

Supporting information

**Highly Efficient Photocatalytic Formic Acid Decomposition to
Syngas under Visible Light using CdS Nanorods Integrated with
Crystalline W₂N₃ Nanosheets**

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Experimental Methods

Materials

Ethylene diamine ($C_2H_8N_2$, 99.0%), thiourea (CH_4N_2S , 99.0%), cadmium chloride hemipentahydrate ($CdCl_2 \cdot 2.5H_2O$, 99.0%), sodium tungstate dihydrate, PVP (K-30), acetic acid ($C_2H_4O_2$, 99.0%), formic acid ($HCOOH$, 98%), and sodium hydroxide ($NaOH$, 96.0%) were purchased from Alfa-Aesar, Aldrich, or sinopharm chemical reagent Co.,Ltd and used without further purification. Millipore water (resistivity: $\sim 18 M\Omega \text{ cm}$) was used when needed.

Synthesis of CdS nanorods

CdS nanorods were synthesized by referring to a previous report of our group. First, 4.62 g (10.125 mmol) $CdCl_2 \cdot 2.5H_2O$ and 4.62 g (30.375 mmol) thiourea (CH_4N_2S) were added into 60 mL ethylene diamine. The mixed solution was transferred into a 100 mL Teflon-lined autoclave. Then the autoclave was sealed and maintained at $160^\circ C$ for 48 h. After cooling down to room temperature, centrifugation was used to collect the yellow precipitate, followed by washing with DI water and ethanol to remove organic residues. The final product was then dried at $60^\circ C$ overnight.

Synthesis of W_2N_3 nanosheets

W_2N_3 nanosheets were synthesized by a simple hydrothermal method and high-temperature calcination in an ammonia atmosphere. First, 330 mg (1 mmol) sodium tungstate dihydrate and 50 mg PVP were added into a mixture of 1 mL acetic acid and 6 mL deionized water. The obtained solution was stirred for 10 min and sonicated for 20 min, and then transferred to a Teflon-lined autoclave. The autoclave was sealed and heated at $200^\circ C$ for 8 h. The obtained white precipitate was washed with DI water and ethanol several times by centrifugation and dried at $60^\circ C$ overnight. Then the powder was placed in a quartz boat and transferred to a tubular furnace. The furnace was heated to $700^\circ C$ with a rate of $2^\circ C/\text{min}$ in an ammonia atmosphere for 3 h and cooled down naturally. The white powder turned black and W_2N_3 nanosheets was successfully synthesized.

Synthesis of CdS/ W_2N_3 photocatalysts

Two steps of grinding and calcining were used to synthesis the composite

CdS/W₂N₃ photocatalysts. In the first step, 95 mg CdS and 5 mg W₂N₃ were added into 30 mL ethanol with stirring for 30 min and sonicating for 10 min. After drying under N₂, the mixture was ground for 20 min. In the second step, the obtained powder was calcined under argon at 300 °C for 1 h with a heating rate of 5 °C/min. Finally, the composite CdS/W₂N₃ (5 wt%) photocatalysts were obtained and kept in a centrifuge tube for further tests. CdS/W₂N₃ photocatalysts with different W₂N₃ weight percentages (0.5, 1, 3, and 10 wt%) were also synthesized by the same method.

Characterization

The scanning electron microscopy (SEM) images of all the samples were acquired using a Zeiss GeminiSEM 500. A FEI Talos F200X electron microscope was used to obtain transmission electron microscopy (TEM) images and energy-dispersive X-ray microscopy (EDX) mappings at an acceleration voltage of 200 kV. A D/max-TTR III was used to record X-ray diffraction (XRD) patterns at a scanning rate of 10° min⁻¹ from 10° to 80° (2θ). Optical absorption properties of all the samples were measured over a SOLID 3700 UV–vis spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 X-ray photoelectron spectrometer. The steady-state photoluminescence (PL) spectra were measured on a Perkin-Elmer LS 55 fluorescence spectrometer with an excitation wavelength of 405 nm.

Photocatalytic FA Decomposition

The photocatalytic activity tests of FA decomposition were carried out in a 50 mL round bottom flask at ambient temperature. The visible light irradiation was provided by a 300 W Xe lamp equipped with a UV cutoff filter ($\lambda > 420$ nm). The typical photocatalytic solution was prepared by dispersing 2 mg photocatalysts in 20 mL mixture of FA and DI water. FA concentration and pH of the solution were adjusted by adding different amounts of FA and NaOH. Before the reaction, the obtained suspension was sonicated and then bubbled with high-purity nitrogen for 20 min to remove the air. The generated gases were determined by gas chromatography (GC-1690, Ar as a carrier gas) equipped with a thermal conductivity detector (TCD). The apparent quantum yield (AQY) was measured using monochromatic 420 nm light.

AQY was calculated using the following equation:

$$\begin{aligned} \text{AQY (\%)} &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number of evolved H}_2\text{ molecules} \times 2}{\text{number of incident photons}} \times 100 \quad (1) \end{aligned}$$

Photoelectrochemical measurements

All the photoelectrochemical measurements were performed using a conventional three-electrode cell with a Pt wire counter electrode, an Ag/AgCl reference electrode, and the photocatalyst-coated FTO as the working electrode. The electrolyte was 0.5 M Na₂SO₄ solution. A CHI 660E electrochemical workstation (CH Instrument Inc., Shanghai) was used to record the electrochemical data. The illumination was provided by a 300 W Xe lamp equipped with a UV cutoff filter ($\lambda > 420$ nm). The ethanol suspension of CdS/W₂N₃ photocatalysts was prepared by adding 2 mg samples into 1 mL ethanol. After being sonicated, the suspension (100 μ L) was dropped onto the surface of FTO. The CdS/W₂N₃ working electrode was obtained after drying at ambient temperature. The CdS working electrode for comparison was prepared by the same way.

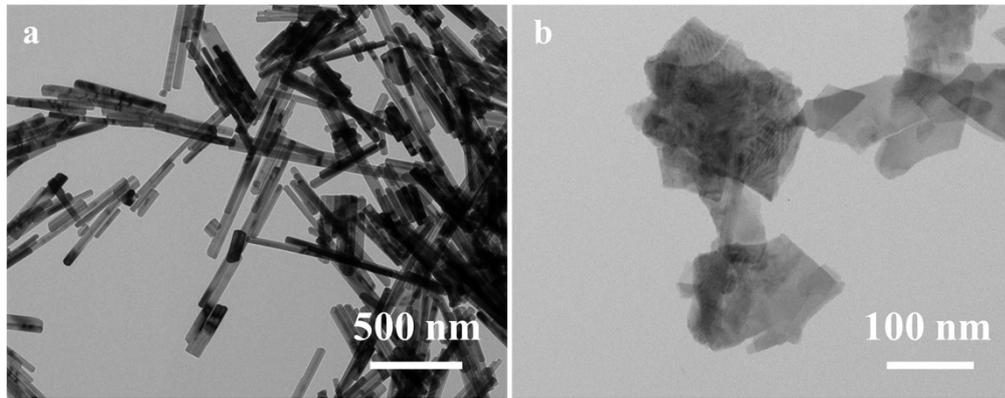


Fig. S1. TEM images of (a) CdS nanorods and (b) W₂N₃ nanosheets.

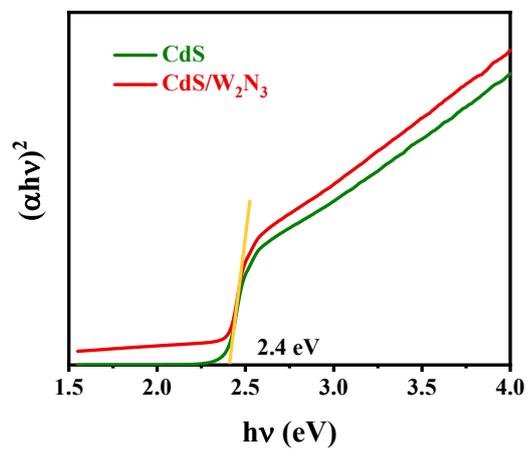


Fig. S2. Plots of $(\alpha hv)^2$ vs photo energy.

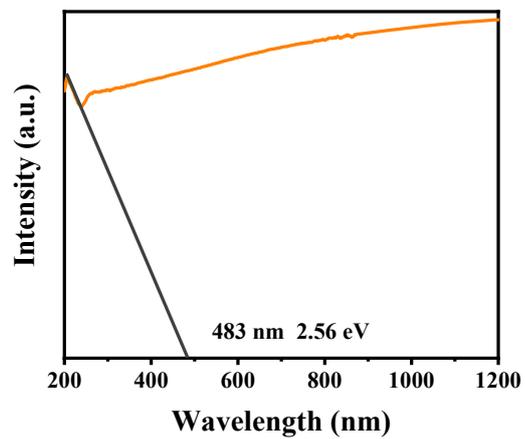


Fig. S3. Diffuse reflectance UV-vis spectra of W_2N_3 nanosheets.

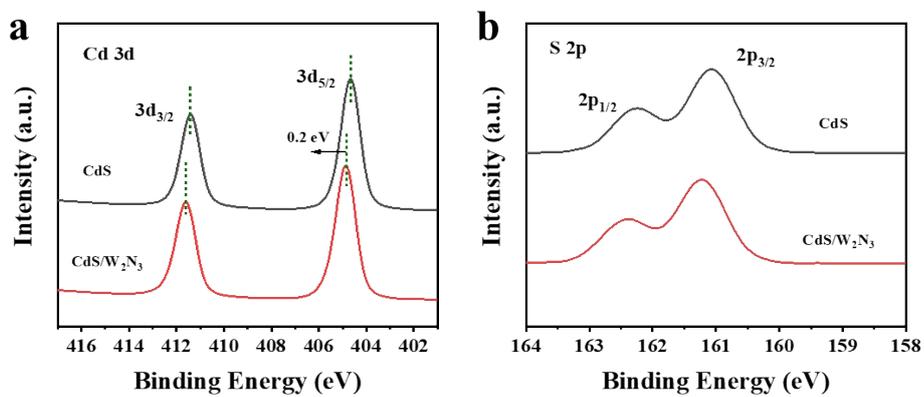


Fig. S4. Comparison of XPS spectra for CdS and 5 wt% CdS/W₂N₃. High-resolution XPS spectra of (a) Cd 3d and (b) S 2p.

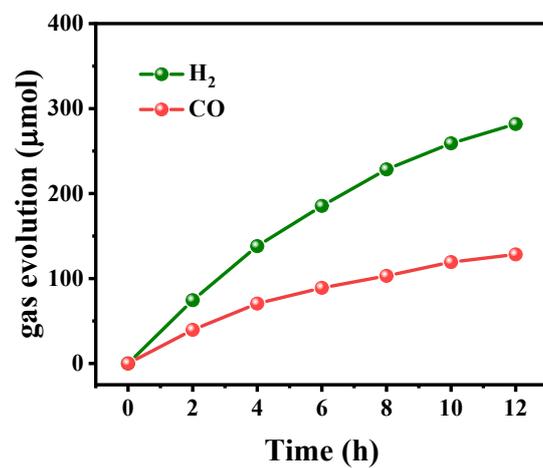


Fig. S5. Photocatalytic H₂ and CO evolution of CdS nanorods in 6 M FA aqueous solution using 2 mg photocatalyst at pH 3.5.

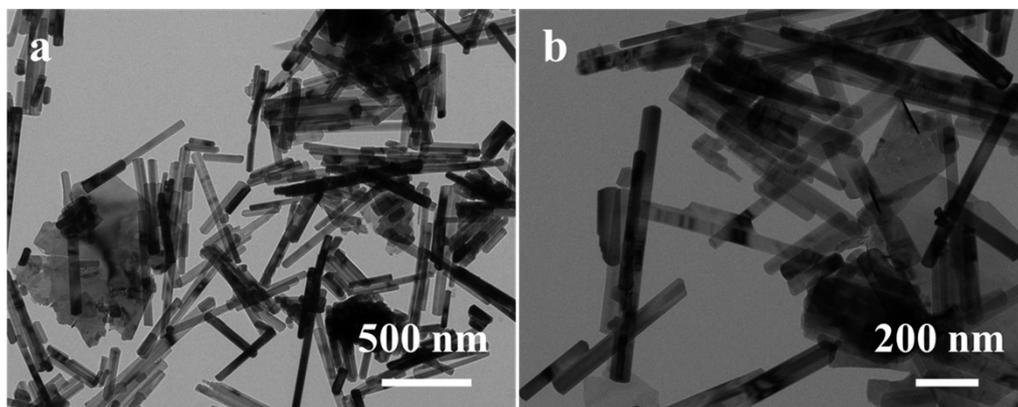


Fig. S6. TEM images after 54 h photocatalysis reaction in 6 M FA aqueous solution using 2 mg photocatalyst at pH 3.5.

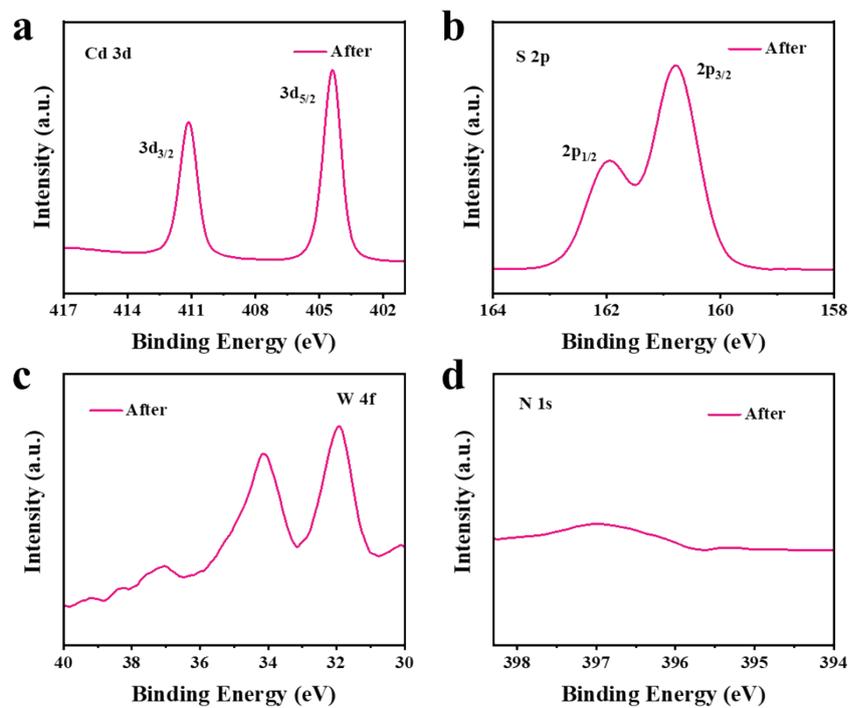


Figure S7. XPS data of 5 wt% CdS/W₂N₃ samples after 54 h stability test in 6 M FA aqueous solution at pH 3.5. High-resolution XPS spectra of (a) Cd 3d, (b) S 2p, (c) W 4f, and (d) N 1s.

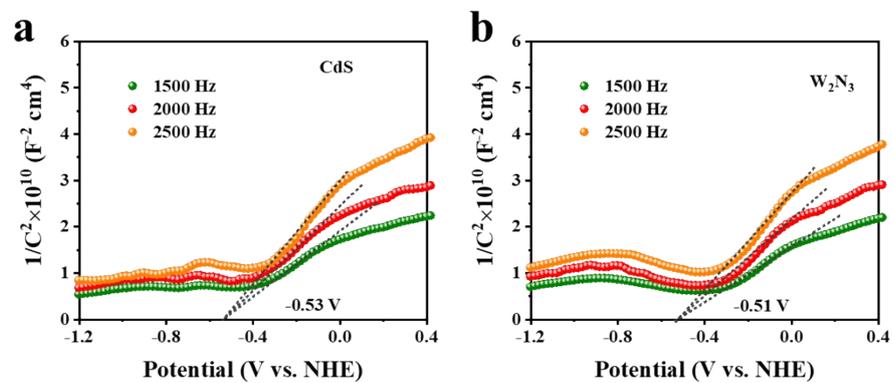


Figure S8. Mott–Schottky plots of (a) CdS nanorods and (b) W₂N₃ nanosheets with different frequency in the dark.

Table S1. The photocatalytic performance with different amount of catalysts. Photocatalytic experiments were carried out in 20 mL formic acid solution (6.0 M) at pH 3.5 using 2 mg photocatalysts.

Amount of catalyst (mg)	H ₂ ($\mu\text{mol h}^{-1}$)	H ₂ ($\mu\text{mol mg}^{-1} \text{h}^{-1}$)	CO ($\mu\text{mol h}^{-1}$)	CO ($\mu\text{mol mg}^{-1} \text{h}^{-1}$)
1	124	124	91	91
2	262	131	207	103.5
5	508	101.6	402	80.4
10	596	59.6	501	50.1

Table S2. Comparison of the H₂ and CO generation rate for photocatalytic formic acid decomposition of the CdS/W₂N₃ with other reported high performance photocatalysts.

catalysts	λ (nm)	H ₂ ($\mu\text{mol mg}^{-1} \text{h}^{-1}$)	AQY (%, H ₂)	CO ($\mu\text{mol mg}^{-1} \text{h}^{-1}$)	AQY (%, CO)	Stability (h)	Reference
FeP@CdS NRs	≥ 420	278	54	0	-	> 96	<i>ACS Appl. Mater. Interfaces</i> 2021 , 13, 23751-23759.
Fe salen/CdS NRs	≥ 420	150	16.8	71.5	9.3	> 30	<i>Angew. Chem.</i> 2020 , 59, 14818-14824.
CdS/CoP@RGO	≥ 420	182	32	trace	-	> 120	<i>Joule</i> 2018 , 2, 549-557.
CoPSA-CdS NRs	> 400	102	6.47	0	-	> 24	<i>Adv. Mater.</i> 2020 , 32,1904249.
Co-Ni/CdS	> 420	32.6	-	0	-	> 18	<i>ChemSusChem</i> 2018 , 11, 2587-2592.
Au _{0.75} Pd _{0.25} /TiO ₂	1 sun	17.7	15.6	0.2	-	> 9	<i>Appl. Catal. B Environ.</i> 2015 , 162, 204-209.
Pd/C ₃ N ₄	> 400	53.4	-	0	-	> 6	<i>Angew. Chem.</i> 2013 , 125, 12038-12041.
Co ²⁺ /CdS QDs	> 420	116	21.2	trace	-	> 168	<i>Angew. Chem. Int. Ed.</i> 2015 , 54, 9627-9631.
CdS/W ₂ N ₃	≥ 420	131	17.6	103.5	16.9	> 54	This work