

Supporting Information

Enhancement of Photocatalytic CO₂ Reduction by In Situ Growth of TiO₂ on Ti₃C₂ MXene

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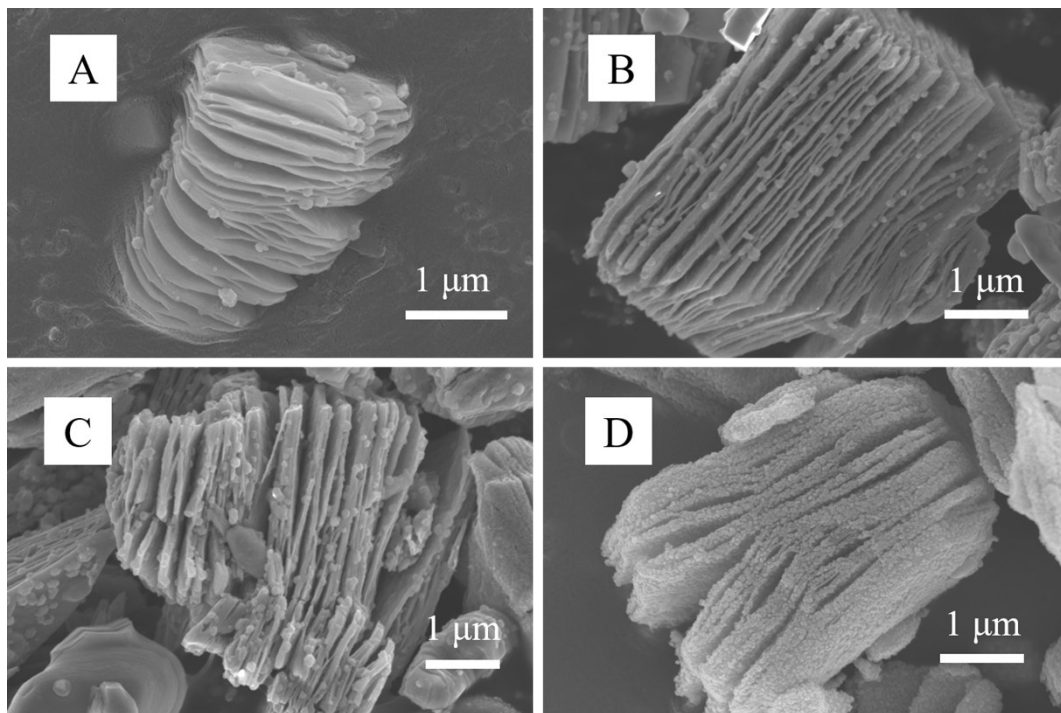


Fig. S1 SEM images of 2%- $\text{TiO}_2/\text{Ti}_3\text{C}_2$ (A), 4%- $\text{TiO}_2/\text{Ti}_3\text{C}_2$ (B), 6%- $\text{TiO}_2/\text{Ti}_3\text{C}_2$ (C), and 10%- $\text{TiO}_2/\text{Ti}_3\text{C}_2$ (D).

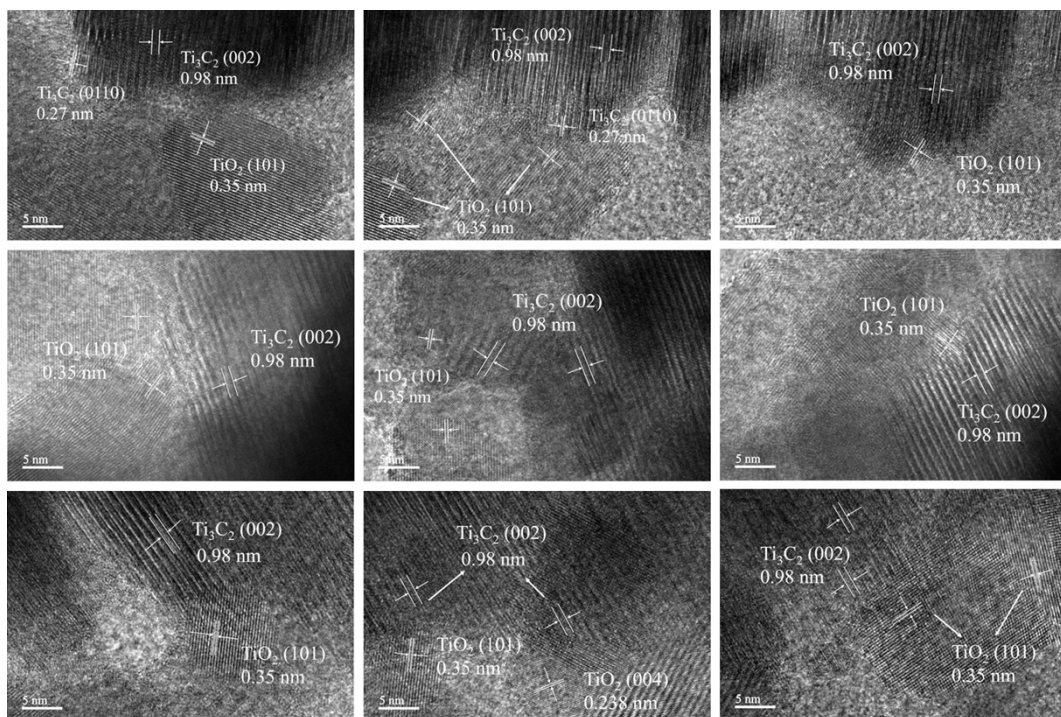


Fig. S2 HRTEM images of 8%- $\text{TiO}_2/\text{Ti}_3\text{C}_2$.

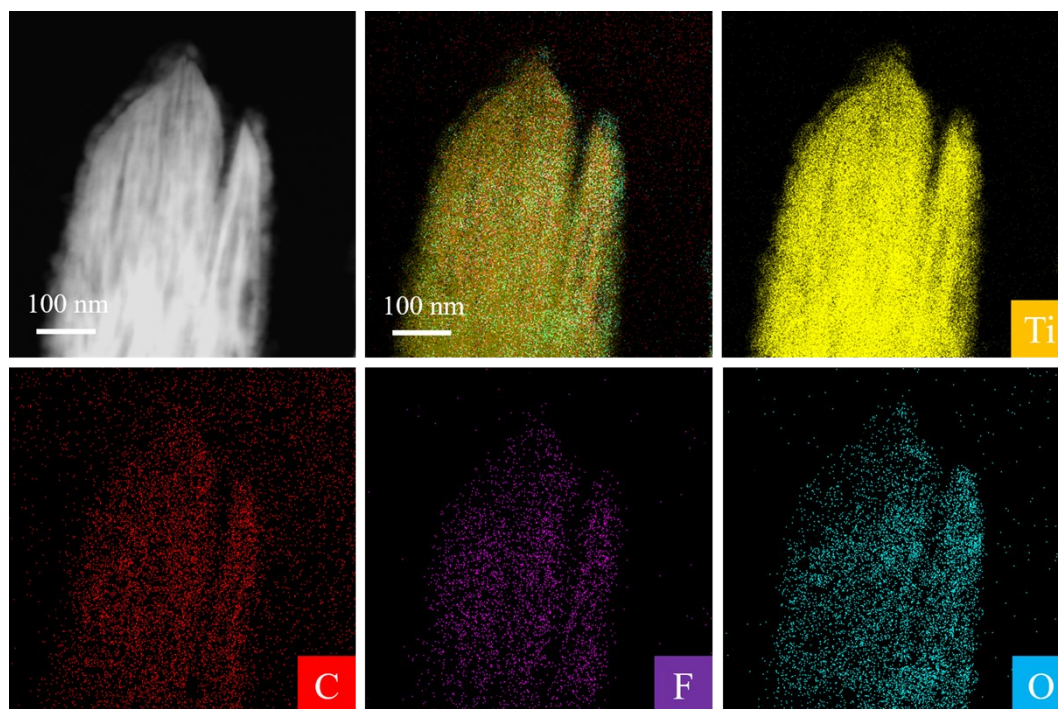


Fig. S3 STEM images and corresponding elemental mappings of 8%-TiO₂/Ti₃C₂.

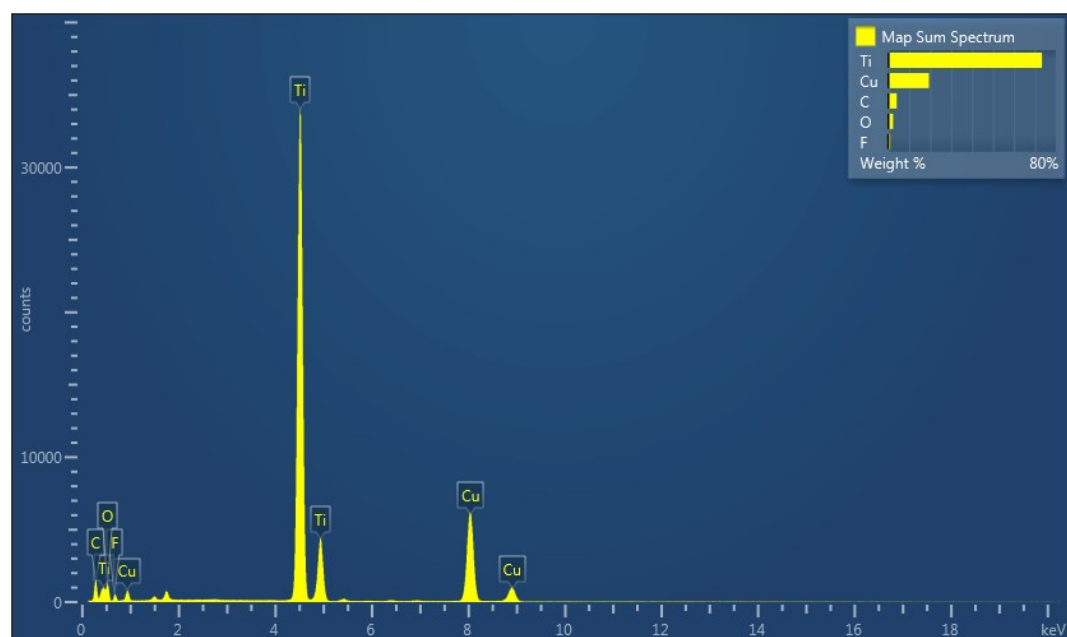


Fig. S4. EDS spectrum of 8%-TiO₂/Ti₃C₂.

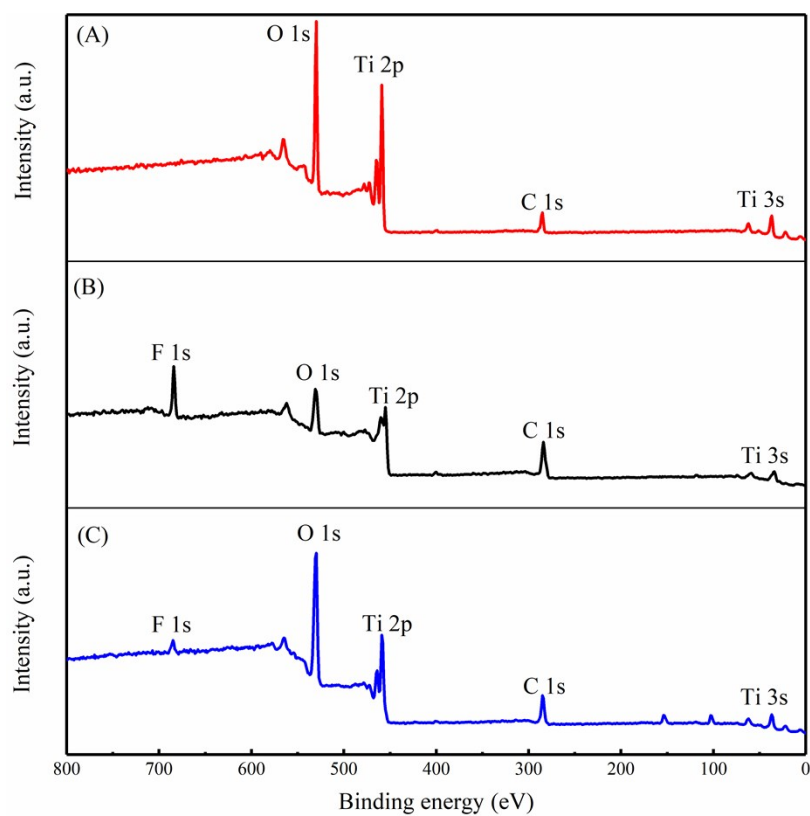


Fig. S5 XPS survey spectra of TiO_2 (A), Ti_3C_2 (B), and 8%- $\text{TiO}_2/\text{Ti}_3\text{C}_2$ (C).

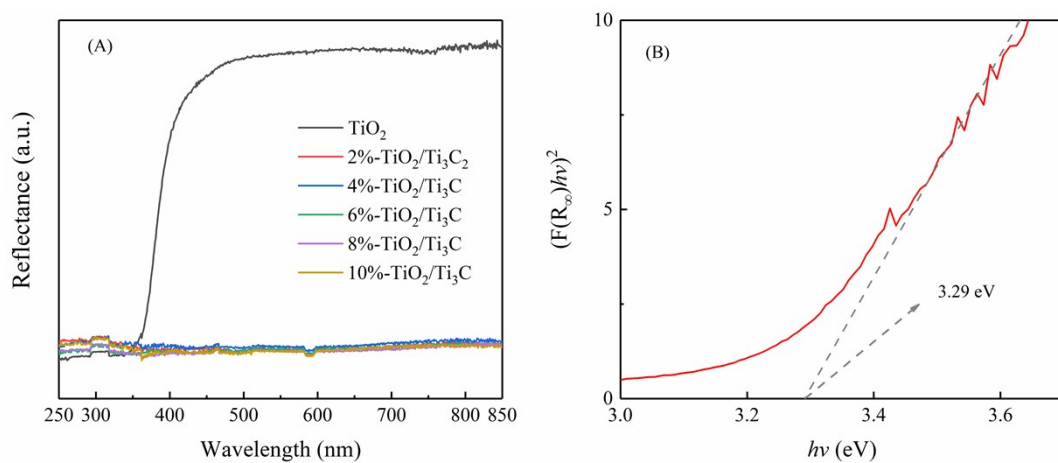


Fig. S6 UV-vis diffuse reflectance spectra of TiO_2 and $\text{TiO}_2/\text{Ti}_3\text{C}_2$ composites (A), the Tauc plots of TiO_2 (B).

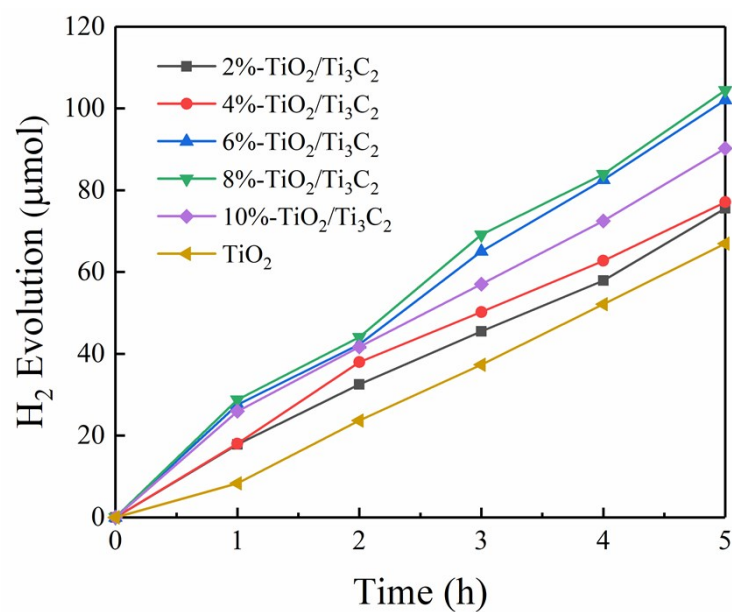


Fig. S7 Photocatalytic H₂ evolution of TiO₂ and TiO₂/Ti₃C₂.

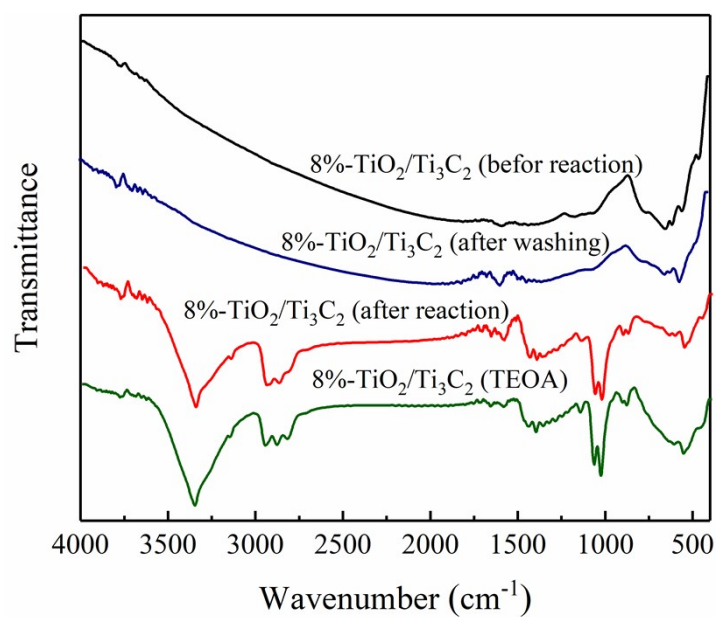


Fig. S8 FTIR spectra of the fresh 8%-TiO₂/Ti₃C₂, 8%-TiO₂/Ti₃C₂ after reaction with and without washing treatment, and 8%-TiO₂/Ti₃C₂ after soaking in TEOA.

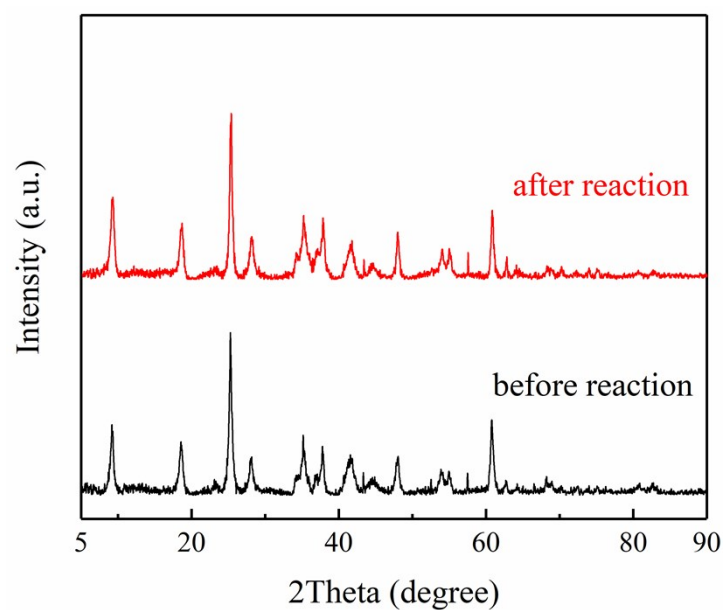


Fig. S9 XRD patterns of 8%-TiO₂/Ti₃C₂ composites before and after reaction.

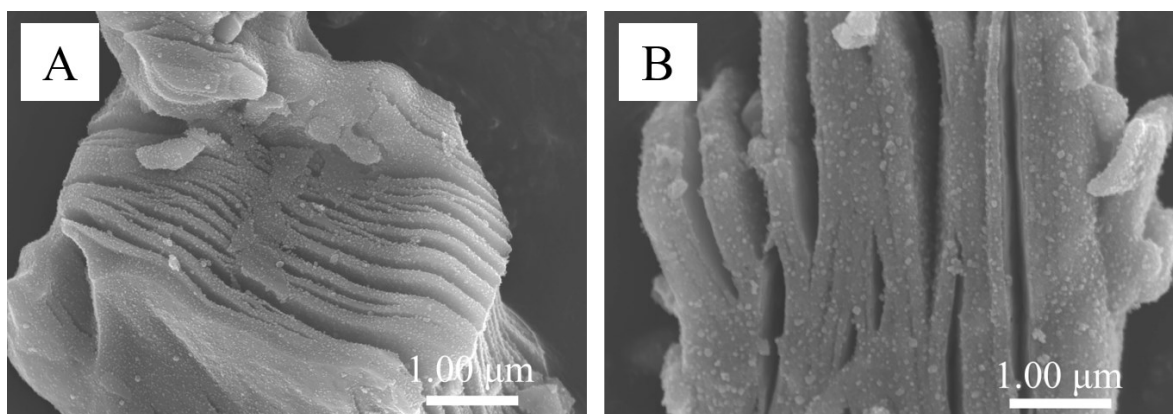


Fig. S10 SEM images of 8%-TiO₂/Ti₃C₂ composite before (A) and after (B) reaction.

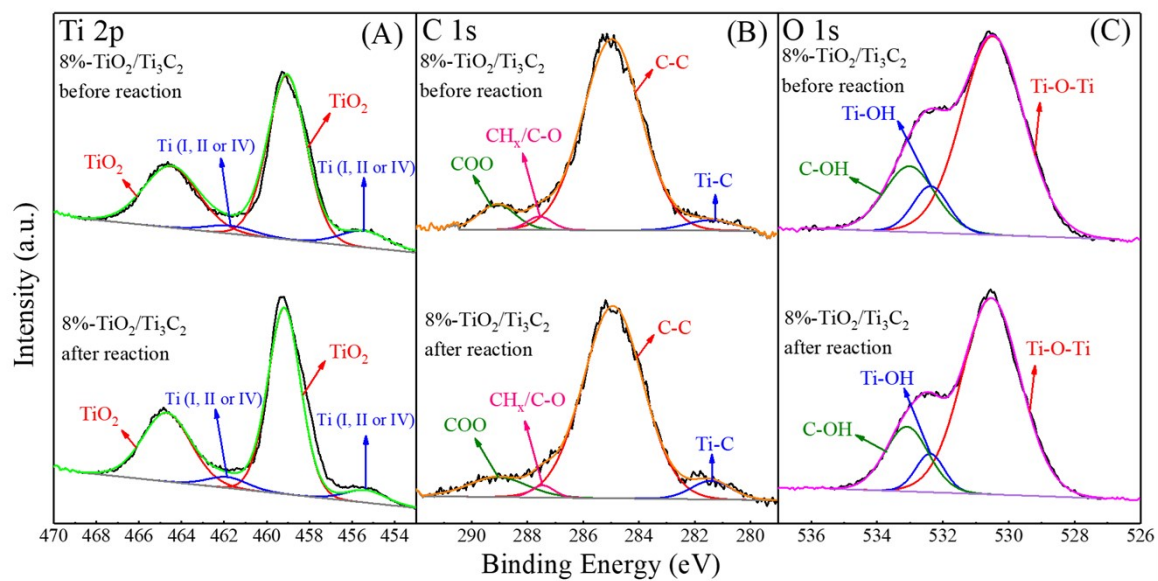


Fig. S11 High-resolution Ti 2p (A), C 1s (B), and O 1s (C) XPS spectra of 8%-TiO₂/Ti₃C₂ composite before and after reaction.

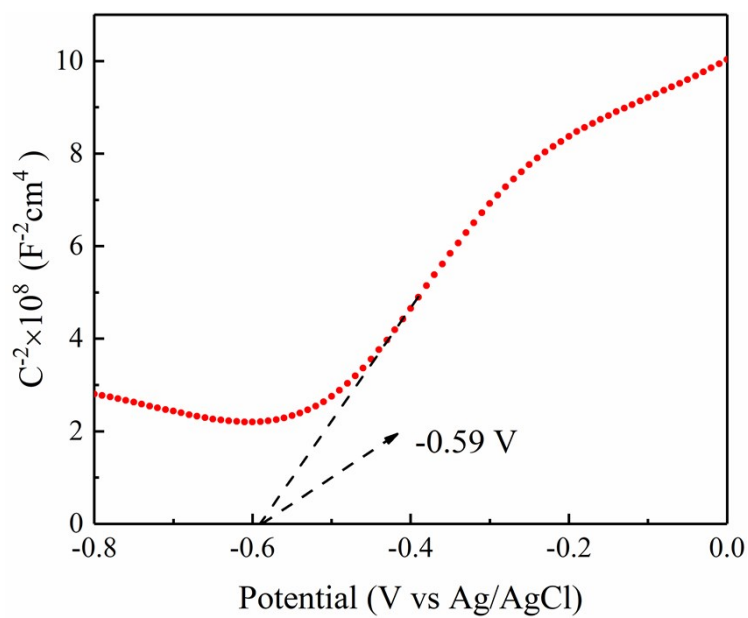


Fig. S12 Mott Schottky plots of TiO₂.

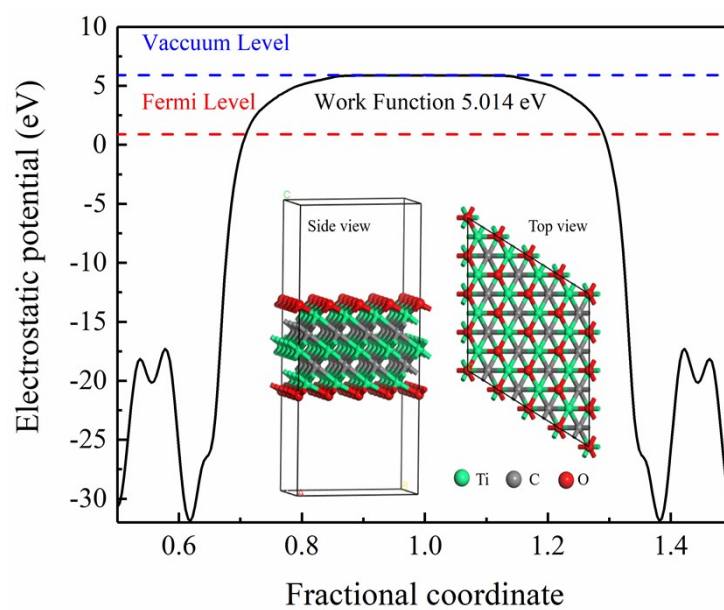


Fig. S13 E_F of Ti_3C_2 with O-termination. The inset is a side and top view of the $4 \times 4 \times 1$ supercell for $\text{Ti}_3\text{C}_2\text{-O}$ model (Green, gray, and red correspond to Ti, C, and O, respectively).

Table S1 Weight ratio of C : O : F : Ti for 8%-TiO₂/Ti₃C₂.

Element	Line Type	k Factor	wt%	atomic %
C	K series	2.769	16.46	37.14
O	K series	2.020	11.00	18.63
F	K series	1.721	3.71	5.29
Ti	K series	1.090	68.82	38.93

Table S2 Pore volume, pore size, and specific surface area of the samples with different TiO₂ content.

Samples	TiO ₂ content (wt %)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	<i>S</i> _{BET} (m ² g ⁻¹)
Ti ₃ C ₂	0.0	0.03	21.85	6.73
2%-TiO ₂ /Ti ₃ C ₂	2.0	0.02	13.88	7.02
4%-TiO ₂ /Ti ₃ C ₂	4.0	0.03	17.30	8.21
6%-TiO ₂ /Ti ₃ C ₂	6.0	0.03	16.20	8.65
8%-TiO ₂ /Ti ₃ C ₂	8.0	0.04	13.34	11.47
10%-TiO ₂ /Ti ₃ C ₂	10.0	0.04	14.54	11.14
TiO ₂	100.0	0.16	9.03	57.89

Table S3 Comparison of the catalytic performance with other photocatalysts for photocatalytic CO₂ reduction reaction.

Photocatalyst	Light source	Sacrificial agent	Products	Activity	Ref
TiO ₂ /Ti ₃ C ₂	500 W Hg lamp	TEOA	CO CH ₄	120.83 μmol h ⁻¹ 15.91 μmol h ⁻¹	This work
g-C ₃ N ₄ /FeTCPP	300 W Xe lamp (420 nm)	TEOA MeCN	CO	54.33 μmol h ⁻¹	[1]
Co(bpy) ₂ Cl ₂	300 W Xe lamp (420 nm)	TEOA MeCN	CO	62.30 μmol h ⁻¹	[2]
LaCoO ₃	300 W Xe lamp (420 nm)	TEOA MeCN	CO	28.50 μmol h ⁻¹	[3]
Zn ₂ GeO ₄ /Mg-MOF-74	300 W Xe lamp	MeCN	CO	0.03 μmol h ⁻¹	[4]
CoP/rGO	300 W Xe lamp (400 nm)	TEOA MeCN	CO	47.33 μmol h ⁻¹	[5]
CoSn(OH) ₆	300 W Xe lamp (420 nm)	TEOA MeCN	CO	18.70 μmol h ⁻¹	[6]

Table S4 Control experiment.

Photocatalyst	Gas reaction	Sacrificial agent	Gas product
8%-TiO ₂ /Ti ₃ C ₂	CO ₂	TEOA	H ₂ , CO, CH ₄
8%-TiO ₂ /Ti ₃ C ₂	CO ₂	None	None
8%-TiO ₂ /Ti ₃ C ₂	Ar	TEOA	H ₂
8%-TiO ₂ /Ti ₃ C ₂	CO ₂	Na ₂ SO ₃	None
8%-TiO ₂ /Ti ₃ C ₂	CO ₂	Methanol	H ₂
Ti ₃ C ₂	CO ₂	TEOA	None
None	CO ₂	TEOA	None

Table S5 FTIR characteristic spectrum of band assignment for 8%-TiO₂/Ti₃C₂ after reaction.

Wavenumber/cm ⁻¹	Description
3354	ν (O-H)
2948	ν_s (C-H)
2879	ν_{as} (C-H)
1635	δ (H-O-H)
1465	γ (C-H)
1038	ν (C-N)

Reference

1. L. Lin, C. Hou, X. Zhang, Y. Wang, Y. Chen and T. He, *Appl. Catal. B: Environmen.*, 2018, **221**, 312-319.
2. Y. n. Yao, Y. Gao, L. Ye, H. Chen and L. Sun, *J. Energy Chem.*, 2018, **27**, 502-506.
3. J. Qin, L. Lin and X. Wang, *Chem. Commun.*, 2018, **54**, 2272-2275.
4. H. Zhao, X. Wang, J. Feng, Y. Chen, X. Yang, S. Gao and R. Cao, *Catal. Sci. & Technol.*, 2018, **8**, 1288-1295.
5. Z.-C. Fu, R.-C. Xu, J. T. Moore, F. Liang, X.-C. Nie, C. Mi, J. Mo, Y. Xu, Q.-Q. Xu, Z. Yang, Z.-S. Lin and W.-F. Fu, *Chem. – A Eur. J.*, 2018, **24**, 4273-4278.
6. X. Lin, Y. Gao, M. Jiang, Y. Zhang, Y. Hou, W. Dai, S. Wang and Z. Ding, *Appl. Catal. B: Environ.*, 2018, **224**, 1009-1016.