Supporting Information

Increasing unsaturated Se number and facilitating atomic hydrogen adsorption of WSe$_{2+x}$ nanodot for improving photocatalytic H$_2$ production of TiO$_2$

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Number of pages: 21

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Supporting Information Content

EXPERIMENTAL SECTION

SI-1 Preparation of g-C$_3$N$_4$ and CdS photocatalysts

The g-C$_3$N$_4$ photocatalyst was obtained by a simple calcination-hydrothermal procedure via using melamine powder as the precursor. According to previous studies, the melamine precursor was calcined at 550 °C for 4 h in ambient atmosphere to obtain the bulk g-C$_3$N$_4$. To increase its specific surface area, the as-prepared g-C$_3$N$_4$ sample was further treated by a hydrothermal method. In briefly, 0.5 g of the calcined g-C$_3$N$_4$ powder was dispersed into 70 mL of deionized water, then stirred at room temperature for 1 h, and finally maintained at 180 °C for 12 h. After cooling down to room temperature, the resulting sample was washed for several times, and then dried at 60 °C for overnight to obtain the g-C$_3$N$_4$ photocatalyst.

The CdS photocatalyst was synthesized by a frequently-used precipitation method. In brief, 140 mL of 0.1 mol L^{-1} Na$_2$S solution was added into 140 mL of 0.1 mol L^{-1} Cd(NO$_3$)$_2$ solution. The resulting suspension was vigorously stirred at room temperature for 2 h and then it was allowed to stay for overnight. The orange-red precipitate was collected by filtration, rinsed with plenty of deionized water, and dried at 60 °C for 24 h to obtain the CdS photocatalyst.

SI-2 Synthesis of Se-enriched WSe$_{2+x}$/g-C$_3$N$_4$ and WSe$_{2+x}$/CdS photocatalysts

The Se-enriched WSe$_{2+x}$-modified CdS and g-C$_3$N$_4$ photocatalysts can be obtained by a similar procedure as the WSe$_{2+x}$/TiO$_2$ via employing CdS and g-C$_3$N$_4$ as

the raw materials, respectively (the preparation process of CdS and g-C$_3$N$_4$ photocatalysts are shown in SI-1). In this case, the mass ratio of W to CdS (or g-C$_3$N$_4$) is regulated to be 3 wt% (W: Se = 1:8). After the suspension is bubbled with nitrogen for 0.5 h, the above system is irradiated via four illuminator (420 nm) to induce the simultaneous photodeposition of Se-rich WSe$_{2+x}$ and its H$_2$-evolution. The hydrogen-generation rate is evaluated by the gas chromatograph (GC-2014C, Shimadzu, TCD). After that, the precipitations are washed and dried in vacuum oven (50 °C, 12 h). In this case, the attained samples are referred as WSe$_{2+x}$/CdS or WSe$_{2+x}$/g-C$_3$N$_4$, respectively.

SI-3 Synthesis of a-MSe$_{2+x}$/TiO$_2$ (M = Cu, Fe, Co, Ni or Mo) photocatalysts

The Se-enriched a-MSe$_{2+x}$-modified TiO$_2$ (M = Cu, Fe, Co, Ni or Mo) photocatalysts were also prepared under identical procedure as the WSe$_{2+x}$/TiO$_2$(3wt%). Herein, the WCl$_5$ was replaced by CuCl$_2$, FeCl$_3$, CoCl$_3$, NiCl$_2$ and MoCl$_5$, respectively.

SI-4 The AQE calculation

The apparent quantum efficiency (AQE) of WSe$_{2+x}$/TiO$_2$(3wt%) photocatalyst is calculated via the following equation:

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

$$= \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\%$$

The average power of the UV light (four 3-W 365 nm) was 19 mW/cm^2, which was

detected by an irradiatometer (UV-B, Beijing Normal University Optical Instrument).

Hence, the AQE can be calculated to be 18.1%.

SI-5 The TON calculation

Turnover number (TON) of WSe_{2+x} nanoclusters for the $WSe_{2+x}/TiO_2(3wt\%)$ photocatalyst is calculated via the following equation:

$$\text{TON} = \frac{2 \times \text{the moles of evolved } H_2}{\text{the moles of cocatalyst on photocatalyst}}$$

According to the inductively coupled plasma-optical emission spectrometry, it is found that the WSe_{2+x} amount in the $WSe_{2+x}/TiO_2(3wt\%)$ is 11.61 wt% (2.67 wt% for W, and 8.94 wt% for Se). Therefore, for 50 mg of the $WSe_{2+x}/TiO_2(3wt\%)$ photocatalyst used in photocatalytic H_2-evolution reaction, the true WSe_{2+x} amount can be calculated to be 5.80 mg, corresponding to 7.25 μmol. In addition, the total amount of H_2 generation of $WSe_{2+x}/TiO_2(3wt\%)$ was 2262.48 μmol for 12 h. Therefore, the TON can be calculated as following: 2262.48 μmol × 2 / 7.25 μmol = 624.13.

SI-6 DFT calculations

The density functional theory (DFT) calculations were carried out by using the Vienna Ab initio Simulation Package (VASP). The exchange–correlation interaction was described by generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional. The energy cutoff and Monkhorst–Pack k-point mesh were set as 450 eV and $3 \times 3 \times 1$, respectively. The convergence threshold was set as 10^{-5} eV for energy and 0.01 eV·Å^{-1} for force. For the construction of surface models, a vacuum of 20 Å was used to ensure that no appreciable interaction occurred between periodic structures. The Gibbs free energy of H atom adsorption (ΔG_{H*}) was defined as $\Delta G_{H*} = \Delta E_{H*} + \Delta E_{ZPE} - T\Delta S_H$. The entropy of H_2 gas at 298 K is 130 J·mol^{-1}·K^{-1}. Therefore, $T\Delta S_H$ was calculated to be –0.20 eV. During the geometry optimization, the bottom half of W and Se atoms were fixed, while other atoms were relaxed. W-vacancy WSe_2 model was constructed by removing a surface W atom in the WSe_2 (001) model. Se-attached WSe_2 model was created via adsorbing a surface Se atom in the WSe_2 (001) model.

SI-7 Photoelectrochemical measurements

The photoelectrochemical properties were conducted on a CHI660E electrochemical workstation (Chenhua Instrument, Shanghai, China) in a standard three-electrode system by using Na_2SO_4 (0.5 M) as the electrolyte solution, where the photocatalyst-coated FTO (fluorine-doped tin oxide substrate), Ag/AgCl and platinum wire act as the working electrode, reference electrode and counter electrode,

respectively. High-purity N_2 was purged into the three-electrode cell for 15 min to remove O_2 before all the testing. The light source was provided by one 3-W LED irradiator (365-nm, Shenzhen Lamplic Science Co. Ltd.).

The working electrodes were prepared on FTO substrate with an active area of about 1.0 cm^2, where the side of FTO glass is protected by Scotch tape. First, FTO glass was washed with deionized water and ethanol for three times, respectively, and then was dried at 40 °C for 12 h. Second, 10 mg of photocatalyst was dispersed into a Nafion-ethanol solution with 1 mL D-520 Nafion (5%, w/w, in water and 1-propanol, Alfa Aesar) and 1 mL anhydrous ethanol, and subsequently ultrasonicated for 30 min to obtain a suspension solution. Finally, the above suspension was coated on the FTO surface to form a uniform film (with a thickness of 5-10 μm) and then dried at 40 °C for 12 h.

The linear sweep voltammetry (LSV) curves were measured at the potential ranging from −0.8 to −1.4 (*vs* Ag/AgCl) with a scan rate of 10 mV s^{-1}. The transient photocurrent responses with time (*i-t* curve) can be achieved at a bias potential of +0.5 V during repeated ON/OFF illumination cycles. The electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 0.001 Hz-10^6 Hz with an ac amplitude of 10 mV at the open circuit voltage.

Table S1 The ICP-OES results (atom %) for different photocatalysts

Samples	Se (at. %)	W (at. %)	Se/W
TiO_2	0	0	0
Se-enriched WSe_{2+x}/TiO_2(3wt%)	8.94	2.67	3.35
Amorphous WSe_2/TiO_2(3wt%)	5.32	2.46	2.16
Crystalline WSe_2/TiO_2(3wt%)	4.83	2.54	1.90

Table S2 Comparisons of photocatalytic H_2-evolution activity for low-cost

cocatalyst-modified TiO_2

Photocatalyst	Cocatalysts	Sacrificial agent	Light source	Activity (μmol/h/g)/AQE	Ref.
TiO_2	WSe_{2+x}	ethanol-water	3 W LED 365 nm	3770.80/18.10%	**This work**
TiO_2	MoS_2	methanol-water	3.5 W LED 365 nm	2443/8.30%	1
TiO_2	NiCoP	methanol-water	300 W Xe lamp	1540	2
TiO_2	MoC	methanol-water	3 W LED 365 nm	504/1.4%	3
TiO_2	Fe-Ni	ethanol-water	500 W Xe lamp λ > 400 nm	361	4
TiO_2	CoS_x	triethanolamine-water	3 W LED 365 nm	2394	5
TiO_2	$a\text{-}CoMoS_x$	ethanol-water	500-W high-pressure mercury lamp	2160	6
TiO_2	Cu_xP	methanol-water	UV-PC Hg lamp	1870/7.70%	7
TiO_2	$Cu(OH)_2$	methanol-water	500 W Xe lamp	1994	8
TiO_2	NiS	methanol	350 W Xe lamp	655	9
TiO_2	Ni	triethanolamine-water	UV-visible	1160	10

Table S3 Fluorescence emission lifetime and relevant percentage data fitted by a

three-exponential function.

Samples	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_3 (ns)	A_3 (%)	Average lifetime (τ_a) (ns)	χ^2
TiO$_2$	0.45	54.11	2.24	42.13	19.60	3.79	8.69	1.08
Se-enriched WSe$_{2+x}$/TiO$_2$	0.40	74.14	3.43	46.85	20.53	15.30	13.89	1.17
Amorphous WSe$_2$/TiO$_2$	0.35	68.91	2.97	23.27	13.76	13.95	10.00	1.15
Crystalline WSe$_2$/TiO$_2$	0.37	63.98	3.26	28.00	15.47	8.02	9.31	1.07

The above fitted parameters are acquired via the following tri-exponential formulas:

$$I_{(t)} = I_0 + A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) + A_3\exp(-t/\tau_3) \tag{1}$$

$$\tau_a = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3) \tag{2}$$

where I_0 is the baseline correction value, A_1, A_2 and A_3 represent the tri-exponential

factors, and τ_1, τ_2, τ_3 and τ_a corresponding the lifetime in various stages (radiation,

non-radiation and energy transfer) and average lifetime, χ^2 is the goodness-of-fit.
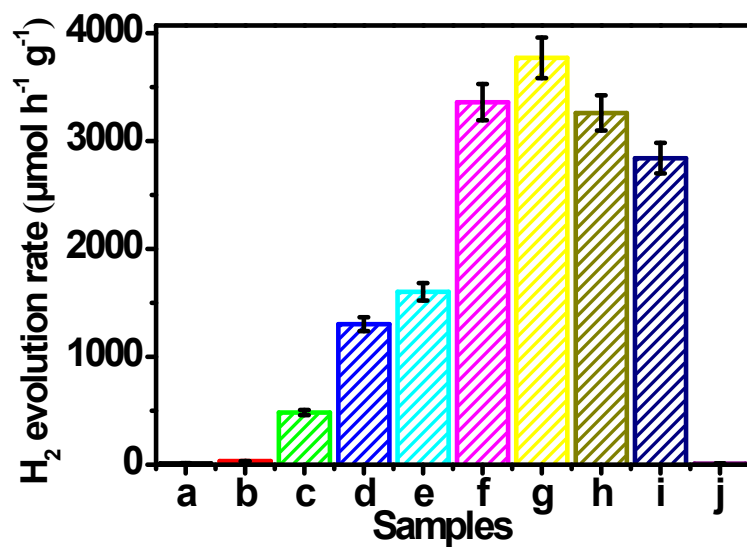
Fig. S1 The effect of Se/W ratios on the H_2-evolution activity of Se-enriched WSe$_{2+x}$/TiO$_2$(3wt%): (a) 0:0; (b) 0:1, (c) 0.2:1, (d) 1:1, (e) 2:1, (f) 4:1, (g) 8:1, (h) 10:1, (i) 12:1, and (j) 8:0.
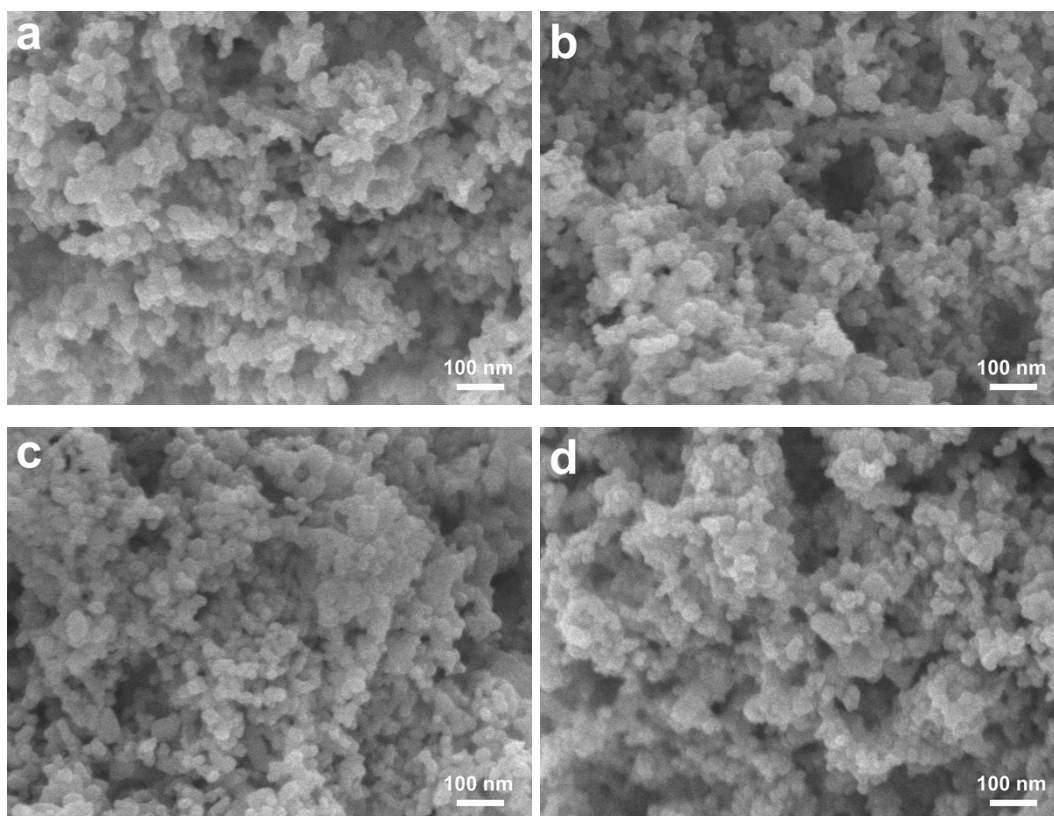
Fig. S2 FESEM images of (a) TiO_2, (b) Se-enriched WSe_{2+x}/TiO_2(3wt%), (c) amorphous WSe_2/TiO_2(3wt%), and (d) crystalline WSe_2/TiO_2(3wt%).
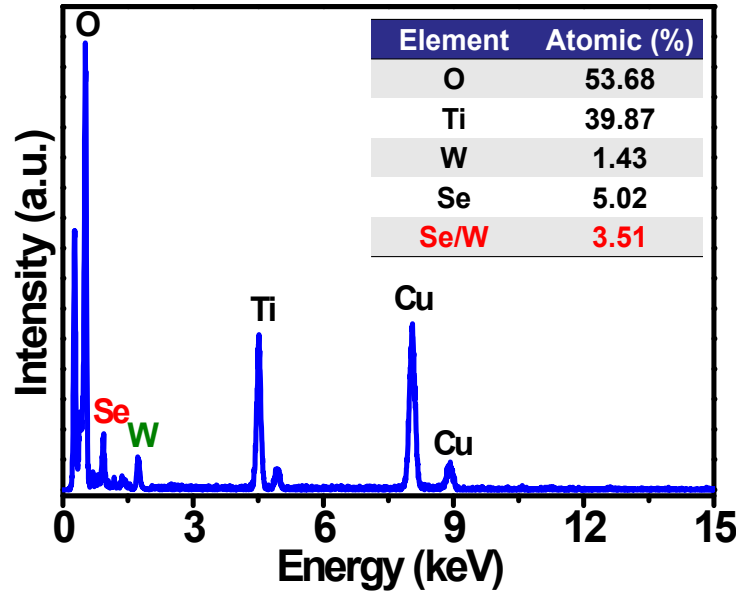
Fig. S3 EDX spectrum of Se-enriched WSe_{2+x}/TiO_2(3wt%).

	Front view	Side view	Top view
Se site			
W site			
W vacancy			
Se adhesion			
W vacancy and Se adhesion			
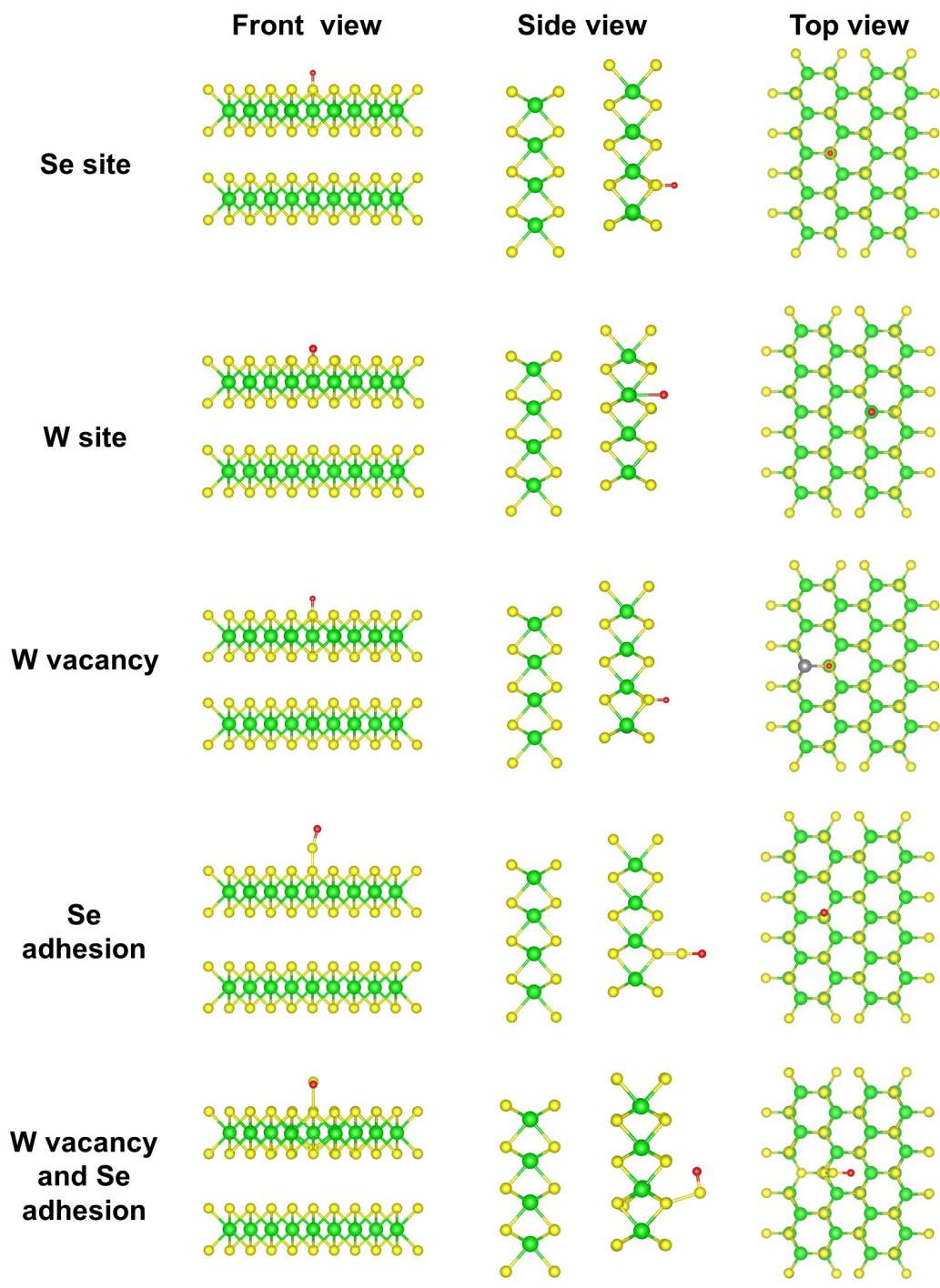
Fig. S4 Structure models from DFT calculations for various WSe$_2$ with different H-adsorbed states (Front, side and top views).
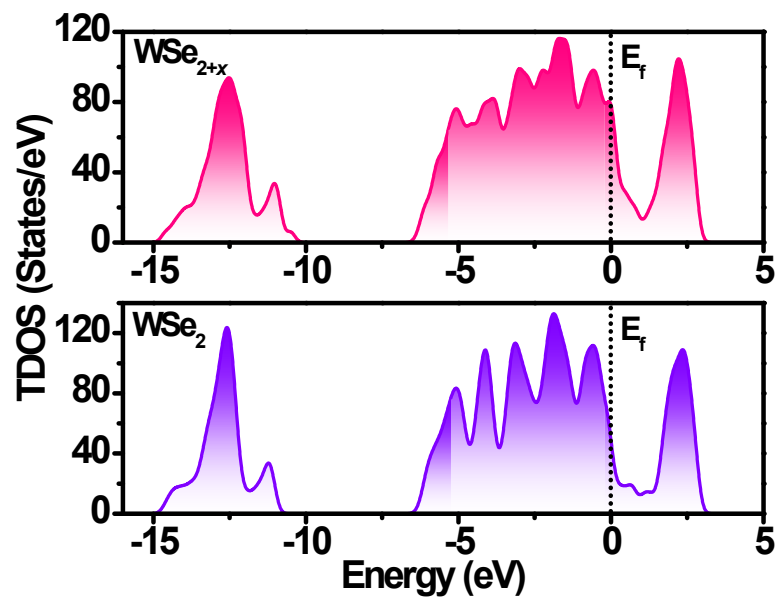
Fig. S5 The total density of states (TDOS) of WSe_2 and WSe_{2+x} with W-vacancy and Se-adhesion.
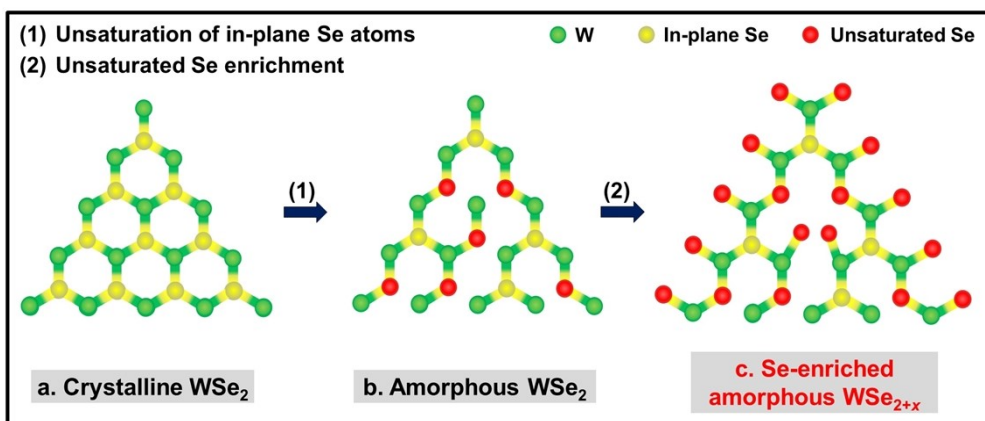
Fig. S6 Schematic illustration of the unsaturated selenium-enriched regulation to increase the active-site number of WSe_{2+x} cocatalyst by (1) unsaturation of in-plane Se atoms and (2) unsaturated Se enrichment.
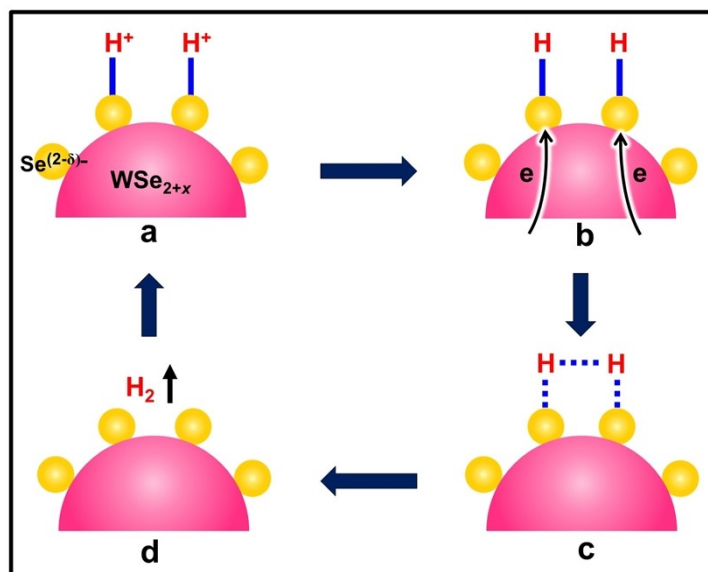
Fig. S7 The detailed interfacial H_2-evolution process on the active $Se^{(2-\delta)-}$ sites of WSe_{2+x}/TiO_2: a) H^+ adsorption; b) H^+ reduction by delivered photoelectrons; c, d) H_2 formation and desorption.

For better understanding the enhanced interfacial H_2-evolution process, a more detailed mechanism showing the hydrogen-evolution route has been proposed (Fig. S7). First, the electron-poor $Se^{(2-\delta)-}$ active sites on WSe_{2+x} cocatalyst can effectively adsorb positive H^+ ions from the reaction system via $Se^{(2-\delta)-}$-H^+ interaction (Fig. S7a). Subsequently, the adsorbed H^+ ions on the WSe_{2+x} surface can be rapidly reduced by the delivered photoelectrons of WSe_{2+x} to form the adsorbed atomic hydrogen ($Se^{(2-\delta)-}$-H_{ads}) on the $Se^{(2-\delta)-}$ sites (Fig. S7b). After that, the adsorbed atomic hydrogen can effectively bond with adjacent atomic hydrogen (Fig. S7c) and finally desorb to produce H_2 gas (Fig S7d). Therefore, the above electron-poor $Se^{(2-\delta)-}$-mediated hydrogen-generation cycle can greatly enhance the photocatalytic hydrogen-production performance of WSe_{2+x}/TiO_2.
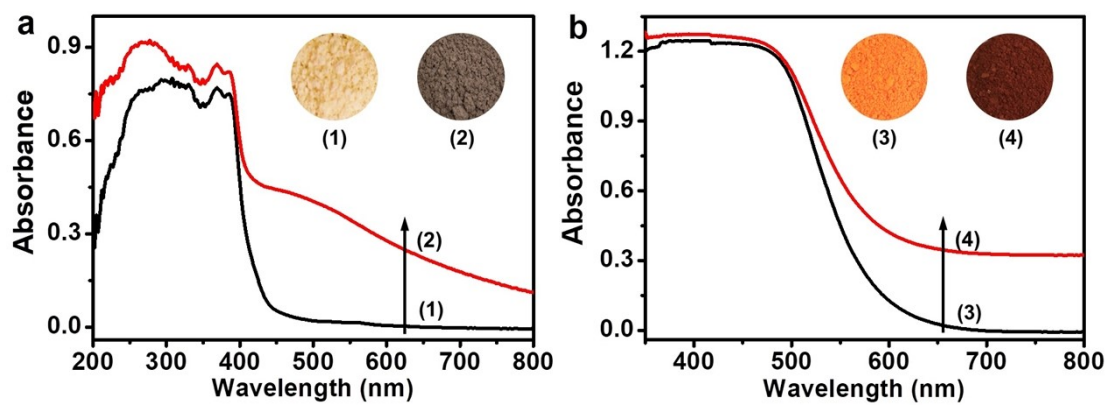
Fig. S8 (a, b) UV-vis absorption spectra of (1) g-C_3N_4, (2) Se-enriched WSe_{2+x}/g-C_3N_4(3wt%), (3) CdS, and (4) Se-enriched WSe_{2+x}/CdS(3wt%).
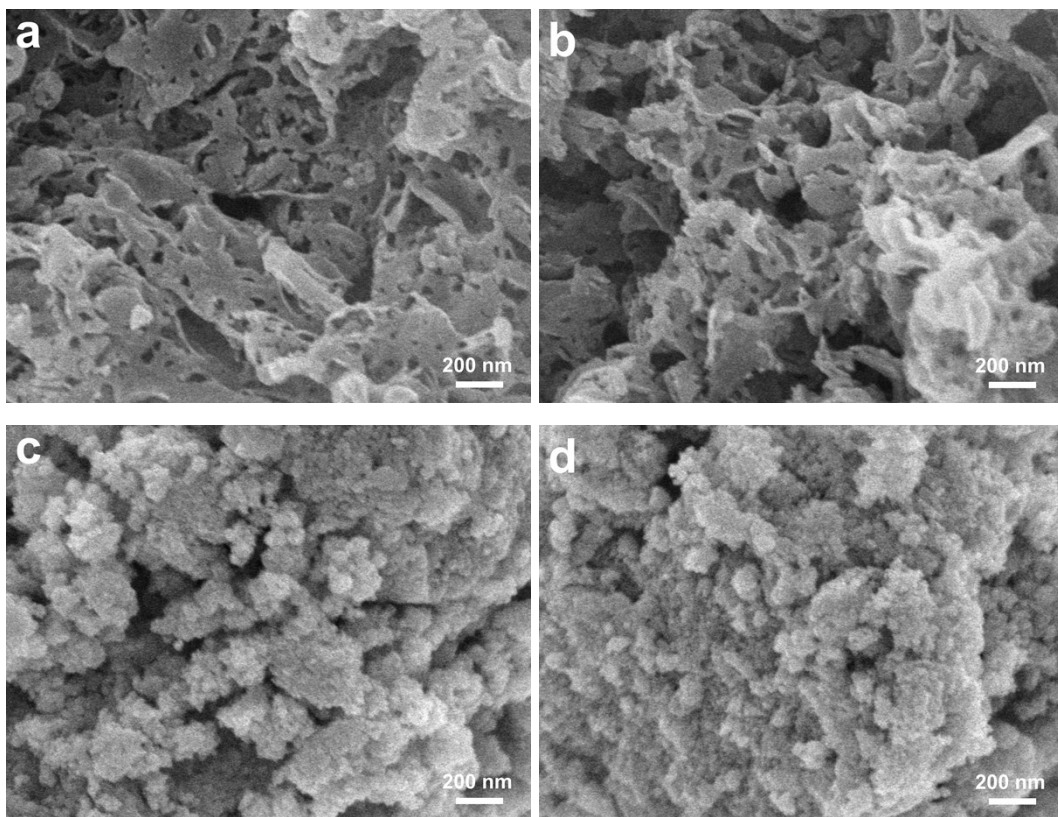
Fig. S9 (a–d) FESEM images of (a) g-C$_3$N$_4$, (b) Se-enriched WSe$_{2+x}$/g-C$_3$N$_4$(3wt%),

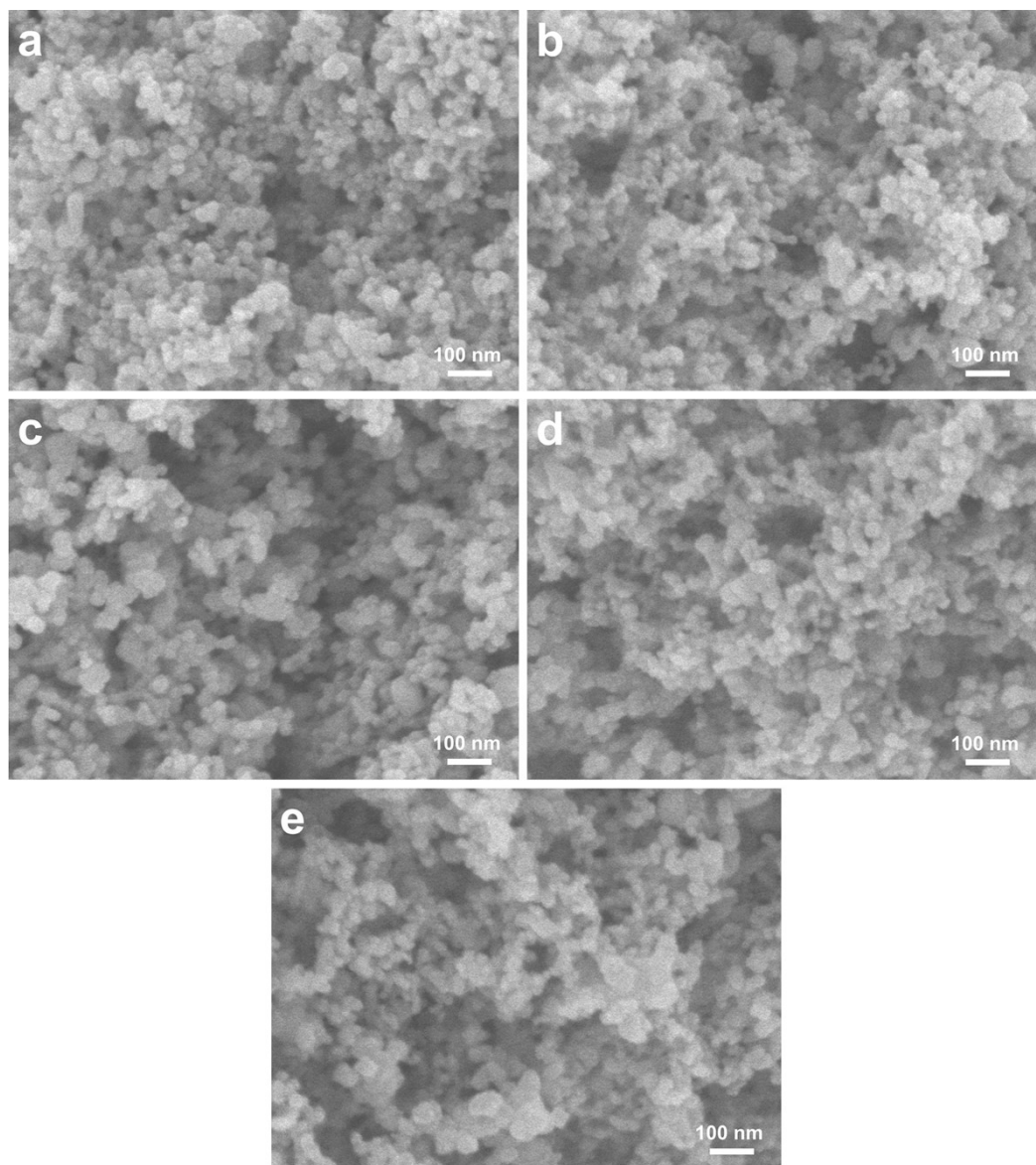(c) CdS, and (d) Se-enriched WSe$_{2+x}$/CdS(3wt%).

Fig. S10 (a–e) FESEM images of selenium-enriched (a) a-CuSe$_{1+x}$/TiO$_2$(3wt%), (b) a-FeSe$_{1+x}$/TiO$_2$(3wt%), (c) a-CoSe$_{1+x}$/TiO$_2$(3wt%), (d) a-NiSe$_{1+x}$/TiO$_2$(3wt%), and (e) a-MoSe$_{2+x}$/TiO$_2$(3wt%).

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