Supporting Information

One-step calcination synthesis of WC-Mo_2C heterojunction nanoparticles as novel H_2-production cocatalysts for enhanced photocatalytic activity of TiO_2

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Number of pages: 13

Number of Figures: 2

Number of Tables: 4

Supporting Information Content **page**

SI Experimental

SI-1 Materials

Titanium dioxide (TiO_2-P25), melamine ($C_3N_3(NH_2)_3$), ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot4H_2O$), ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$), sodium sulfide ($Na_2S\cdot9H_2O$), cadmium nitrate ($Cd(NO_3)_2\cdot4H_2O$), Zinc nitrate ($Zn(NO_3)_2\cdot6H_2O$), methanol ($CH_3OH$), sodium sulfate ($Na_2SO_4$), and lactic acid ($CH_3CH(OH)COOH$) were of analytical grade from Shanghai Chemical Reagent Ltd. (PR China) and used without further purification.

SI-2 Preparation of WC-Mo_2C@C(1:2)/TiO_2(5 wt%), WC-Mo_2C@C(4:3)/TiO_2(5 wt%) and WC-Mo_2C@C(4:1)/TiO_2(5 wt%) photocatalysts

To compare the photocatalytic hydrogen-production performance of TiO_2 modified by different cocatalysts with different mole ratios of W/Mo, WC-Mo_2C@C(1:2)/TiO_2(5 wt%), WC-Mo_2C@C(4:3)/TiO_2(5 wt%) and WC-Mo_2C@C(4:1)/TiO_2(5 wt%) photocatalysts were prepared by a facile electrostatic self-assembly approach. In a brief, 2.5 mg of the previous hetero-phase WC-Mo_2C@C(1:2), WC-Mo_2C@C(4:3) and WC-Mo_2C@C(4:1) were dispersed into TiO_2 methanol solution (50 mg of TiO_2 in 80 ml of methanol solution) under sonication for 0.5 h to acquire WC-Mo_2C@C(1:2)/TiO_2(5 wt%), WC-Mo_2C@C(4:3)/TiO_2(5 wt%) and WC-Mo_2C@C(4:1)/TiO_2(5 wt%) composite samples, respectively. According to the results in Fig. S1, the resultant WC-Mo_2C@C(4:3)/TiO_2(5 wt%) exhibited the highest photocatalytic performance. Therefore, in this study, the WC-Mo_2C@C(4:3)/TiO_2 was simplified as the WC-Mo_2C@C/TiO_2 in the following text.

SI-3 Characterization

Microstructures and morphologies of the as-prepared samples were conducted by X-ray diffraction (XRD) ((D/MAXRB, RIGAKU, Japan), Raman microscope (InVia, Renishaw, UK), and Transmission electron microscopy (TEM and HRTEM) (Talos F200S, Thermo Fisher, USA). Elemental analyses of photocatalysts were measured via X-ray photoelectron spectroscopy (XPS) ((ESCALAB 250Xi, Thermo Scientific, USA) with Al Kα source and inductively coupled plasma (ICP) (Prodigy 7, LEEMAN LABS, USA). UV-vis spectrophotometer (UV-2450, Shimadzu, Japan) was used to characterize the optical absorption property.

SI-4 Photocatalytic H_2 production activity

Photocatalytic hydrogen evolution activity was evaluated with 50 mg of photocatalyst in 80 mL methyl alcohol (10 vol%) solution in a Pyrex glass reaction cell under four LEDs (3 W, 365 nm, Shenzhen Lamplic Science Co. Ltd., China). The system was degassed under the N_2 atmosphere for 15 min. After four 365 nm-LED lamps irradiated the system, 400 μL of gas was injected into a gas chromatograph (Shimadzu, GC-2014C, Japan) with a thermal conductivity detector and a 5 Å molecular sieve column. The apparent quantum efficiency (AQE) was calculated according to the following the equation S1:

$$
\begin{aligned}
\mathrm{AQE}(\%) &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\
&= \frac{\text{number of evolved } \mathrm{H_2} \text{ molecules} \times 2}{\text{number of incident photons}} \times 100
\end{aligned}
\tag{S1}
$$

SI-5 Photoelectrochemical measurements

Photoelectrochemical (PEC) curves were measured on an electrochemical analyzer (CHI660E, China) in a standard three-electrode configuration. The prepared samples were loaded on fluorine-doped tin oxide (FTO) conductor glass, a standard Ag/AgCl electrode and the platinum foil as the working electrodes, reference electrode and counter electrode, respectively, with Na_2SO_4 (0.5 mol L^{-1}) as the electrolyte solution. The method of working electrodes was the same as in our previous works. Linear sweep voltammetry (LSV) curves were obtained in the potential ranging of -1.0 to -1.6 V with a scan rate of 10 mV s^{-1}. Transient photocurrent responses with time (*i-t* curves) were recorded at 0.5 V bias potential during periodic ON/OFF illumination cycles under a 3W LED lamp (365 nm), and electrochemical impedance spectroscopy (EIS) curves were conducted at the frequency range of 0.01-10^5 Hz with an ac amplitude of 10 mV under the open-circuit voltage.

SI-6 DFT computational methods

The first principle calculations were carried out by using the Vienna Ab initio Simulation Package (VASP). Generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was selected to describe the exchangecorrelation interaction. The energy cutoff and Monkhorst–Pack k-point mesh were set as 450 eV and 3 × 3 × 1, respectively. The convergence threshold was set as 10^{-5} eV for energy and 0.01 eV·$Å^{-1}$ for force. To eliminate interactions between periodic structures, a vacuum of 20 Å was added. The Gibbs free energy of H atom adsorption (ΔG_{H*}) was defined as following the equation S2:

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H \tag{S2}$$

where ΔE_H, ΔE_{ZPE}, $T\Delta S_H$ are the differential hydrogen ΔE_H adsorption energy, the change in zero point energy and entropy between the adsorbed hydrogen and molecular hydrogen in gas phase, respectively, and T is the temperature. The term $T\Delta S_H$ was calculated to be -0.20 eV. Mo_2C model was composed of 64 Mo atoms and 32 C atoms. During the geometry optimization, the bottom half of Mo and C atoms were fixed, while other atoms were relaxed. To simulate the hetero-phase structure of WC-Mo_2C, the WC-Mo_2C model was constructed by replacing two adjacent Mo atoms with one W atom.

Table S1. The element compositions and contents of various samples according to ICP results.

Samples	Mo (wt%)	W (wt%)	W:Mo molar ratio	$WC:Mo_2C$ molar ratio
Mo_2C@C	75.1	-	-	-
WC-Mo_2C@C(1:2)	47.9	19.8	1:4	1:2
WC-Mo_2C@C(4:3)	29.6	37.9	2:3	4:3
WC-Mo_2C@C(4:1)	15.2	54.4	2:1	4:1
WC@C	-	68.8	-	-

Table S2. The element components of various samples according to XPS results.

Samples	Mo	C	Ti	O	$Mo:TiO_2$ wt%
TiO_2	-	52.89	16.32	30.79	-
$WC\text{-}Mo_2C@C/TiO_2$	0.24	32.68	20.95	45.03	1.8

Table S3. The H_2-evolution performance and apparent quantum efficiency (AQE) of various samples.

Sample	H_2-evolution activity (μmol h^{-1} g^{-1})	AQE (%)
TiO_2	10	0.03
Mo_2C@C/TiO_2(5 wt%)	254	0.78
WC-Mo_2C@C/TiO_2(0.5 wt%)	350	1.05
WC-Mo_2C@C/TiO_2(1 wt%)	762	2.28
WC-Mo_2C@C/TiO_2(5 wt%)	903	2.70
WC-Mo_2C@C/TiO_2(10 wt%)	781	2.34
WC@C/TiO_2(5 wt%)	357	1.08
WC-Mo_2C@C(1:2)/TiO_2(5 wt%)	738	2.21
WC-Mo_2C@C(4:3)/TiO_2(5 wt%) (WC-Mo_2C/TiO_2(5 wt%))	903	2.70
WC-Mo_2C@C(4:1)/TiO_2(5 wt%)	672	2.16

Table S4. The apparent quantum efficiency (AQE) for various photocatalysts

Photocatalyst	Method	Light source	Sacrificial agent	H_2-production rate ($\mu mol\ h^{-1}g^{-1}$)	AQE %	Ref.
Mo_2C/TiO_2	calcination	Xe (300 W)	triethanolamine	39400 (25 times)	12.3	R1
rGO-Mo_2C/TiO_2	sonication	LED (365 nm 3W)	methanol 10 vol%	880 (88 times)	2.64	R2(our work)
MoC-Mo_2C@C/TiO_2	sonication	LED (365 nm 3 W)	methanol 10 vol%	918 (91 times)	2.7	R3(our work)
MoC@C/TiO_2	sonication	LED (365 nm 3 W)	methanol 10 vol%	504 (50 times)	1.43	R4(our work)
Mo_2C/TiO_2	calcination	mercury lamp (387 nm 125 W)	deionized water	52.5 (15 times)	-	R5
Mo_2C@C/CdS	sonication	Xe (420 nm 300 W)	lactic acid 10 vol %	5543 (26 times)	-	R6
MoS_2/TiO_2	hydrolysis calcination	LED (365 nm 3.5W)	methanol 20 vol%	2443 (10 times)	8.3	R7
MoS_2/TiO_2	hydrothermal	LED (3 W 360 nm)	methanol 10 vol%	2145 (36 times)	6.4	R8
MoN/TiO_2	mechanically mixing	Xe (300 W)	ethanol 20 vol%	2034 (40 times)	-	R9
WC-Mo_2C@C/TiO_2	sonication	LED (365 nm 3 W)	methanol 10 vol%	903 (90.3 times)	2.70	This work

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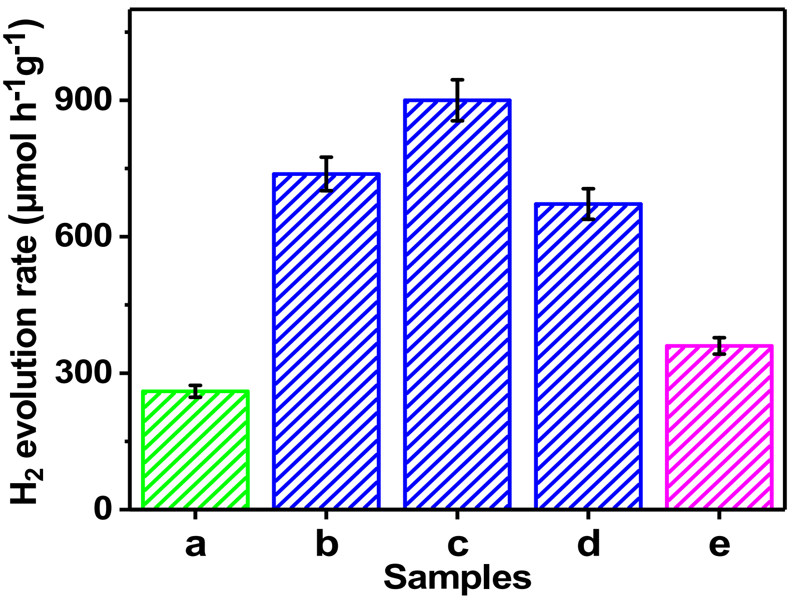

Fig. S1. The photocatalytic H_2-evolution activity of (a) Mo_2C@C/TiO_2(5 wt%), (b) WC-Mo_2C@C(1:2)/TiO_2(5 wt%), (c) WC-Mo_2C@C(4:3)/TiO_2(5 wt%), (d) WC-Mo_2C@C(4:1)/TiO_2(5 wt%), (e) WC@C/TiO_2(5 wt%).

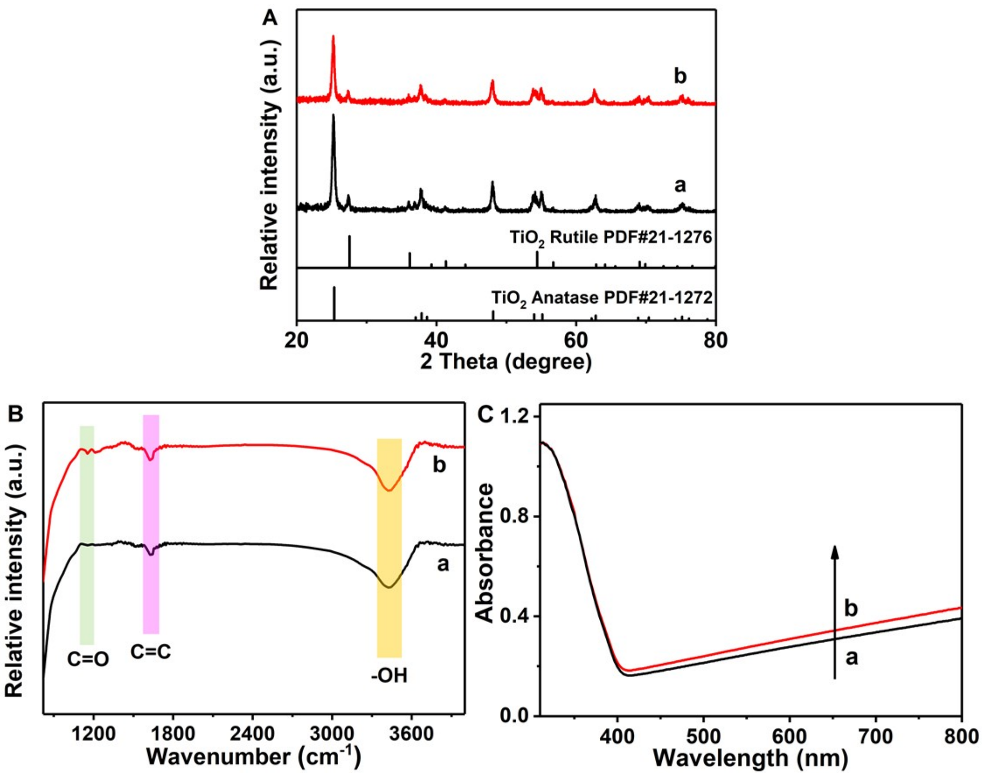

Fig. S2. (A) XRD patterns, (B) FTIR spectra, and (C) UV-vis spectra for the WC-Mo_2C@C/TiO_2(5 wt%) sample: (a) before and (b) after photocatalytic H_2 evolution.