Electronic Supplementary Information

Photoredox-catalyzed biomass intermediate conversion

integrated with H_2 production over $Ti_3C_2T_x/CdS$ composites

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Experimental Section Synthesis of Ti₃C₂T_x colloid

 $Ti_3C_2T_x$ nanosheets (NSs) colloid was prepared as described previously.^{S1} In detail, multilayered $Ti_3C_2T_x$ was firstly synthesized by etching Ti_3AlC_2 powders (1 g) in a mixture of LiF (1 g) and HCl (9 mol L⁻¹, 10 mL) for 24 h at 35 °C. The product was washed with DI water until the pH of the supernatant was above 6. The multilayered $Ti_3C_2T_x$ powder was then added into 200 mL of DI water and delaminated by bath sonication for 1 h under argon (Ar) flow. After centrifugation for 1 h at 3500 rpm, the dark green supernatant was collected. The concentration of the delaminated $Ti_3C_2T_x$ was determined by filtering the supernatant with a known volume through a Celgard membrane and measuring the weight of the film after drying. The delaminated $Ti_3C_2T_x$ colloid was then diluted to obtain a concentration of 1.75 mg mL⁻¹.

Materials characterizations

The morphology of the samples was determined by field emission scanning electron microscopy (FESEM) on a Hitachi New Generation cold field emission SEM SU-8200 spectrophotometer. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were analysed using a JEOL model JEM 2010 EX instrument at an acceleration voltage of 200 kV. The X-ray diffraction (XRD) patterns of samples were measured on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation in the 2 θ ranging from 10° to 80° at a scan rate of 0.02° s⁻¹. The optical properties of samples were characterized by UV-vis diffuse reflectance spectroscopy (DRS) using UV-vis spectrophotometer (Cary 500, Varian Co.) in which BaSO₄ was employed as a reference in the range of 400-800 nm. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCA Lab 250 spectrometer, which was made of a monochromatic Al Ka as the X-ray source, a hemispherical analyser, and a sample stage with multiaxial adjustability to obtain the surface composition of the samples. All the binding energies were calibrated by the C 1s peak at 284.8 eV. The photoluminescence spectra (PL) for samples were analysed on an Edinburgh Analytical Instrument F900 spectrophotometer with an excitation wavelength of 375 nm. To ensure the comparability of the PL spectra, the experimental parameters, including the excitation wavelength, slit width and the amount of the samples, were identical. The photoelectrochemical analysis and Mott–Schottky curve were composed of conventional three-electrode, a quartz cell containing 30 mL Na₂SO₄ (0.5 M) aqueous solution. A Pt plate (10 mm × 10 mm) was used as the counter electrode, Ag/AgCl as reference electrode. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass that was cleaned by ultrasonication in ethanol for 30 minutes and dried at 80 °C. 5 mg of the sample was dispersed in 0.5 mL of N, N-dimethylformamide (DMF) to get slurry by ultrasonication. The slurry was spread onto FTO glass, whose side part was previously protected using Scotch tape. After air drying, the working electrode was further dried at 100 $\,^{\circ}$ C for 2 h to improve adhesion. Then, the scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin. The electrochemical impedance spectroscopy (EIS) experiments were conducted on an electrochemical workstation (Autolab, PGSTAT204) in the electrolyte of 0.5 M KCl aqueous solution containing 0.01 M K_3 [Fe(CN)₆]/ K_4 [Fe(CN)₆] (1:1) under open-circuit potential conditions. The cyclic voltammograms (CV) were measured in the same solution in the three-electrode cell as that of the EIS measurements. The cathodic polarization curves were obtained using the linear sweep voltammetry (LSV) technique with a scan rate of 5 mV s⁻¹ in 0.1 M Na₂SO₄ aqueous solution. Zeta potential (ξ) of the sample was determined by dynamic light scattering analysis (Zeta sizer 3000HSA) at room temperature.



Fig. S1 Field-emission scanning electron microscopy (FESEM) images of the Ti_3AlC_2 powders (a) and $Ti_3C_2T_x$ nanosheets (NSs) (b).

Note: Fig. S1a shows the irregular blocky morphology of Ti_3AlC_2 powders, and $Ti_3C_2T_x$ exhibits a sheet-like structure in **Fig. S1b**.



Fig. S2 Zeta potential of $Ti_3C_2T_x$ NSs.



Fig. S3 FESEM images of 0.25%Ti₃C₂T_x/CdS (a), 0.5%Ti₃C₂T_x/CdS (b), 1%Ti₃C₂T_x/CdS (c) and 5%Ti₃C₂T_x/CdS (d).



Fig. S4 Transmission electron microscopy (TEM) image of the $Ti_3C_2T_x/CdS$ composites.



Fig. S5 Tauc plot for optical band gap of CdS.

Note: To calculate the band gap energy, the following formula is used:^{S2}

$$(\alpha h v)^2 = K \cdot (h v - E_g)$$

where α is the absorption coefficient, hv is the photon energy, K is a constant, E_g is the band gap energy. As shown in **Fig. S5**, the band gap of CdS is evaluated to be 2.2 eV.



Fig. S6 Time-dependent conversion of furfural alcohol over the samples of CdS and 0.5%Ti₃C₂T_x/CdS under visible light irradiation ($\lambda > 420$ nm).



Fig. S7 The selectivity of furfural over CdS and $Ti_3C_2T_x/CdS$ composites with different contents of $Ti_3C_2T_x$.



Fig. S8 High performance liquid chromatography (HPLC) analysis chromatogram of the liquid product over 0.5%Ti₃C₂T_x/CdS under visible light irradiation ($\lambda > 420$ nm) for 10 h. **Note:** Furfural alcohol and furfural can be respectively measured by HPLC. After 10 h of visible light irradiation, most of the furfural alcohol was converted to furfural.



Fig. S9 X-ray diffraction (XRD) patterns (a) and UV–vis diffuse reflectance spectra (DRS) (b) of fresh and used $Ti_3C_2T_x/CdS$ composites.

Table. S1 Control experiments for photocatalytic conversion of furfural alcohol to furfural and hydrogen (H_2) over 0.5%Ti₃C₂T_x/CdS composites.

Entry	Catalyst	hv	Solvent	Yield of H ₂ (µmol g ⁻¹)	Yield of Furfural (µmol g ⁻¹)
1	0.5%Ti ₃ C ₂ T _x /CdS	+	Deionized (DI) Water	773.04	765.95
2	0.5%Ti ₃ C ₂ T _x /CdS	-	DI Water	0	0
3	-	+	DI Water	0	0
4	Ti ₃ C ₂ T _x	+	DI Water	0	0
5	0.5%Ti ₃ C ₂ T _x /CdS	+	Acetonitrile	0	249.59
6 ^a	0.5%Ti ₃ C ₂ T _x /CdS	+	DI Water	361.65	820.07
7 ^b	0.5%Ti ₃ C ₂ T _x /CdS	+	DI Water	860.82	427.86

a: carbon tetrachloride (CCl_4) as scavenger for photogenerated electrons

b: triethanolamine (TEOA) as scavenger for photogenerated holes

+: with visible light irradiation

-: without visible light irradiation



Fig. S10 Cyclic voltammograms (CV) of CdS and $Ti_3C_2T_x/CdS$.

Table.	S2 Kinetic	analvsis o	f emission	decay for	CdS and	Ti ₃ C ₂ T ₂ /CdS.
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	τ ₁ /ns	Rel %	τ₂/ns	Rel %	X ²	T _{average} /ns
CdS	0.86	57.51	8.58	42.49	1.059	7.92
Ti₃C₂T _x /CdS	0.63	49.90	5.74	50.10	1.065	5.23



Fig. S11 Mott-Schottky curve of CdS.

Note: The conduction band (CB) of CdS, as calculated from the horizontal axis intercepts of the linear region, is -0.65 V (versus the normal hydrogen electrode, NHE).⁵³



Fig. S12 Valence-band (VB) X-ray photoelectron spectroscopy (XPS) spectrum of CdS. **Note:** The position of VB for CdS is measured as 1.61 eV.^{S4}

References

S1 M. Ghidiu, M. R. Lukatskaya, M.-Q. Zhao, Y. Gogotsi and M. W. Barsoum, *Nature*, 2014, **516**, 78. S2 N. Zhang, S. Liu, X. Fu and Y.-J. Xu, *J. Phys. Chem. C*, 2011, **115**, 9136-9145.

S3 X. Lin, S.-H. Li, K.-Q. Lu, Z.-R. Tang and Y.-J. Xu, New J. Chem., 2018, 42, 14096-14103.

S4 M. Ji, R. Chen, J. Di, Y. Liu, K. Li, Z. Chen, J. Xia and H. Li, *J. Colloid Interface Sci.*, 2019, **533**, 612-620.