Supporting Information

Efficient and Stable Solar Hydrogen Generation of Hydrophilic Rhenium-Disulfide-Based Photocatalysts *via* Chemically Controlled Charge Transfer Paths

Jianmin Yu,^{†,‡,1} Sohyeon Seo,^{†,‡,1} Yongguang Luo,^{†,‡} Yan Sun,[§] Simgeon Oh,^{†,§} Chau T. K. Nguyen, ^{†,‡} Changwon Seo, ^{†,§} Ji-Hee Kim, ^{†,§} Joonsoo Kim^{†,§} and Hyoyoung Lee^{*,†,‡,§}

[†]Centre for Integrated Nanostructure Physics (CINAP), Institute of Basic Science (IBS), Suwon 16419, Republic of Korea, [‡]Department of Chemistry, Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea, [§]Department of Energy Science, Sungkyunkwan University, Suwon, 16419, Republic of Korea.

* E-mail: hyoyoung@skku.edu

^IThe authors contribute equally to the work.



Figure S1. (a) Ultraviolet-visible (UV-vis) spectrum of ReS_2 -C₆H₅COOH nanosheets in a solution. (Inset) Optical image of ReS_2 -C₆H₅COOH solution in a tube. (b),(c) XPS spectra of Re 4f (M: metallic-state Re) and S 2p core level peak regions for ReS_2 powder (upper panel) and ReS_2 -C₆H₅COOH nanosheets (lower panel), respectively. (d) FT-IR spectra of bulk ReS_2 powder and ReS_2 -C₆H₅COOH nanosheets. (e) Scanning TEM (STEM) image of ReS_2 -C₆H₅COOH nanosheets. (f) EDS mapping image of ReS_2 -C₆H₅COOH, the correspondent EDS spectrum and element analysis. (g) Element mappings corresponding to (f).

In the XPS spectra, the Re atoms in ReS₂–C₆H₅COOH nanosheets showed two peaks $(4f_{7/2} \text{ and } 4f_{/5/2} \text{ at } 42.1 \text{ eV} \text{ and } 44.5 \text{ eV}, \text{ respectively})$, and these were positively shifted by 0.3 eV from the typical binding energy of Re⁴⁺ in ReS₂ nanosheets.¹ In addition, the S 2p peaks corresponding to the S 2p_{3/2} and S 2p_{1/2} states of ReS₂–C₆H₅COOH nanosheets were positively shifted to 162.6 and 163.7 eV, respectively, from those of ReS₂ nanosheets (162.4 and 163.6 eV). These results implied that Re atoms became positively charged due to the functionalization of ReS₂ nanosheets with –C₆H₅COOH.^{2,3}



Figure S2. (a) Survey scan of X-ray photoelectron spectroscopy (XPS) for ReS_2 –BzO-TiO₂. (b)-(d) XPS spectra of O 1s, C 1s and Ti 2p of TiO₂, ReS_2 –C₆H₅COOH and ReS_2 –BzO–TiO₂, respectively. (e),(f) HR-TEM image and the correspondent EDS element mappings of ReS_2 –BzO-TiO₂, respectively. (g) Cross-sectional element profiles as marked with yellow line. (h) EDS spectrum and element analysis corresponding to (f).



Figure S3. (a) X-ray diffraction (XRD) spectra of each material (Bulk ReS₂, ReS₂–BzO–TiO₂, ReS₂–C₆H₅COOH nanosheets and TiO₂). (b) Raman spectra corresponding to different ratios (wt%) of ReS₂–C₆H₅COOH nanosheets to TiO₂. (c) FT-IR spectra of each material. ReS₂–BzO– TiO₂ exhibits typical peaks (carboxylate C=O and C–O at 1735 and 1400 cm⁻¹, respectively) for chemical binding between ReS₂–C₆H₅COOH and TiO₂ in the zoomed-in spectra. (d) Diffuse reflectance UV-Vis spectra of ReS₂–C₆H₅COOH nanosheets, ReS₂–BzO–TiO₂ and TiO₂.



Figure S4. (a),(b) The hydrogen generation rate in log scale corresponding to Figure 2(a),(b). (c),(d) The hydrogen generation rate under (c) 1-sun light and (d) LED-light in each photocatalyst (against the amount of catalysts). The left and right graphs in (c),(d) were plotted in linear scale and log scale, respectively.



Figure S5. Plots for average hydrogen-production of each photocatalyst with regard to (a) amounts of ReS₂ nanosheets in each catalyst and (b) total amounts of each catalyst under sunlight irradiation (1-sun). The average rates against the amount of catalysts for the hydrogen generation of the ReS₂–BzO–TiO₂ (1:4) exhibited 1.9 mmol $g_{cat}^{-1} h^{-1}$ (per gram of ReS₂–BzO–TiO₂), while the ReS₂–C₆H₅COOH nanosheets and the pristine TiO₂ obtained average rates of 0.038 and 0.089 mmol $g_{cat}^{-1} h^{-1}$, respectively. Hydrogen production of 1.9 mmol h^{-1} per gram of the ReS₂–BzO–TiO₂ TiO₂ is over 21-fold higher than that of the native TiO₂.



Figure S6. (a),(b) UV-vis spectra for the photooxidation of RhB under LED-light (395–405 nm) by photocatalysts of (a) TiO_2 and (b) ReS_2 –BzO–TiO₂. (c),(d) UV-vis spectra for the photooxidation of RhB under (c) 1 sun and (d) LED-light (395–405 nm) by photocatalysts of physically mixed bulk ReS_2/TiO_2 and physically mixed ReS_2 –C₆H₅COOH/TiO₂ as a function of irradiation time. (e),(f) Plots of relative concentration of RhB for each photocatalyst under 1-sun light and LED-light, respectively, as a function of irradiation time.



Figure S7. (a)-(d) EPR spectral changes of the DMPO-'OH adduct produced by each photocatalyst with/without RhB after 5-min irradiation of 1-sun light.



Figure S8. (a)-(c) UV-vis spectra of RhB adsorption on photocatalysts. For the photocatalyst/RhB_{ads} measurement, solid films of each photocatalyst prepared on fluorine doped tin oxide (FTO) glasses were immersed into RhB solution for 30 min. UV-vis absorption of each film was measured after washing with DI water, ethanol, and acetone thoroughly. (d) A scheme of the RhB structure according to possible adsorption paths through functional groups.



Figure S9. (a) Plots of TOC measurements and (b) HPLC spectra for photocatalytic activity tests using RhB. In HPLC spectra (@525 nm), each peak was defined with RhB, N,N-diethyl-N'-ethylrhodamine (DER), N-ethylrhodamine (ER), and rhodamine (Rh).

The gradual blue shifts of the absorption maximum was coursed by the N-demethylation of Rh.B during irradiation. The blue shifts of RhB were defined with generation of N,N-diethyl-N'-ethylrhodamine (DER), N,N-diethylrhodamine (DR), N-ethylrhodamine (ER), and rhodamine (Rh).⁴ In the presence of TiO₂, the absorption peak of RhB solution decreased slowly and the absorption band shifted from 554 to 551 nm within 30 min irradiation, the percentage of RhB was reduced to 67.6% and the percentage of DER was increased to 32.4%. On the other hand, the absorption peak of RhB completely disappeared as the photodegradation reaction proceeded in the presence of ReS₂–BzO–TiO₂ and ReS₂-CH₅COOH/TiO₂. The percentage of Rh was 100% for ReS₂–BzO–TiO₂, while the percentage of ER, Rh was 58.1% and 41.9% for ReS₂-CH₅COOH/TiO₂, respectively. Consequently, this phenomenon revealed that the ReS₂–BzO–TiO₂ can up to 100% after irradiation 30min.



Figure S10. (a),(b) HR-TEM images of bulk $\text{ReS}_2/\text{TiO}_2$ and $\text{ReS}_2-\text{C}_6\text{H}_5\text{COOH}/\text{TiO}_2$ in the physical mixtures, respectively. (c) Water contact angles of $\text{ReS}_2-\text{C}_6\text{H}_5\text{COOH}$ nanosheets and bulk ReS_2 , bulk $\text{ReS}_2/\text{TiO}_2$, $\text{ReS}_2-\text{C}_6\text{H}_5\text{COOH}/\text{TiO}_2$ and $\text{ReS}_2-\text{BzO}-\text{TiO}_2$. (d) H₂ production plots per gram of ReS_2 for the physical mixtures of $\text{ReS}_2-\text{C}_6\text{H}_5\text{COOH}$ $_2/\text{TiO}_2$ with different ratios (wt%) of $\text{ReS}_2-\text{C}_6\text{H}_5\text{COOH}$ to TiO_2 . (e) H₂ production plots of two-phase TiO₂ (composed of 75% anatase and 25% rutile phases). Hydrothermally treated TiO₂ was prepared by the hydrothermal condensation reaction of pristine TiO₂.



Figure S11. (a) H₂ production plots of ReS₂–C₆H₅COOH/single-phase TiO₂. The H₂ production performance of both ReS₂–C₆H₅COOH/single-phase TiO₂ photocatalysts was relatively lower than that ReS₂–BzO–TiO₂. (b) FT-IR spectra of each material. Zoomed-in spectra exhibit unspecified peaks (carboxylate C=O and C–O at 1735 and 1400 cm⁻¹, respectively) for chemical binding between ReS₂–C₆H₅COOH and single-phase TiO₂. Consequently, chemical junctions between TiO₂ and ReS₂–C₆H₅COOH were not clearly detected. (c)-(f) XPS characterizations of ReS₂–C₆H₅COOH/single-phase TiO₂. As compared with two-phase TiO₂ (Figure S2b), both of single-phase anatase and rutile TiO₂ showed relatively small amounts of Ti–OH, which were involved in hydrothermal condensation reactions between TiO₂ and ReS₂–C₆H₅COOH.



Figure S12. (a) Valence band XPS spectra, UPS spectra (secondary energy cutoff), and a Tauc plot of the indirect bandgap for bulk ReS₂. (b),(c) Tauc plots of the indirect bandgap for ReS₂– C_6H_5COOH , TiO₂, and ReS₂–BzO–TiO₂ from Kubelka-Munk functions converted by diffuse reflectance UV-vis spectra of each material (E_g = bandgap energy, E_B = binding energy). (d) UPS spectra for Fermi edge of each material.



Figure S13. (a),(b) Energy band diagrams estimated by combinations of (a) UPS, diffuse reflectance UV-vis spectroscopy (DRS), and valence band XPS spectra and (b) UPS and DRS spectra. E_F indicates energy of the Fermi level. (c),(d) Proposed energy band diagrams of type II and Z-scheme, respectively for combinations of two semiconductors (S1,S2: semiconductors, E_c : conduction band energy, E_v : valence band energy, and E_F : energy of Fermi level).



Figure S14. (a) A H₂ production plot of non-functionalized ReS₂ NS/TiO₂ in a 40 ml mixture solvent of water and methanol at a volume ratio of 1:1 under 1-sun. (b) A TEM image of ReS₂ NS/TiO₂. ReS₂ NS was prepared by tip-sonication of bulk ReS₂ in DMF and followed by centrifugation.



Figure S15. Photoelectrochemical properties of photocatalysts obtained in 0.5 M Na₂SO₄ (pH 7.2). (a),(b) Linear sweep voltammograms and Nyquist plots of the impedance spectra for each photocatalyst, respectively. Linear sweep votammetry (LSV) was conducted at the scan rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were performed at 0.3

 $V_{Ag|AgCl}$ for 0.1 Hz–100 kHz with 10 mV. Inset in (b) depicts the equivalent circuit;⁵ R_s is the solution resistance, R_{ct} represents the charge transfer resistance, while the double layer capacitance, the Warburg impedance, and the constant phase element are denoted as C_{dl} , Z_w , and CPE, respectively. ReS₂–BzO–TiO₂ exhibited relatively high photocurrents and low charge transfer resistance as compared with other photocatalysts. (c) Transient photocurrent response as a function of 1-sun light irradiation at 1.0 $V_{Ag|AgCl}$ in 0.5 M Na₂SO₄. (d) Transient absorption decays (pump beam: 350 nm, 1.5 mW). (e) PL emission (excitation = 375 nm). (f) Transient PL decays (laser: 488 nm, 200 μ W).



Figure S16. (a) DRS spectra of pristine TiO_2 and Pt/TiO_2 . The arrow indicates a red-shift of the absorption edge. (b) The rates of hydrogen generation of Pt/TiO_2 , TiO_2 , and ReS_2 –BzO–TiO₂ under LED (395–405 nm)-light.

Supporting calculation I: Density functional theory (DFT)

DFT calculation was performed to understand changes in electronic structures for each condition from pure anatase TiO_2 and ReS_2 to ReS_2 –BzO–TiO₂;



(a)-(e) Calculated DOS of (a) anatase TiO₂, (b) molecule-TiO₂, (c) ReS₂, (d) molecule-ReS₂ (functionalized ReS₂), (e) ReS₂–BzO–TiO₂. (f),(g) Comparison of each DOS. (h) Partial DOS plots of (e). Due to the binding of ReS₂-molecule, the conduction band consisting of Ti-3d and O was shifted to the left in DOS of ReS₂–BzO–TiO₂. At the same time, ReS₂-molecule formed energy levels in the forbidden band. The energy required to transition from VBM through the forbidden band to CBM was reduced.

First-principles have been employed to investigate the electronic structure properties, based on density functional theory in our systems with the projector augmented wave (PAW) method.⁶ The exchange-functional has been treated using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional.⁷ The energy cutoff for the plane wave basis expansion has been set to 400 eV and the force on each atom less than 0.05 eV/Å was set for convergence criterion of geometry relaxation. The surface and interface structure have been choose using the 2x2x1 Monkhorst and Pack k-point sampling. The effective value of U=4.36 eV was performed to describe the Ti 3d orbitals. The surfaces with slab strucutres has been established using equilibrium bulk geometry. These slabs were separated from their periodic images normal to the surface by a minimum vacuum gap of 12 Å, to give a pseudo-2D periodic system. In addition, spin polarized was also considered in our systems.

Supporting calculation II: the apparent quantum yield (AQY)

The apparent quantum yield (AQY) was calculated using equations (1) and (2).³

AQY(%)

 $= \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100$

AQY(%)

 $= \frac{2 \times Number of H_2 molecules}{\frac{Light absorbed by the photocatalyst}{The average photon energy} \times t} \times 100$

(I) Solar simulator (1 Sun)

The photocatalysts were irradiated by a solar simulator (Oriel Sol3A Class AAA) with an AM 1.5 filter for 3 h. The average incident irradiation was determined to be 1000 W·m⁻², and the area of the photoreactor was 33 cm². The bandgaps of TiO₂ and ReS₂–BzO–TiO₂ as estimated from DRS analysis were 3.10 eV and 1.3 eV, respectively. Therefore, unbound and free electron hole pairs can be generated at 250 nm < λ < 400 nm and 250 nm < λ < 953 nm, respectively. The average photonic wavelengths were λ_{TiO2} = 325 nm and $\lambda_{ReS2-BzO-TiO2}$ = 601 nm.

Light absorbed by the photocatalyst = 1000 $Wm^{-2} \times 0.0033 m^2 = 3.3 Js^{-1}$

The average photon energy
$$(TiO_2) = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} Js \times 3 \times 10^8 ms^{-1}}{325 \times 10^{-9} m} = 6.116 \times 10^{-19} Js$$

The average photon energy
$$(ReS_2) = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} Js \times 3 \times 10^8 ms^{-1}}{601 \times 10^{-9} m} = 3.307 \times 10^{-19} Js^{-10}$$

The average amounts of hydrogen gas production within 1 h for TiO_2 and ReS_2 –BzO–TiO₂ were 0.083 mmol/g_{cat} and 1.900 mmol/g_{cat}, respectively.

$$AQY_{\text{TiO2}}(\%) = \frac{2 \times 0.083 \times 10^{-3} \ mol \times 6.022 \times 10^{23} \ mol^{-1}}{\frac{3.3 \ Js^{-1}}{6.116 \times 10^{-19} \ J}} \times 3600 \ s \qquad \times 100 = 0.51\%$$

In addition, the average amounts of hydrogen gas production within 1 h for ReS_2 -BzO-TiO₂ were 9.5 mmol h⁻¹ per gram of ReS_2 .

Thus,

$$AQY_{\text{ReS2-BzO-TiO2}}(\%) = \frac{2 \times 9.5 \times 10^{-3} \text{ mol} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{\frac{3.3 \text{ Js}^{-1}}{3.307 \times 10^{-19} \text{ J}} \times 3600 \text{ s}} \times 100 = 32 \%$$

(II) LED (395-405 nm)

The photocatalysts were irradiated using a light-emitting diode (LED) lamp with a 395–405 nm wavelength (20 W) for 6 h. The average incident irradiation was determined to be 1301 $W \cdot m^{-2}$, and the area of the photoreactor was 33 cm².

Light absorbed by the photocatalyst = 1301 $Wm^{-2} \times 0.0033 m^2 = 4.29 Js^{-1}$

The average photon energy $=\frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} Js \times 3 \times 10^8 ms^{-1}}{400 \times 10^{-9} m} = 4.97 \times 10^{-19} J$

The average amounts of hydrogen gas production in 1 h for TiO_2 and ReS_2 –BzO–TiO₂ were 0.022 mmol/g_{cat} and 0.80143 mmol/g_{cat}, respectively.

$$AQY_{\text{TiO2}}(\%) = \frac{2 \times 0.022 \times 10^{-3} \ mol \times 6.022 \times 10^{23} \ mol^{-1}}{\frac{4.29 \ Js^{-1}}{4.97 \times 10^{-19} \ J}} \times 3600 \ s \qquad \times 100 = 0.085\%$$

$$AQY_{\text{ReS2-BzO-TiO2}}(\%) = \frac{2 \times 0.80143 \times 10^{-3} \text{ mol} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{\frac{4.29 \text{ Js}^{-1}}{4.97 \times 10^{-19} \text{ J}} \times 3600 \text{ s}} \times 100 = 3.11\%$$

In addition, the average amounts of hydrogen gas production within 1 h for ReS_2 –BzO–TiO₂ was 4.0 mmol h⁻¹ per gram of ReS_2 . Thus,

$$AQY_{\text{ReS2-BzO-TiO2}}(\%) = \frac{2 \times 4.00715 \times 10^{-3} \text{ mol} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{\frac{4.29 \text{ Js}^{-1}}{4.97 \times 10^{-19} \text{ J}} \times 3600 \text{ s}} \times 100 = 15.55\%$$

Supporting calculation III: Solar to hydrogen (STH) conversion efficiency

Solar-to-hydrogen conversion (STH) efficiency is defined as the amount of chemical (H₂) energy produced against the incident solar energy.⁸ The STH efficiency of each photocatalyst was calculated using the following equation:

 $\eta_{\text{STH}}(\%) = \left[\frac{\text{Chemical energy produced}}{\text{Solar energy input}}\right] \\ \eta_{\text{STH}}(\%) \\ = \left[\frac{\text{Rate of } H_2 \text{ production} \times \Delta G_{H_2 O \to H_2 + \frac{1}{2} O_2}}{\text{Total incident solar power} \times \text{Electrode Area}}\right] \\ \eta_{\text{STH}}(\%) \\ = \left[\frac{(\text{mmol } H_2 \text{ S}^{-1}) \times (237000 \text{ J mol}^{-1})}{P_{Tatal}(\text{mW } \text{ cm}^{-2}) \times \text{Area } (\text{ cm}^2)}\right]_{\text{AM } 1.5\text{G}} \\ \eta_{\text{STH}}(TiO_2)_{catalyst} = \left[\frac{(0.083 \text{ mmol}/3600 \text{ s}) \times (237000 \text{ J mol}^{-1})}{3.3 \times 1000 \text{ mJ } \text{S}^{-1}}\right]_{\text{AM } 1.5\text{G}} \times 100\% \\ = 0.17 \% \\ \eta_{\text{STH}}(ReS_2 - BzO - TiO_2)_{catalyst} \\ = \left[\frac{(1.900 \text{ mmol}/3600 \text{ s}) \times (237000 \text{ J mol}^{-1})}{3.3 \times 1000 \text{ mJ } \text{S}^{-1}}\right]_{\text{AM } 1.5\text{G}} \times 100\%$

$$\eta_{\text{STH}} (ReS_2 - BzO - TiO_2)_{ReS_2} = \left[\frac{(9.500 \text{ mmol}/3600 \text{ s}) \times (237000 \text{ J mol}^{-1})}{3.3 \times 1000 \text{ mJ S}^{-1}} \right]_{\text{AM 1.5G}} \times 100\%$$
$$= 19 \%$$



Supporting additional analysis I: Sacrificial agent effect on photocatalytic H₂ production.

 H_2 production plots (under 1-sun) of each photocatalyst in terms of sacrificial agents; (a) methanol and (b) 0.25 M Na₂S/0.35 M Na₂SO₃. Even though ReS₂-C₆H₅COOH showed relatively higher performance in Na₂S/Na₂SO₃ than others, the H₂ production value of ReS₂-BzO-TiO₂ in methanol was much higher than that of ReS₂-C₆H₅COOH in Na₂S/Na₂SO₃. Therefore, methanol was chosen as a sacrificial agent rather than Na₂S/Na₂SO₃.





(a)-(d) XPS characterization of ReS_2 –BzO–TiO₂ after photocatalytic reactions. XPS spectra of each element showed no significant changes after photocatalytic reactions. (e) TEM image of pristine TiO₂. The blue dotted line indicates interparticle (or interphase) junctions. (f) TEM image of ReS_2 –BzO–TiO₂ after photocatalytic reactions. The blue dotted lines indicate junctions between anatase and rutile phases.

Supporting additional analysis III: Phase information of ReS₂–BzO–TiO₂ after 6-cyclic H₂ production reactions (as shown in Figure 2d).



XRD spectra of ReS₂–BzO–TiO₂ before and after the 6-cyclic H₂ production reaction.

Supporting Table S1: Performance comparison between our catalyst system and previously reported TMDs/TiO₂ photocatalysts for hydrogen evolution.

Photocatalyst	Sacrificial	Light source	Photoactivity	Ref.
	agents		[µmol g ⁻¹ h ⁻¹]	
Molecular-linked ReS ₂ -BzO-TiO ₂ hybrid	50 vol% methanol/H ₂ O	AM 1.5 solar power system	9500	This
TiOr@PoSt	20 vo10/	Blue LED	4000	Rof 9
110 ₂ @ReS ₂	methanol/H ₂ O	500 w Xe lamp	1404	Kel.
MoS ₂ /TiO ₂ edge-on heterostructures	20 vol% methanol/H ₂ O	300 W Xe lamp	4300	Ref. ¹⁰
Nitrogen doped- TiO _{2-x} @MoS ₂ core- shell nanocomposites	20 vol% methanol/H ₂ O	AM 1.5 solar power system	1882	Ref. ¹¹
TiO ₂ -MoS ₂ (1T) hybrid	25 vol% methanol/H ₂ O	300 W Xe Lamp, $\lambda < 400$	~2000	
TiO ₂ -MoS ₂ (2H) hybrid		nm	~175	Ref. ¹²
TiO ₂ /1T–WS ₂	25 vol%	300 W Xe source	2570	
TiO ₂ /2H–WS ₂	methanol/H ₂ O	with an AM 1.5 filter	225	Ref. ¹³
MoS ₂ @TiO ₂ -15wt%	TEOA	300 W Xe source with an AM 1.5 filter	2160	Ref. ¹⁴
MoS ₂ /TiO ₂ (0.14 wt%) hybrids	25 vol% methanol/H ₂ O	UV light , $\lambda = 365 \text{ nm}$	2443	Ref. ¹⁵
2D-2D SnS ₂ /TiO ₂ nanosheet heterojunctions	50 vol% methanol/H ₂ O	300 W Xe lamp	652.4	Ref. ¹⁶
TiO ₂ nanofiber	0.35M Na ₂ S	300 W Xe lamp,	1680 (λ > 320 nm);	Ref. ¹⁷
@MoS ₂ nanosheets	and 0.25M Na ₂ SO ₃	$\lambda = 320-780$ nm	490 (λ > 420 nm)	
2D-2D MoS ₂ /TiO ₂ nanocomposites	10 vol% methanol/H ₂ O	300 W Xe lamp	2145	Ref. ¹⁸
a-MoSx@MPA-TiO ₂ colloidal nanodots	20 vol% methanol/H ₂ O	$300 \text{ W Xe lamp} \\ (\lambda > 300 \text{ nm})$	259.2	Ref. ¹⁹

REFERENCES

1. Jariwala, B.; Voiry, D.; Jindal, A.; Chalke, B. A.; Bapat, R.; Thamizhavel, A.; Chhowalla, M.;

Deshmukh, M.; Bhattacharya, A. Synthesis and Characterization of ReS₂ and ReSe₂ Layered Chalcogenide Single Crystals. *Chem. Mater.* **2016**, *28*, 3352-3359.

 Tong, J.; Han, X.; Wang, S.; Jiang, X. Evaluation of Structural Characteristics of Huadian Oil Shale Kerogen Using Direct Techniques (Solid-State ¹³C NMR, XPS, FT-IR, and XRD). *Energ. Fuel.* 2011, 25, 4006-4013.

3. Lee, H.; Bak, S.; An, S. J.; Kim, J. H.; Yun, E.; Kim, M.; Seo, S.; Jeong, M. S.; Lee, H. Highly Efficient Thin-Film Transistor *via* Cross-Linking of 1T Edge Functional 2H Molybdenum Disulfides. *ACS Nano* **2017**, *11*, 12832-12839.

4. Yu, K.; Yang, S.; He, H.; Sun, C.; Gu, C.; Ju, Y. Visible Light-Driven Photocatalytic Degradation of Rhodamine B over NaBiO₃: Pathways and Mechanism. *J. Phys. Chem. A* **2009**, *113*, 10024-10032.

5. Nkosi, D.; Pillay, J.; Ozoemena, K. I.; Nouneh, K.; Oyama, M. Heterogeneous Electron Transfer Kinetics and Electrocatalytic Behaviour of Mixed Self-Assembled Ferrocenes and SWCNT Layers. *Phys. Chem. Chem. Phys.* **2010**, *12*, 604-613.

6. Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758-1775.

7. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

8. Kim, J. H.; Hansora, D.; Sharma, P.; Jang, J. W.; Lee, J. S. Toward Practical Solar Hydrogen Production-An Artificial Photosynthetic Leaf-to-Farm Challenge. *Chem. Soc. Rev.* **2019**, *48*, 1908-1971.

9. Wang, X.; Chen, B.; Yan, D.; Zhao, X.; Wang, C.; Liu, E.; Zhao, N.; He, F. Distorted 1T-ReS₂ Nanosheets Anchored on Porous TiO₂ Nanofibers for Highly Enhanced Photocatalytic Hydrogen Production. ACS Appl. Mater. Interfaces 2019, 11, 23144-23151.

10. He, H.; Lin, J.; Fu, W.; Wang, X.; Wang, H.; Zeng, Q.; Gu, Q.; Li, Y.; Yan, C.; Tay, B. K.; Xue, C.; Hu, X.; Pantelides, S. T.; Zhou, W.; Liu, Z. MoS₂/TiO₂ Edge-On Heterostructure for Efficient Photocatalytic Hydrogen Evolution. *Adv. Energy Mater.* **2016**, *6*, 1600464.

11. Liu, X.; Xing, Z.; Zhang, Y.; Li, Z.; Wu, X.; Tan, S.; Yu, X.; Zhu, Q.; Zhou, W. Fabrication of 3D Flower-Like Black N-TiO_{2-X}@MoS₂ for Unprecedented-High Visible-Light-Driven Photocatalytic Performance. *Appl. Catal. B* **2017**, *201*, 119-127.

12. Bai, S.; Wang, L.; Chen, X.; Du, J.; Xiong, Y. Chemically Exfoliated Metallic MoS₂ Nanosheets: A Promising Supporting Co-Catalyst for Enhancing the Photocatalytic Performance of TiO₂ Nanocrystals. *Nano Res.* **2014**, *8*, 175-183.

13. Mahler, B.; Hoepfner, V.; Liao, K.; Ozin, G. A. Colloidal Synthesis of 1T-WS₂ and 2H-WS₂ Nanosheets: Applications for Photocatalytic Hydrogen Evolution. *J. Am. Chem. Soc.* **2014**, *136*, 14121-14127.

14. Hu, X.; Lu, S.; Tian, J.; Wei, N.; Song, X.; Wang, X.; Cui, H. The Selective Deposition of MoS₂ Nanosheets onto (101) Facets of TiO₂ Nanosheets with Exposed (001) Facets and Their Enhanced Photocatalytic H₂ Production. *Appl. Catal. B* **2019**, *241*, 329-337.

 Wang, W.; Zhu, S.; Cao, Y.; Tao, Y.; Li, X.; Pan, D.; Phillips, D. L.; Zhang, D.; Chen, M.;
Li, G.; Li, H. Edge-Enriched Ultrathin MoS₂ Embedded Yolk-Shell TiO₂ with Boosted Charge Transfer for Superior Photocatalytic H₂ Evolution. *Adv. Funct. Mater.* **2019**, *29*, 1901958.

Sun, L.; Zhao, Z.; Li, S.; Su, Y.; Huang, L.; Shao, N.; Liu, F.; Bu, Y.; Zhang, H.; Zhang, Z.
Role of SnS₂ in 2D–2D SnS₂/TiO₂ Nanosheet Heterojunctions for Photocatalytic Hydrogen
Evolution. ACS Appl. Nano Mater. 2019, 2, 2144-2151.

17. Liu, C.; Wang, L.; Tang, Y.; Luo, S.; Liu, Y.; Zhang, S.; Zeng, Y.; Xu, Y. Vertical Single or

Few-Layer MoS₂ Nanosheets Rooting into TiO₂ Nanofibers for Highly Efficient Photocatalytic Hydrogen Evolution. *Appl. Catal. B* **2015**, *164*, 1-9.

Yuan, Y.-J.; Ye, Z.-J.; Lu, H.-W.; Hu, B.; Li, Y.-H.; Chen, D.-Q.; Zhong, J.-S.; Yu, Z.-T.;
Zou, Z.-G. Constructing Anatase TiO₂ Nanosheets with Exposed (001) Facets/Layered MoS₂
Two-Dimensional Nanojunctions for Enhanced Solar Hydrogen Generation. *ACS Catal.* 2015, *6*, 532-541.

19. Chang, K.; Pang, H.; Hai, X.; Zhao, G.; Zhang, H.; Shi, L.; Ichihara, F.; Ye, J. Ultra-Small Freestanding Amorphous Molybdenum Sulfide Colloidal Nanodots for Highly Efficient Photocatalytic Hydrogen Evolution Reaction. *Appl. Catal. B* **2018**, *232*, 446-453.