c) ReS$_x$-2H, (d) ReS$_x$-3H and (e) ReS$_x$-4H.

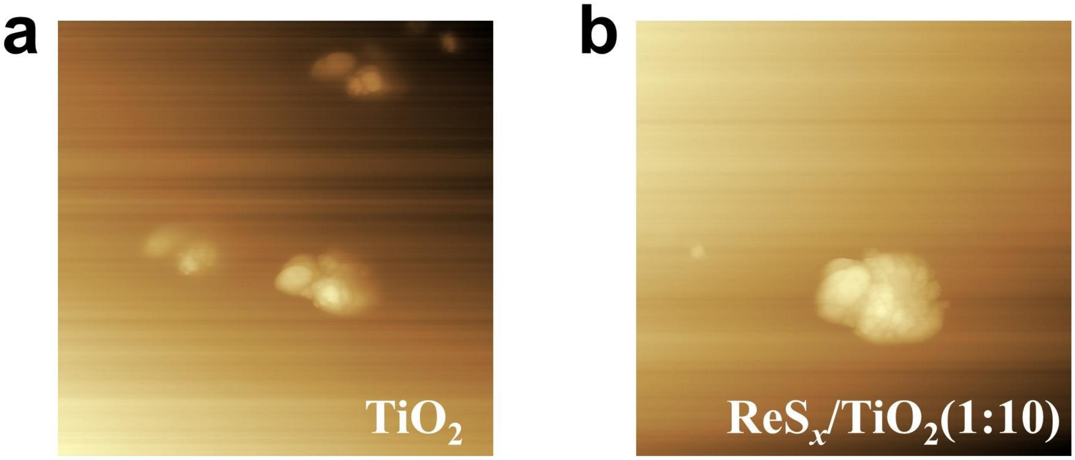

Fig. S4. AFM topographies of (a) TiO_2 and (b) $ReSx/TiO_2$(1:10).

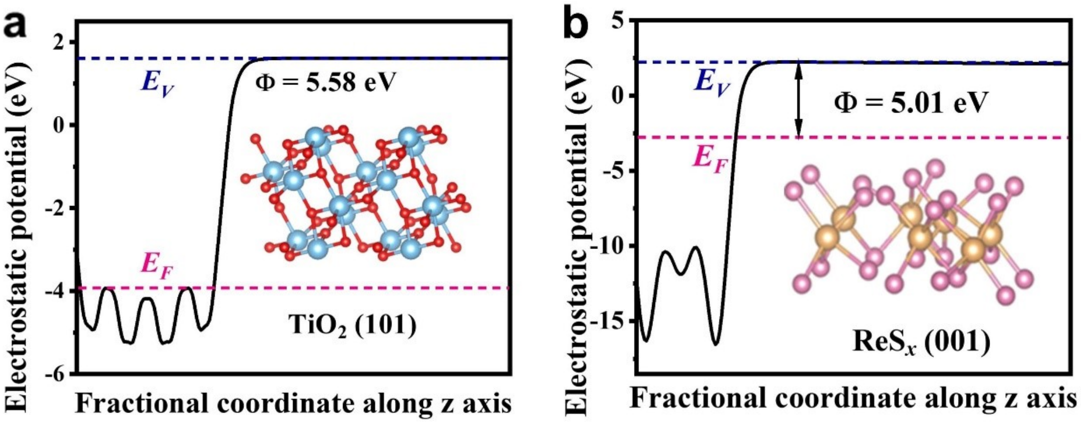

Fig. S5. The calculated electrostatic potentials of (a) TiO_2 and (b) ReS_x.

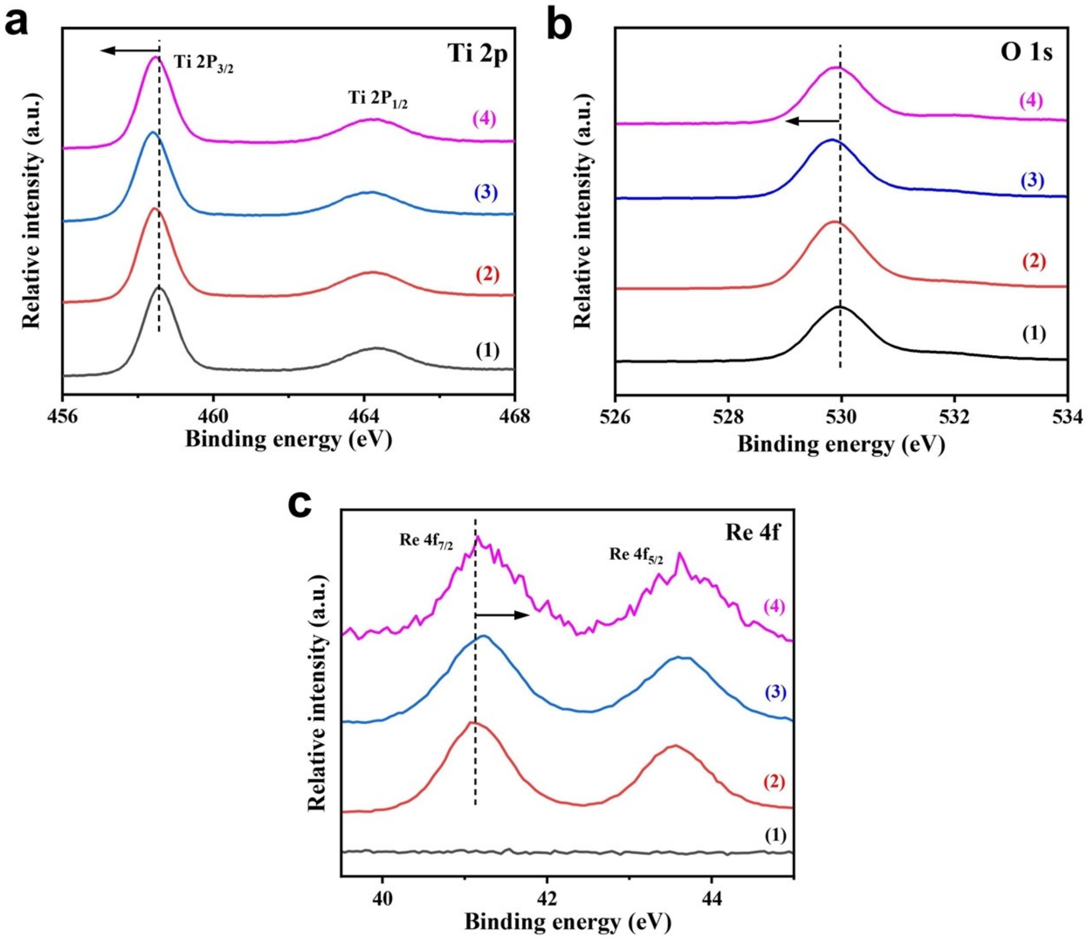

Fig. S6. High-resolution XPS spectra of (a) Ti 2p, (b) O 1s and (c) Re 4f for (1) TiO$_2$, (2) ReS$_x$/TiO$_2$(1:2), (3) ReS$_x$/TiO$_2$(1:10), and (4) c-ReS$_2$/TiO$_2$.

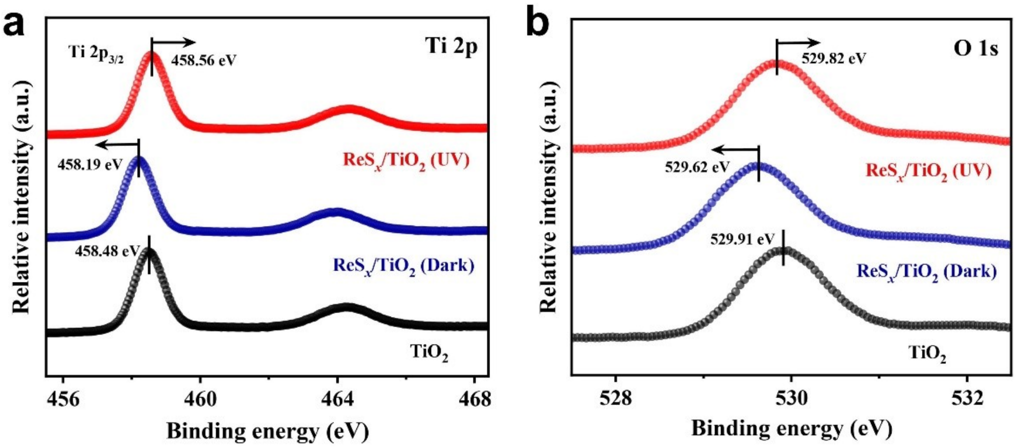

Fig. S7. In-situ irradiated XPS results of (a) Ti 2p and (b) O 1s for ReS$_x$/TiO$_2$(1:10) photocatalyst.

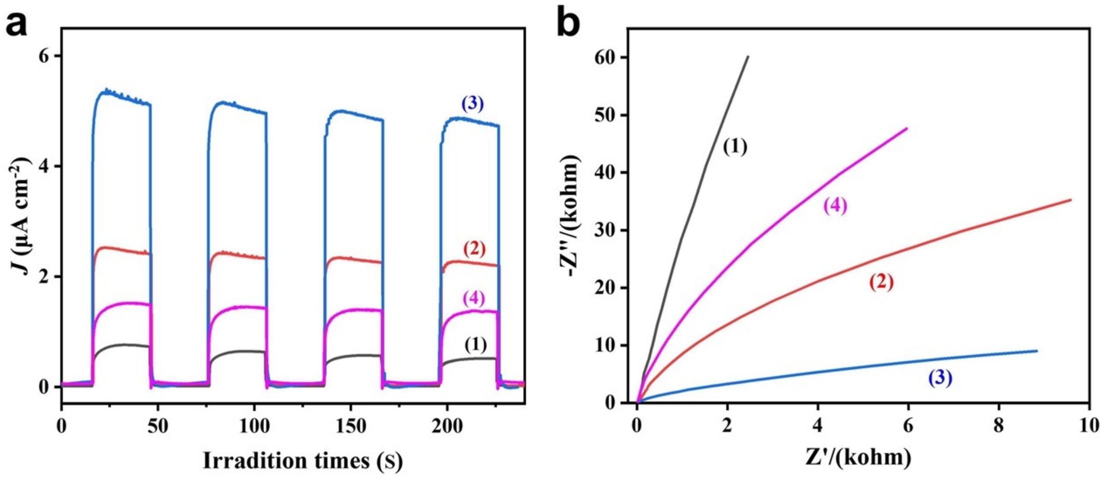

Fig. S8. (a) Photocurrent curves and (b) EIS spectra of (1) TiO_2, (2) ReS_x/TiO_2(1:2), (3) ReS_x/TiO_2(1:10), and (4) c-ReS_2/TiO_2.