Synergy of surface fluorine and oxygen vacancy of TiO_2 nanosheets for O_2 activation in selective photocatalytic organic transformation

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Table S1 Distribution of atomic contents of various elements on the photocatalyst surface.

Sample	Element name	Atomic %
TiO_2-B-0h	C 1s	14.58
	Ti 2p	23.23
	O 1s	53.17
	F 1s	9.02
TiO_2-B-4h	C 1s	11.12
	Ti 2p	22.21
	O 1s	51.07
	F 1s	8.49
TiO_2-B-6h	C 1s	11.17
	Ti 2p	22.06
	O 1s	51.47
	F 1s	7.95
TiO_2-B-18h	C 1s	12.5
	Ti 2p	21.17
	O 1s	54.84
	F 1s	1.53

Table S2 Distribution of base sites over the different TiO_2 photocatalysts obtained by CO_2-TPD.

Entry	photocatalyst	Alkalinity (mL/g)			
		Weak	Medium	Strong	Total
1	TiO_2-B-0h	7.8	2.7	0.54	11.0
2	TiO_2-B-2h	3.8	6.3	0	10.1
3	TiO_2-B-4h	1.7	4.4	0	6.1
4	TiO_2-B-6h	1.7	4.5	0	6.2
5	TiO_2-B-18h	2.1	5.9	0	8.0

Table S3 Distribution of acidic sites over the different TiO_2 photocatalysts obtained by NH_3-TPD

Entry	photocatalyst	Acidity (μmol/g)			
		Weak	Medium strong	Strong	Total
1	TiO_2-B-0h	28.5	31.4	51.6	111.5
2	TiO_2-B-2h	34.5	37.6	65.1	137.2
3	TiO_2-B-6h	32.6	36.0	61.9	130.4
4	TiO_2-B-18h	31.1	40.5	47.0	118.6

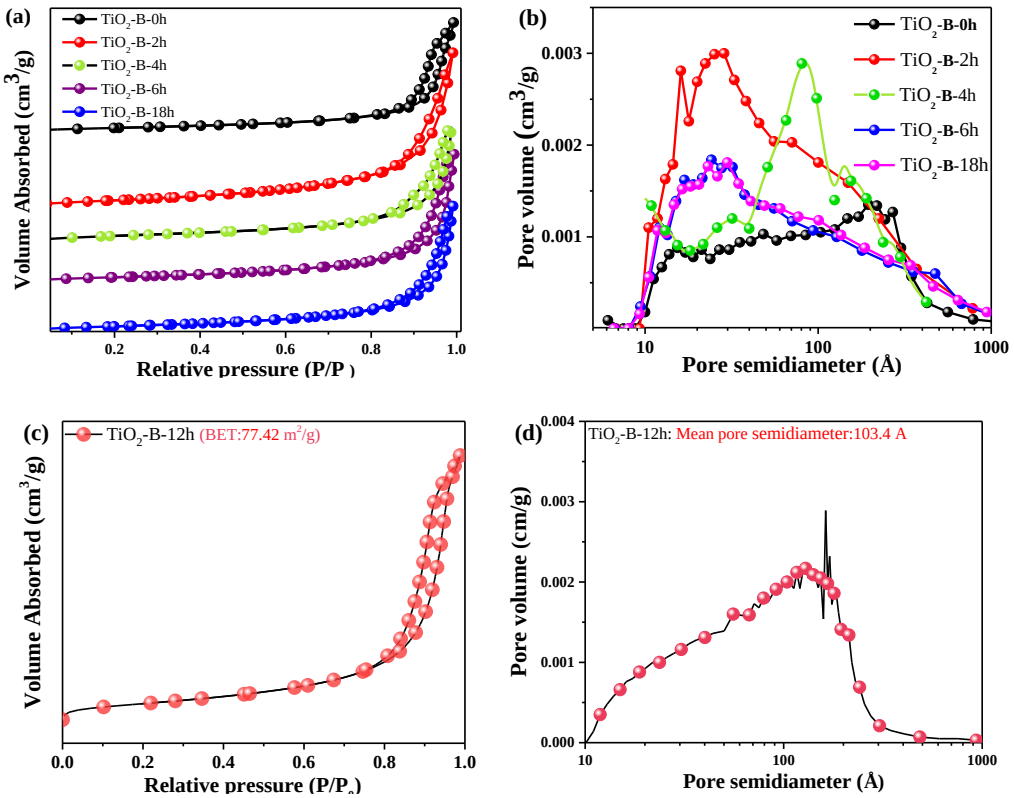

Fig. S1 The isothermal curves and pore size distribution diagram of BJH desorption over different TiO_2 photocatalysts treated with 0.1mol/L of NaOH solution for different times.

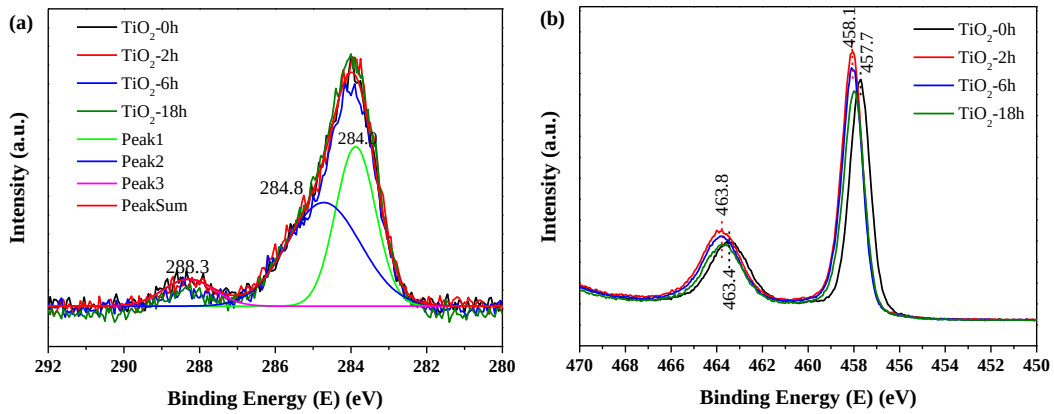

Fig. S2 High-resolution XPS spectra of C1s and Ti2p.

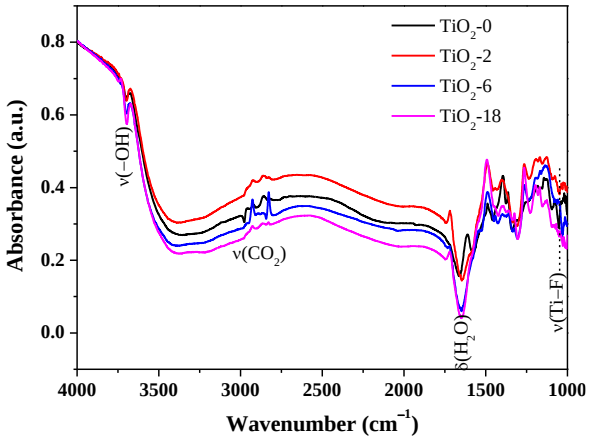

Fig. S3 FTIR spectra of the photocatalysts.

Surface fluorine is further confirmed from FTIR analysis that shows a Ti−F stretching vibration at the 1050 cm^{-1}.[1]

[1] A. Biswas, A. Chakraborty, N. R. Jana, *ACS Appl. Mater. Interfaces*, 2018, **10**, 1976.

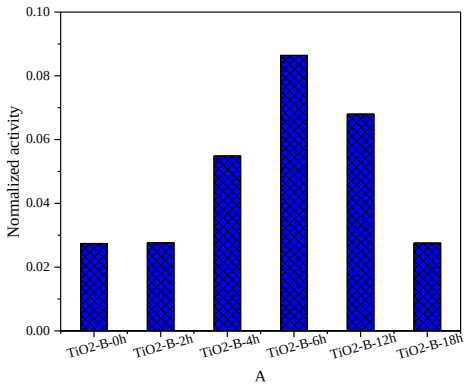

Figure S4 Normalized reaction constants of photocatalytic hydrogen evolution.

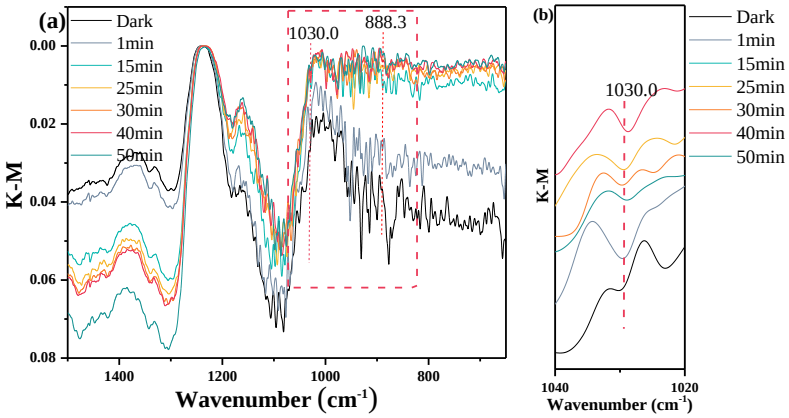

Fig. S5 FTIR spectra of TiO_2-B-6h under UV-vis light.

The photocatalyst was treated at 150 ºC for 30 min in vacuum to eliminate the adsorbed water molecules and other gaseous molecules. The measurement: 30 ºC in N_2, molecular oxygen flow was introduced into the in situ reaction cell and lasted for 40 min, to achieve the saturated adsorption of O_2. The system then was degassed for 40 min to remove the O_2 molecules that were not been adsorbed on the photocatalyst, and the IR spectrum was collected. The reaction was performed under irradiation of ultraviolet visible light, and the IR spectra was recorded continuously, lasting for 50 min.

The band at about 1030 cm^{-1} can be assigned to the O_2^-.[2,3] The fluctuated change of band at 889 cm^{-1} indicates the generation and consumption of superoxide anion.

[2] L. Vaska, *Accounts Chem. Res.*, 1976, **9**, 175.
[3] C. Mao, H, Cheng, H. Tian, H. Li, W.-J. Xiao, H. Xu, J. Zhao, L. Zhang, *Appl. Catal. B- Environ.,* 2018, **228**, 87.

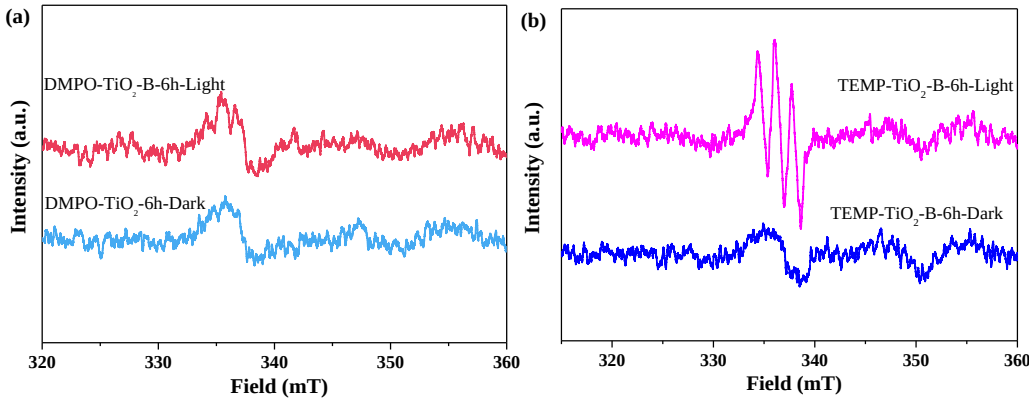

Fig. S6 (a, b) EPR signals generated over TiO_2-B-6h nanosheets, using DMPO and TEMP to capture the superoxide species and singlet oxide in acetonitrile, respectively.

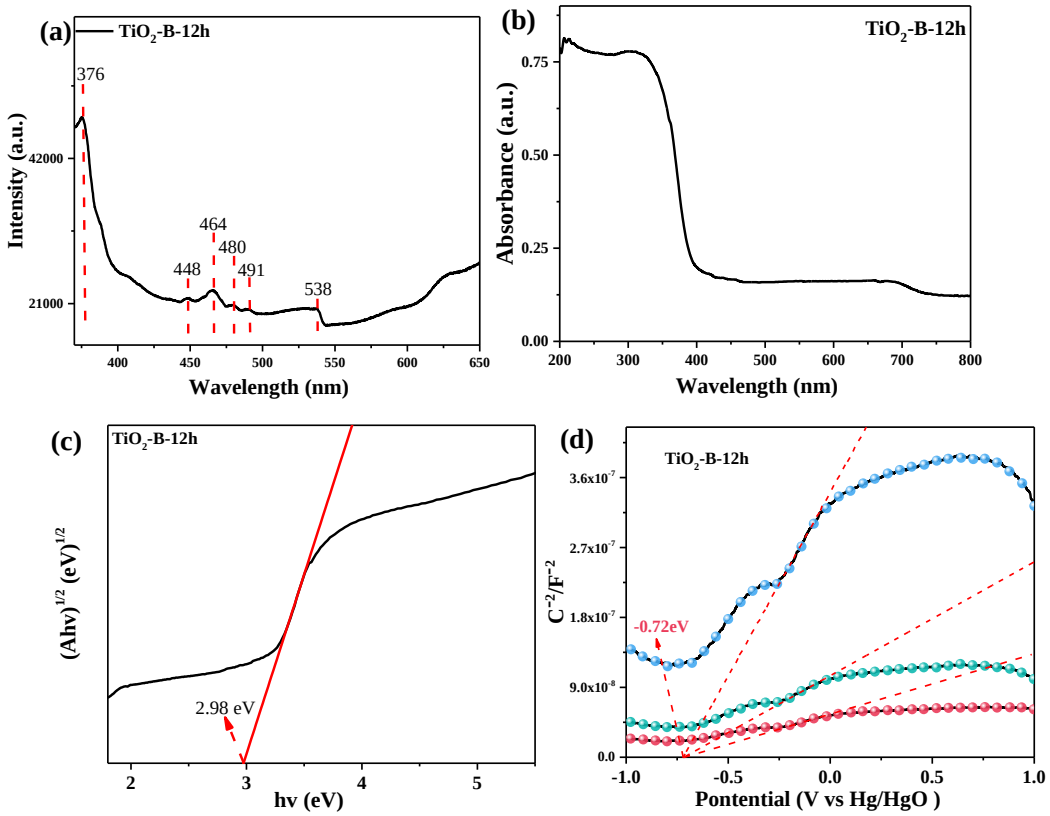

Fig. S7 (a) PL spectra, (b) UV-vis diffused reflectance spectra, (c) Tauc-plot, and (d) Mott-Schottky plots of TiO_2-B-12h photocatalyst.