Electronic Supplementary Information

Fabrication of brookite@anatase heterojunction TiO_2 via phase transformation from metal organic frameworks for enhanced photocatalytic hydrogen evolution and TCH degradation

Weina Song, [a, #] Yamin Liu, [a, #] Yongli Dong, [a]* Xue Han, [a] Mei Mu, [a] Yan Chen, [b] Wenyan Wang, [a] Pei Wang, [a] and Wei Li [b]*

[a] *School of Environmental and Chemical Engineering, Heilongjiang University of Science and Technology, Harbin 150080, PR China*

[b] *Department of Chemistry, Fudan University, Shanghai 200433, PR China*

[#] *These authors make equal contribution to this work*

* *Corresponding author: Yonglidong163@163.com (Y. Dong); weilichem@fudan.edu.cn (W. Li)*

Experimental section

1. Electrochemical measurements

All the electrochemical tests of electrochemical impedance spectroscopy (EIS), transient photocurrent response and Mott-Schottky plots were performed on CHI660E electrochemical workstation with a standard three-electrode system with the photocatalyst-coated FTO as the working electrode, Pt plate as the counter electrode, and a saturated calomel electrode as a reference electrode at room temperature. Na_2SO_4 solution (0.25 M) was used as the electrolyte. The as-synthesized samples (2 mg) were added into 1 mL ethanol and10 uL Nafion mixed solution, and the working electrodes were prepared by dropping the suspension (200 uL) onto an FTO glass substrate electrode surface and dried at room temperature.[1]

2. Regulation of time factor for the heterophase junction TiO_2

In a typical synthetic procedure, the terephthalic acid (3 g, 18 mmol) and tetrabutyl titanate (1.56 mL, 4.5 mmol) were added into a solution of dimethylformamide (54 mL, extra-dry) mixed with dry methanol (6 mL). The mixture was stirred gently for 1 hour at room temperature to obtain a uniform solution. Subsequently, the solution was introduced in a 100 mL Teflon liner and performed solvothermal reaction at 200 °C for 1, 2, 4, 8, 12, 16, 20 hours, respectively. The obtained white solid was washed with DMF and ethanol thoroughly in order to remove excess unreacted raw materials, and dried at 60 °C for 6 hours. Heterophase junction TiO_2 catalysts synthesized under 200 °C were marked as MT-200-BA-X (X = 1, 2, 4, 8, 12, 16, 20, representing synthesis time of 1 h, 2h, 4h, 8 h, 12 h, 16 h, 20 h, respectively.

To determine the relative contents of brookite and anatase, all the MT-200-BA-X samples were examined by X-ray diffraction (XRD). The XRD patterns (Fig. S1) were collected by using a

scanning speed of 0.24°/min in the 2θ range of 22-34°. The phase content of a sample can be calculated from the integrated intensities of anatase (101) and brookite (121) peaks. The weight fraction of brookite (W_B) and anatase (W_A) can be calculated from: $W_B = k_B A_B/(k_B A_B + k_A A_A)$ and $W_A = k_A A_A/(k_B A_B + k_A A_A)$, and the weight ratio of brookite to anatase ($W_B : W_A$) can be calculated by $W_B : W_A = k_B A_B : k_A A_A$, where A_A and A_B represent the integrated intensity of the anatase (101) and rutile (110) peaks, respectively, k_A and k_B are two coefficients ($k_A = 0.886$ and $k_B = 2.721$).[2]

Table S1

Photocatalytic and adsorption performance of MT-200-BA catalyst for the degradation of TCH with different concentration.

TCH concentration (mg L^{-1})	Adsorption rate (%)		Photodegradation rate (%)
	30 min	60 min	
20	83.1	85.7	14.2
40	58.5	62.2	37.8
60	31.8	34.5	60.6
80	18.6	20.1	71.4
100	12.1	13.0	70.6

Table S2

Photocatalytic and adsorption performance for TCH degradation (100 g L^{-1}) upon various MT-200-BA-X samples.

Sample	Adsorption rate (%)		Photodegradation rate (%)
	30 min	60 min	
MT-200-BA-1	47.9	48.6	16
MT-200-BA-2	48.1	51.0	37.1
MT-200-BA-4	42.4	44.0	39.4
MT-200-BA-8	38.4	42.4	49.8
MT-200-BA-12	31.5	36.1	53.5
MT-200-BA-16	17.7	22.0	66.5
MT-200-BA-20	13.3	13.3	70.6

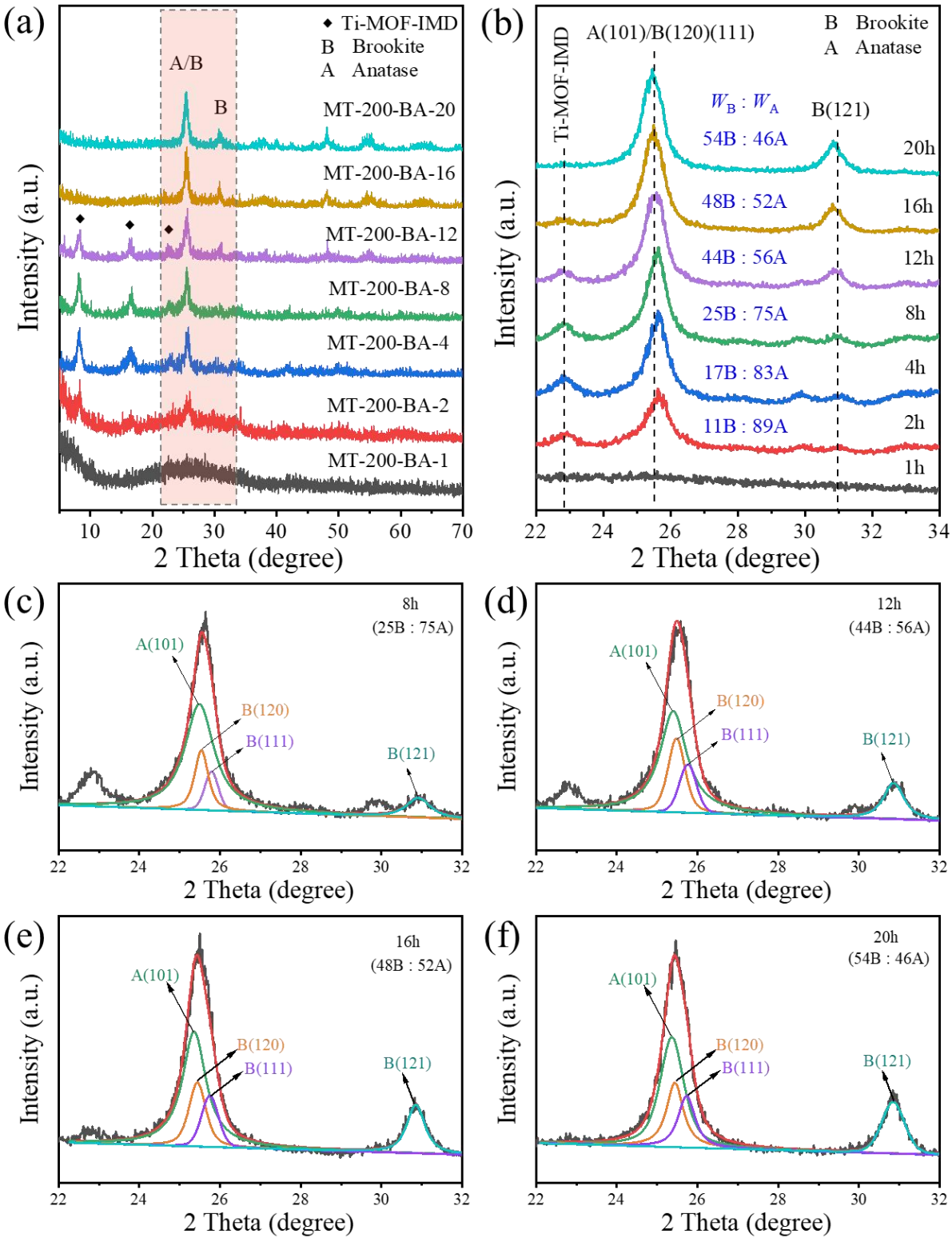

Fig. S1 (a) Wide angle XRD and (b) selected range slow scanning XRD patterns of MT-200-BA-X (X = 1, 2, 4, 8, 12, 16 and 20) samples prepared at different synthesis times, and deconvolution of XRD patterns of MT-200-BA-8 (c), MT-200-BA-12 (d), MT-200-BA-16 (e) and MT-200-BA-20 (f).

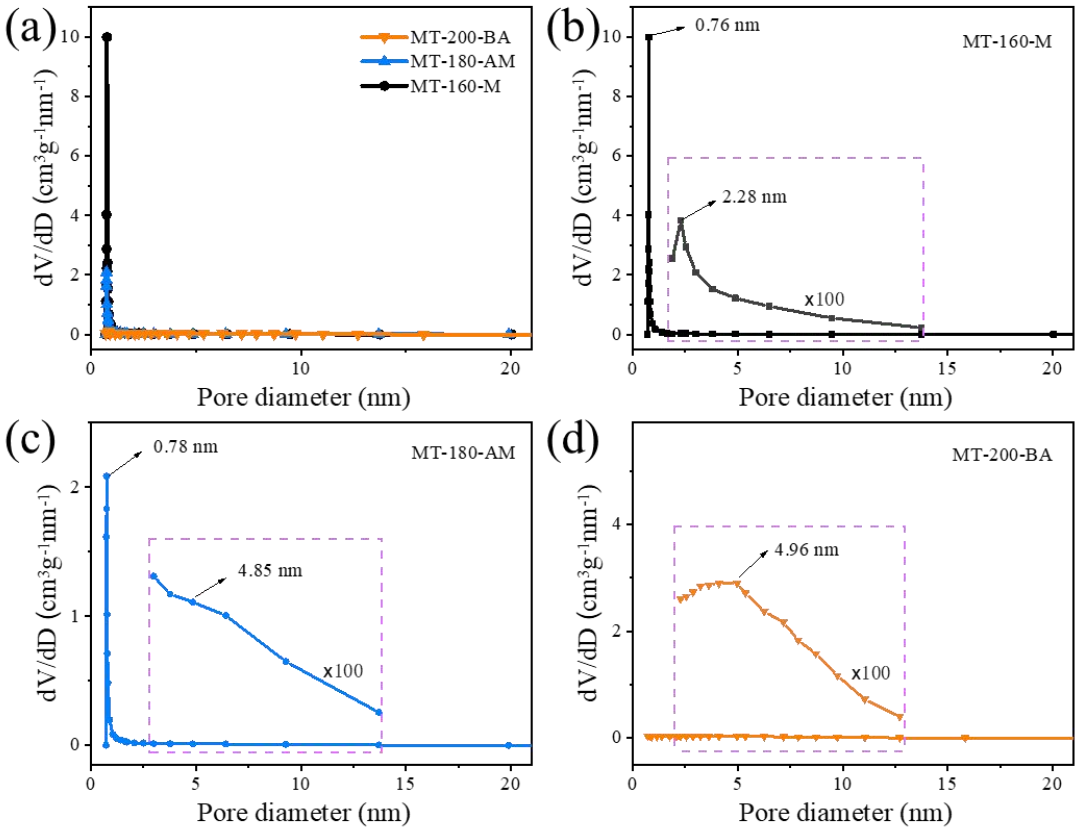

Fig. S2 (a) The pore size distributions and separately magnified curves of MT-160-M (b), MT-180-AM (c) and (d) MT-200-BA samples.

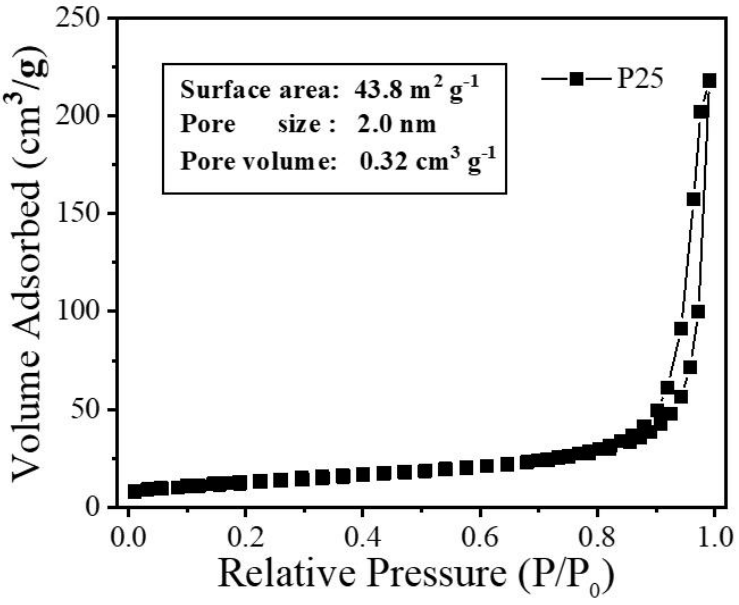

Fig. S3 N_2 adsorption-desorption isotherms of commercial P25 catalyst.

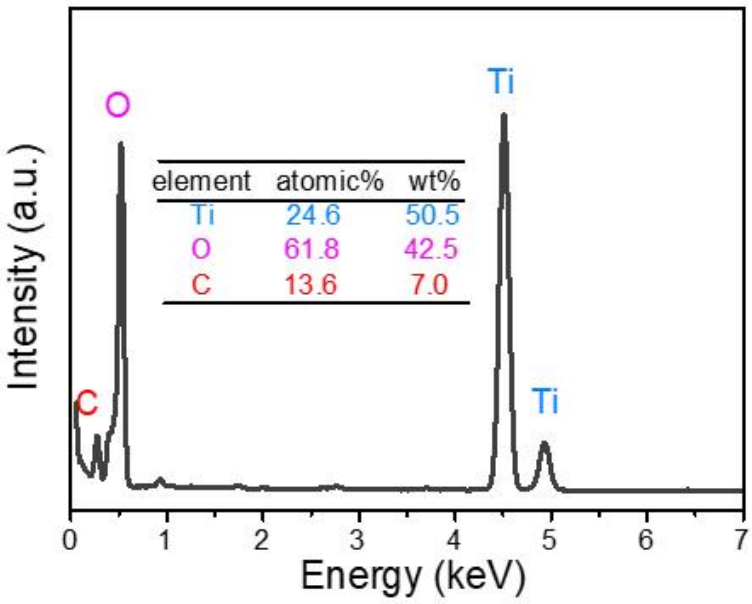

Fig. S4 EDS analysis results of MT-200-BA sample.

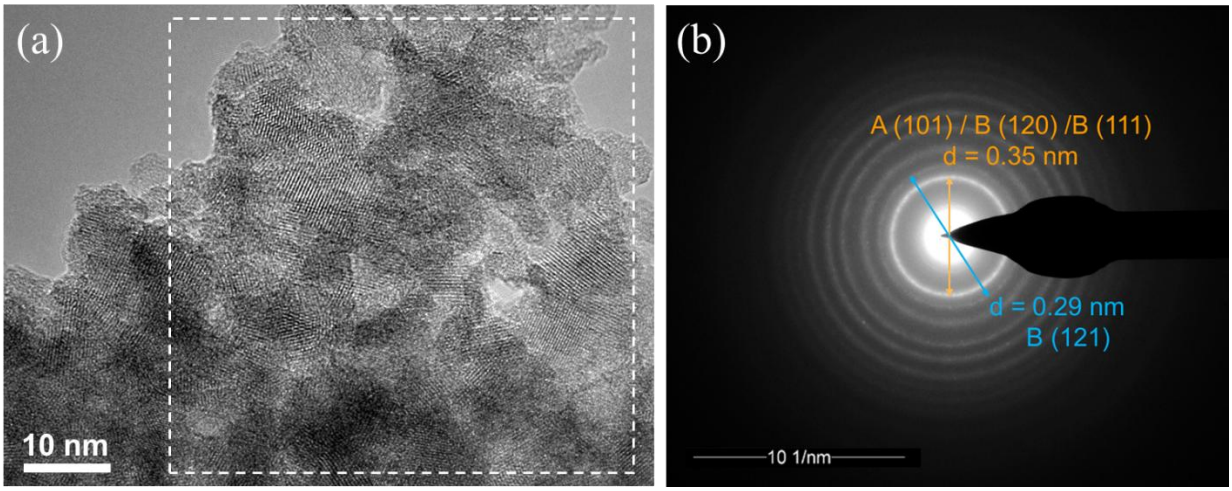

Fig. S5 (a) TEM image and (b) SAED pattern of the MT-200-BA sample

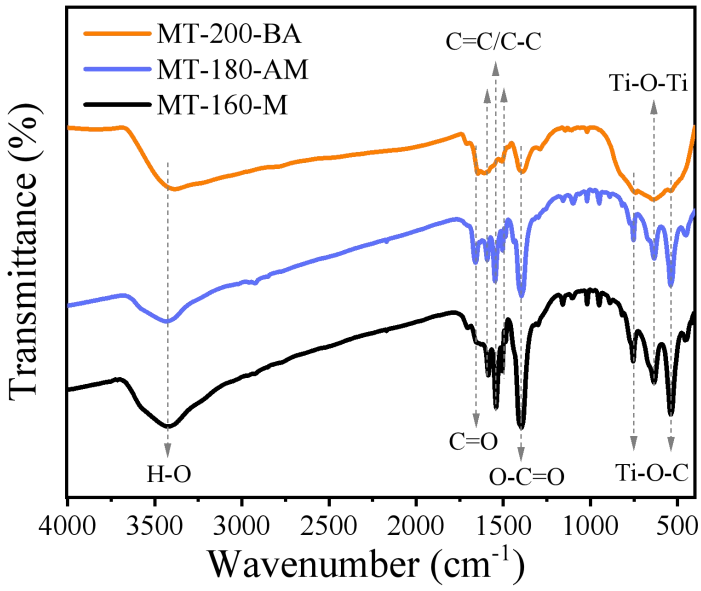

Fig. S6 FT-IR spectra of MT-160-M, MT-180-AM and MT-200-BA.

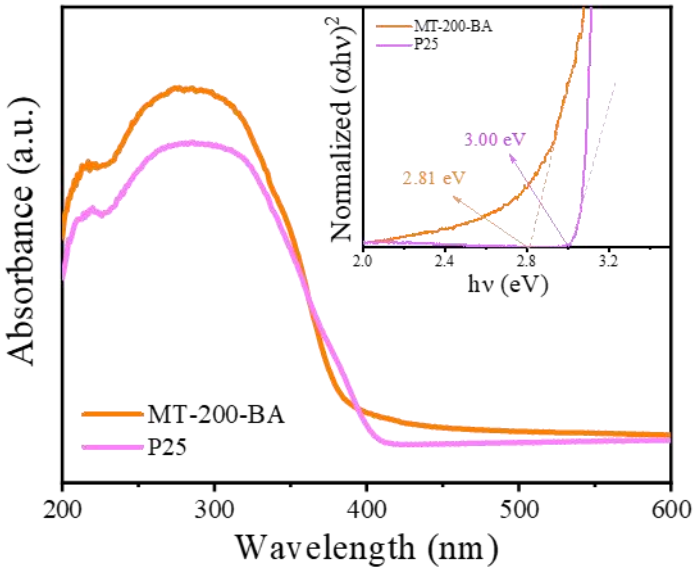

Fig. S7 UV-vis DRS spectra of P25 and MT-200-BA, and corresponding band gap energies calculated by using the Tauc plot method (inset).

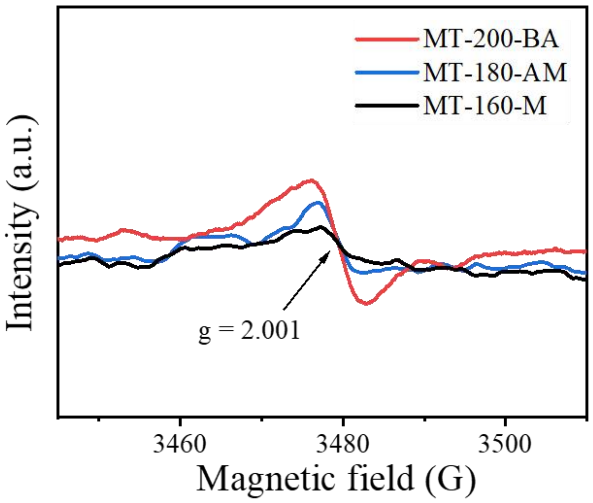

Fig. S8 EPR profiles of MT-160-M, MT-180-AM and MT-200-BA samples.

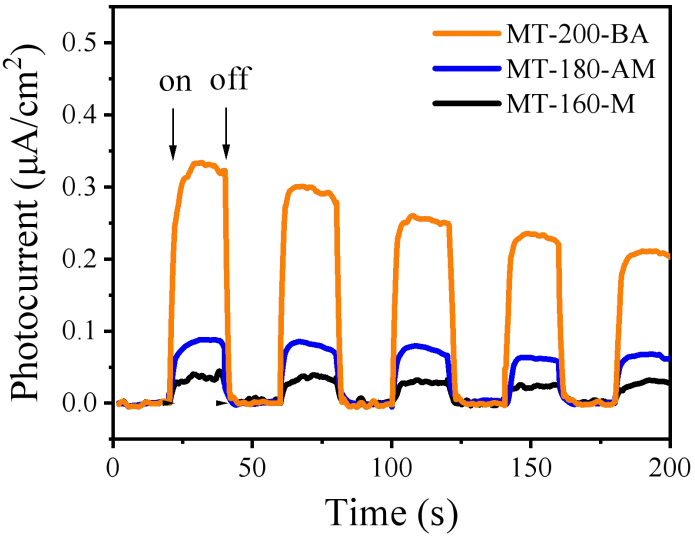

Fig. S9 Transient photocurrent measurements for MT-160-M, MT-180-AM and MT-200-BA on FTO substrate in a 0.2 M Na_2SO_4 electrolyte.

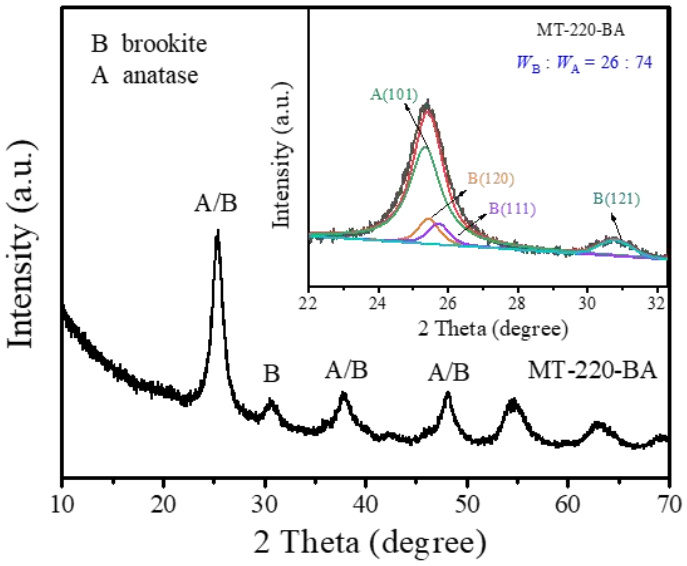

Fig. S10 XRD pattern of the MT-220-BA reference sample prepared at solvothermal temperature of 220 ℃, the inset is deconvolution of XRD pattern of MT-220-BA.

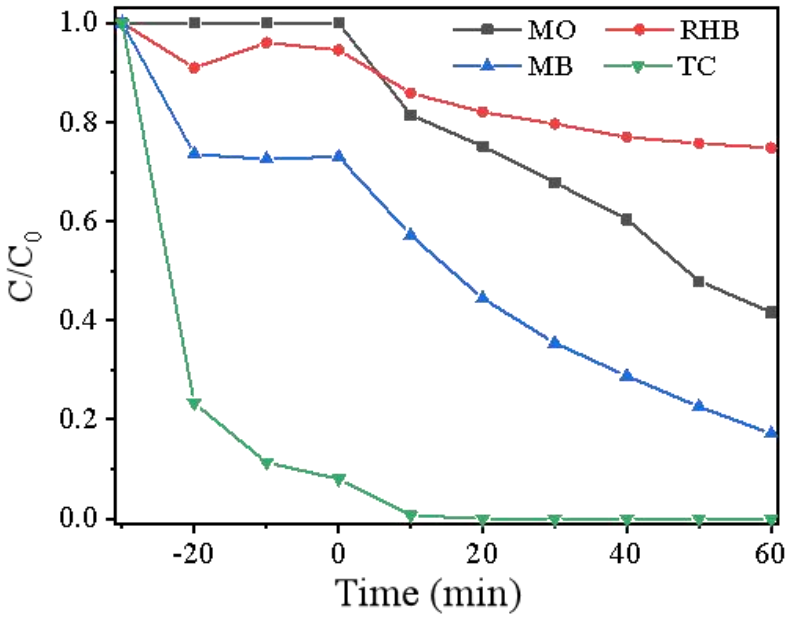

Fig. S11 Photocatalytic degradation of MO, RHB, MB and TCH pollutants in solution (20 mg L^{-1}) upon MT-200-BA sample.

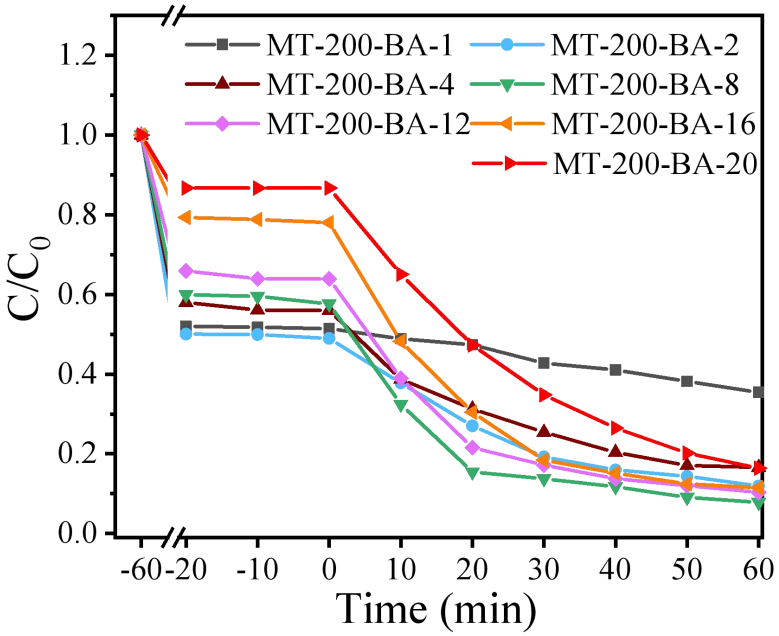

Fig. S12 Photocatalytic degradation of TCH over various MT-200-BA-X samples at a concentration of 100 mg L^{-1}.

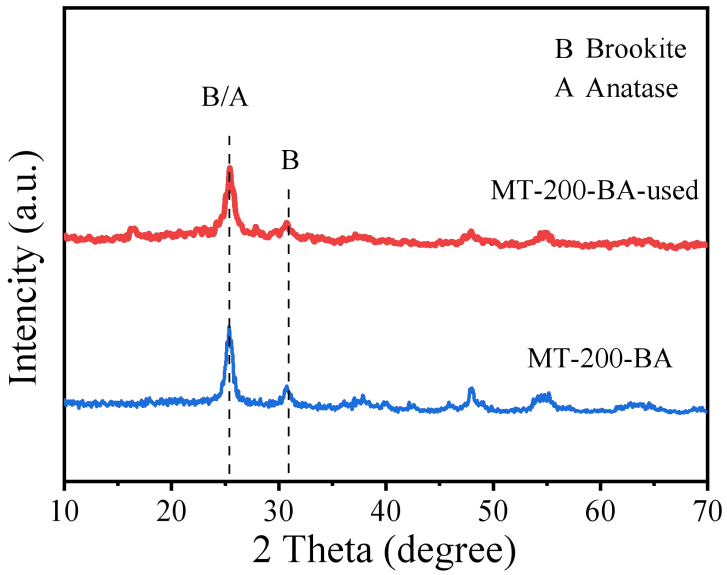

Fig. S13 XRD patterns of MT-200-BA and MT-200-BA-used samples.

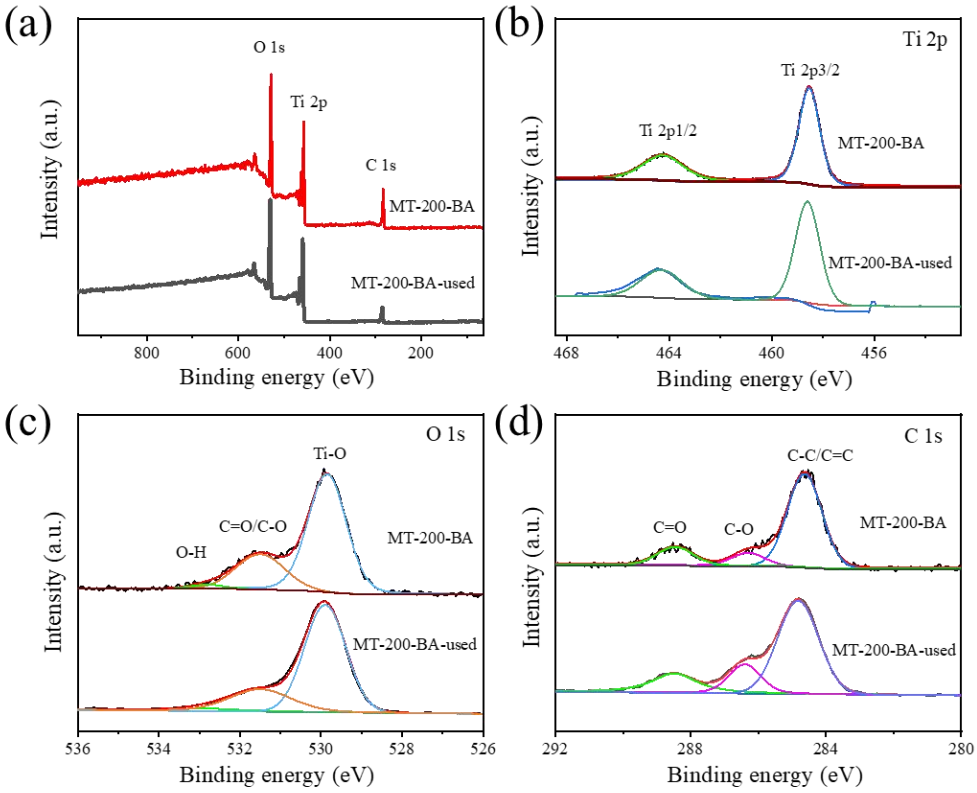

Fig. S14 (a) XPS survey spectra, (b) Ti 2p, (c) O 1s and (d) C 1s spectra of MT-200-BA and MT-200-BA-used samples.

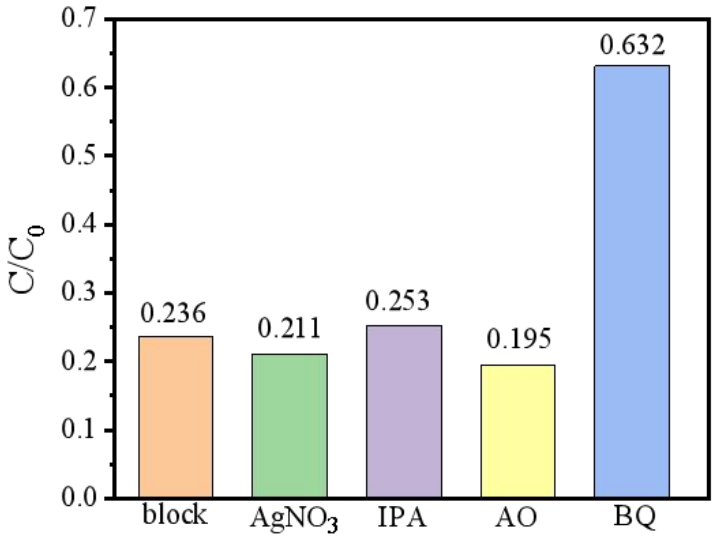

Fig. S15 Trapping experiments of active species during photocatalytic degradation of TCH (100 mg/L) over MT-200-BA under Xe light irradiation.

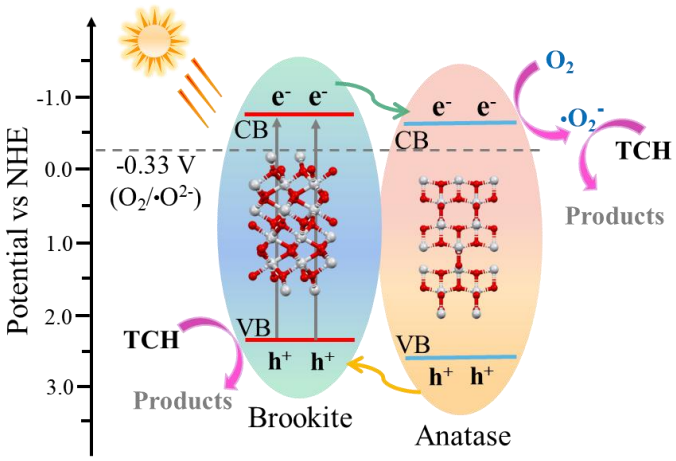

Fig. S16 The possible mechanism schematic for photocatalytic TCH degradation upon MT-200-BA under light irradiation.

References

[1] F. Zhang, J. Sheng, Z. Yang, X. Sun, H. Tang, M. Lu, H. Dong, F. Shen, J. Liu, Y Lan, *Angew. Chem. Int. Edit.*, 2018, **57**, 12106–12110.

[2] H. Zhang, J. Banfield, *J. Phys. Chem. B*, 2000, **104**, 3481–3487.