# *Electronic Supplementary Information for*

## Wet-chemical intercalation of Bi$_4$TaO$_8$Br with self-adaptive structural deformation for enhanced photocatalytic performance

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### 1. Preparation of modified Bi$_4$TaO$_8$Br

*1.1. Materials*

Bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O, ≥99.0%) and tantalum oxide (Ta$_2$O$_5$, 99.5%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., bismuth oxide (Bi$_2$O$_3$) was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd., sodium chloride (NaCl, AR) , potassium chloride (KCl, AR) and potassium bromide (KBr, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd., polyvinylpyrrolidone K 30 (PVP, K30) was purchased from Bide Pharmatech Ltd., sodium borohydride (NaBH$_4$) was purchased from Wuhan Geao Chemical Technology Co., Ltd.

## 1.2. Synthetic experiment

### 1.2.1. Synthesis of BiOBr

In a typical procedure, $Bi(NO_3)_3 \cdot 5H_2O$ and KBr with a molar ratio of 1:1 were respectively dissolved in 40 mL deionized water and stirred. Then, the bromine salt solution was slowly dropwise added to the bismuth salt solution, the mixture was stirred for 1 h and ultrasonic dissolution 10 min. The mixture was poured into a 100 mL Teflon-lined stainless autoclave and hydrothermal reaction was adopted at 150 °C for 10 h. Finally, the collected precipitates were washed several times with ethanol and deionized water, and dried at 60 °C for 10 h.

### 1.2.2. Synthesis of $Bi_4TaO_8Br$

2D $Bi_4TaO_8Br$ nanosheets were prepared by the molten salt method. Mixed BiOBr, $Bi_2O_3$ and $Ta_2O_5$ with a molar ratio of 1:2:3 and ground for 15 min, then NaCl and KCl (molar ratio of $Ta_2O_5$: BiOBr: $Bi_2O_3$: NaCl: KCl is 1:2:3:30:30) were added and ground for 30 min to get a uniform mixture. Finally, the mixture was heated at 700 °C under air condition for 14 h at a ramp rate of 2 °C/min in muffle furnace. After the muffle furnace naturally cooled to room temperature, the obtained yellow $Bi_4TaO_8Br$ powder was washed several times with hot water and ethanol and dried at 60 °C for 10 h.

### 1.2.3. Synthesis of the modified $Bi_4TaO_8Br$

In this study, modified $Bi_4TaO_8Br$ was synthesized by using the above prepared $Bi_4TaO_8Br$ as precursor and $NaBH_4$ as insertion agent. In detail,0.20 g of $Bi_4TaO_8Br$ and 0.40 g of PVP were added to 20 mL of deionized water, and the solution was stirred at a fixed speed for 40 min to obtain solution A. After that, $NaBH_4$ with different masses

(the mass ratio of NaBH$_4$ to BTOB is 3%, 10% and 17%) was quickly added in 20 mL deionized water and sealed, then the ultrasonic dissolution and shaking were conducted to the mixture simultaneously, the entire process lasts for 30 s to obtain solution B. Next, solution B was added to solution A quickly drop by drop, and the mixed solution was sealed and stirred at another fixed speed for 1 h. Finally, the collected solution was washed several times with deionized water and the samples were lyophilized in a vacuum freeze dryer for 12 h. It should be noted that the stirring speed of the solution is the same during the preparation of modified samples with different proportions.

## 2. Characterization

The XRD diffraction patterns of the prepared samples were determined by AXS D8 ADVANCE from Bruker, Germany. The morphology and structural of the samples were characterized by scanning electron microscopy and transmission electron microscopy, the model of SEM is HITACHI, SU8010, and the model of TEM is Talos F200x from Thermo Fisher Scientific. XPS method was used for studying the chemical environment of the electronic structure composition and surface state of catalyst materials, the instrument is K-alpha from Thermo Scientific, America. The BET test by the V-sorb 2800P instrument from Gold APP Instruments Corporation China which was applied to the analysis of the surface area and pore structure of materials. Ultraviolet visible diffuse reflectance spectroscopy (DRS) was used to characterize the optical absorption properties of semiconductor materials and the model of instrument is UV-2600. By using a Fluoromax-4P fluorescence spectrometer to compare the separation efficiency of photogenerated electrons and holes in various catalyst samples.

The Bruker EMXplus-6/1 paramagnetic resonance spectrometer was used to characterize the oxygen vacancies which in the prepared samples. Transient photocurrent, electrochemical impedance spectroscopy and Mott-Schottky curve were tested on electrochemical workstation of CH Instruments.

## 3. Photocatalytic measurements

The photocatalytic properties of all catalysts were measured by using the photodegradation method for different pollutants. Photocatalytic experiments were conducted in a multi path photochemical reaction system and the model of instrument is PCX50B from Beijing Perfect Optical Technology Co. In detail, a 5 W white LED is used as visible light source. Typically, 20 mg of sample was dispersed in 10 mg/L of different pollutants solution for photocatalytic activity testing. The residual concentration of pollutant was determined by using UV visible spectrophotometer.

# 4. Supplementary results and discussion

*4.1 Morphology analysis*
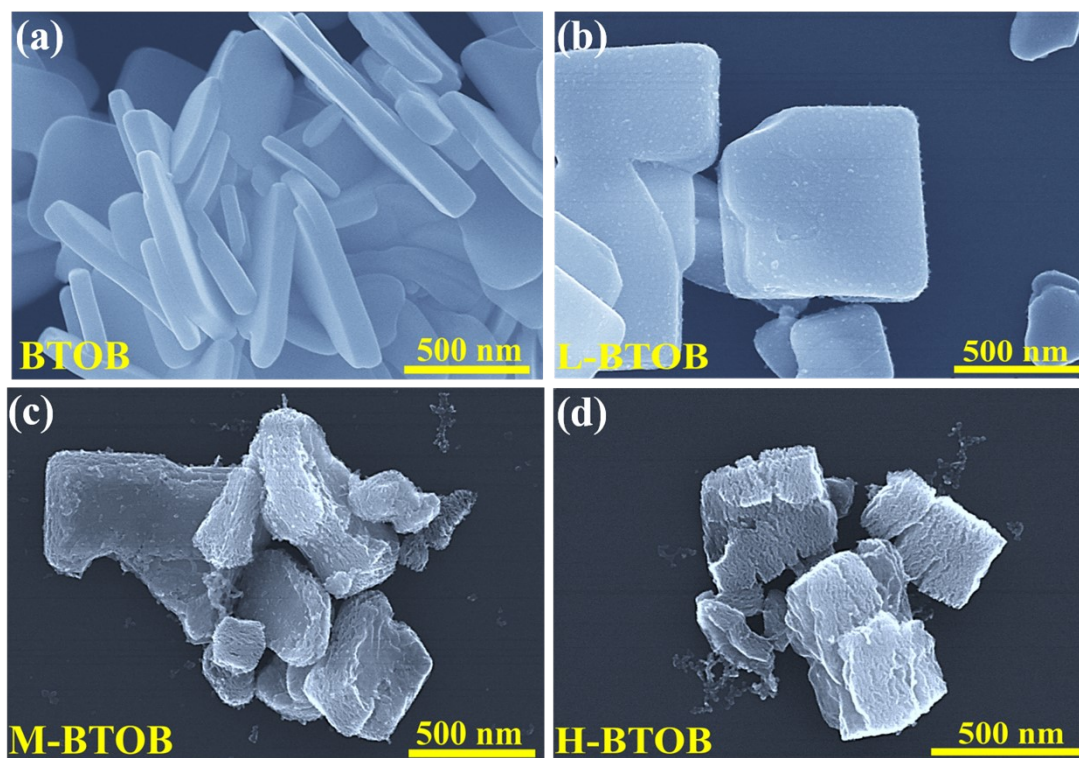


**Fig. S1** The SEM images of (a) BTOB, (b) L-BTOB, (c) M-BTOB, (d) H-BTOB
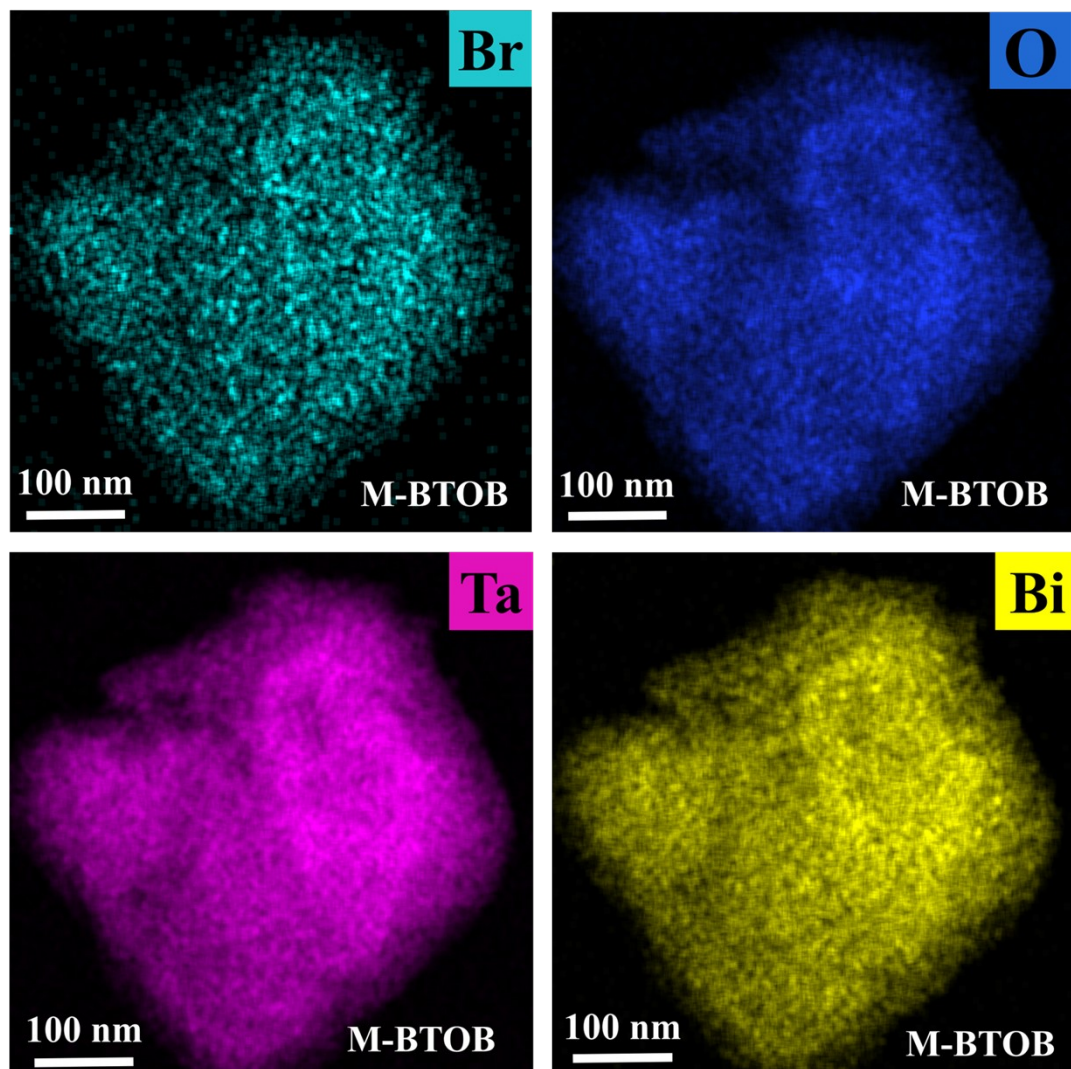
*4.2 Element analysis*



**Fig. S2** TEM-EDS elemental mapping images of M-BTOB.
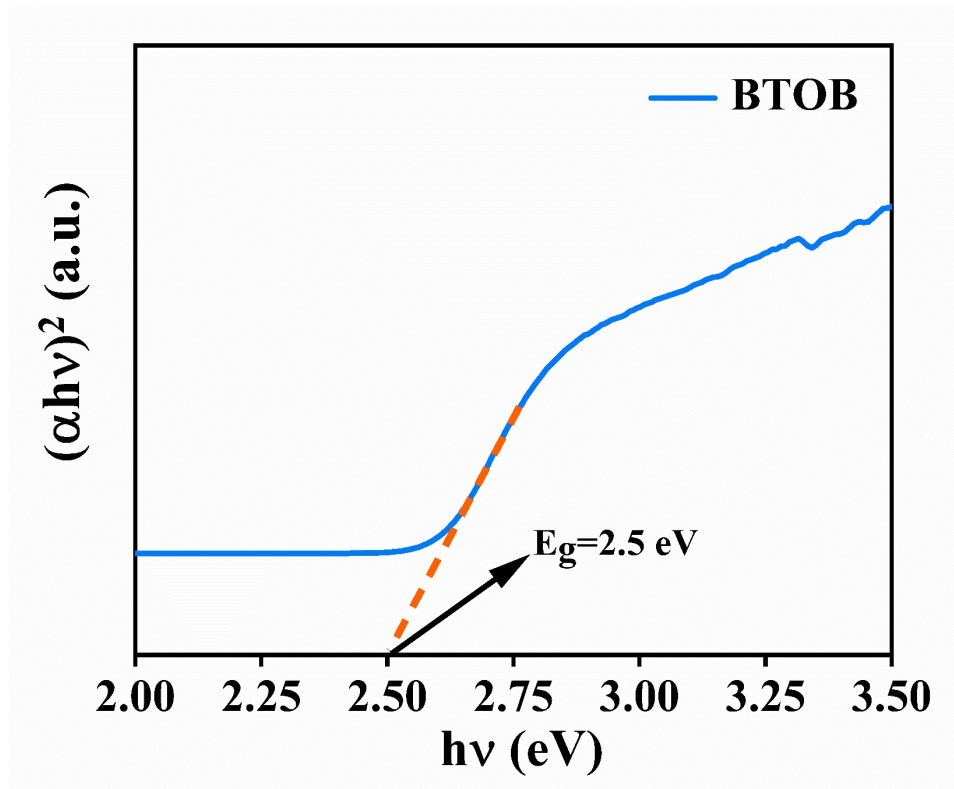
*4.2 Bandgap analysis*



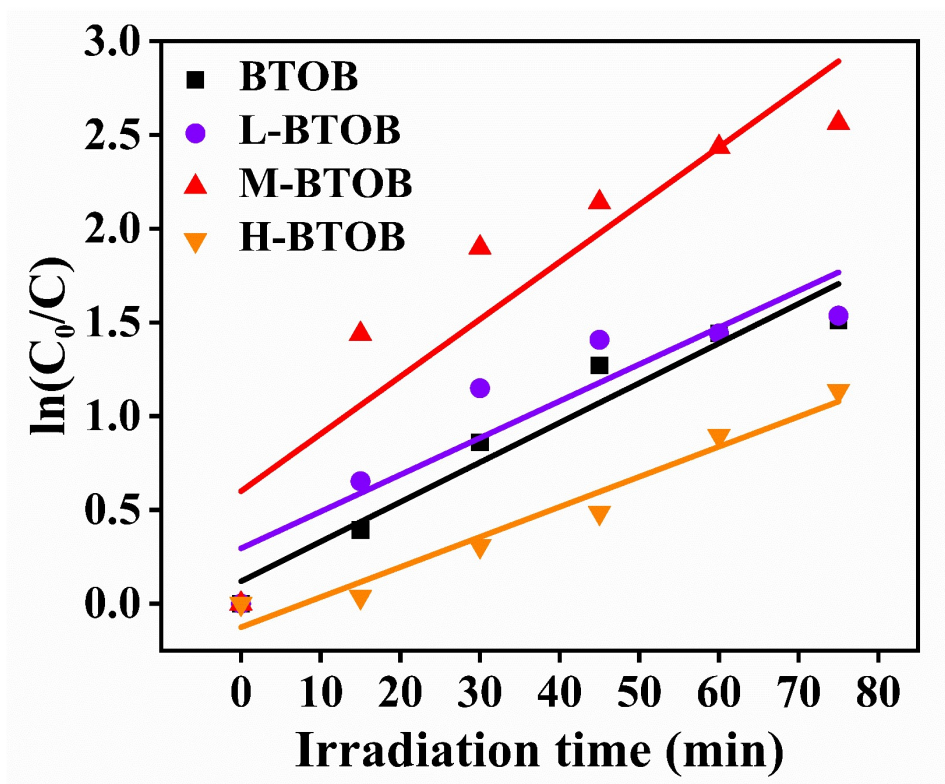**Fig. S3** The band gap of BTOB.

*4.3 Degradation rate analysis*



**Fig. S4** Kinetics curves.

*4.4 BET and porous structure analysis*
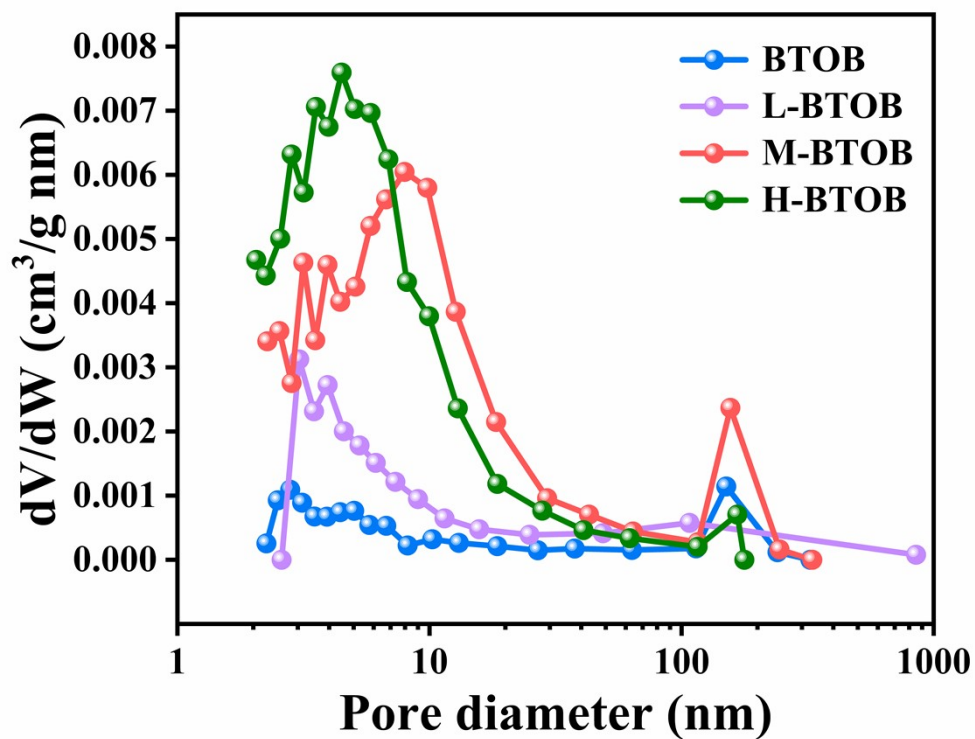
*4.4.1 Pore diameter distribution*



**Fig. S5** BJH pore diameter distribution of samples.

*4.4.2 Detailed data of adsorption*

**Table S1** BET surface area and Zeta potential of samples

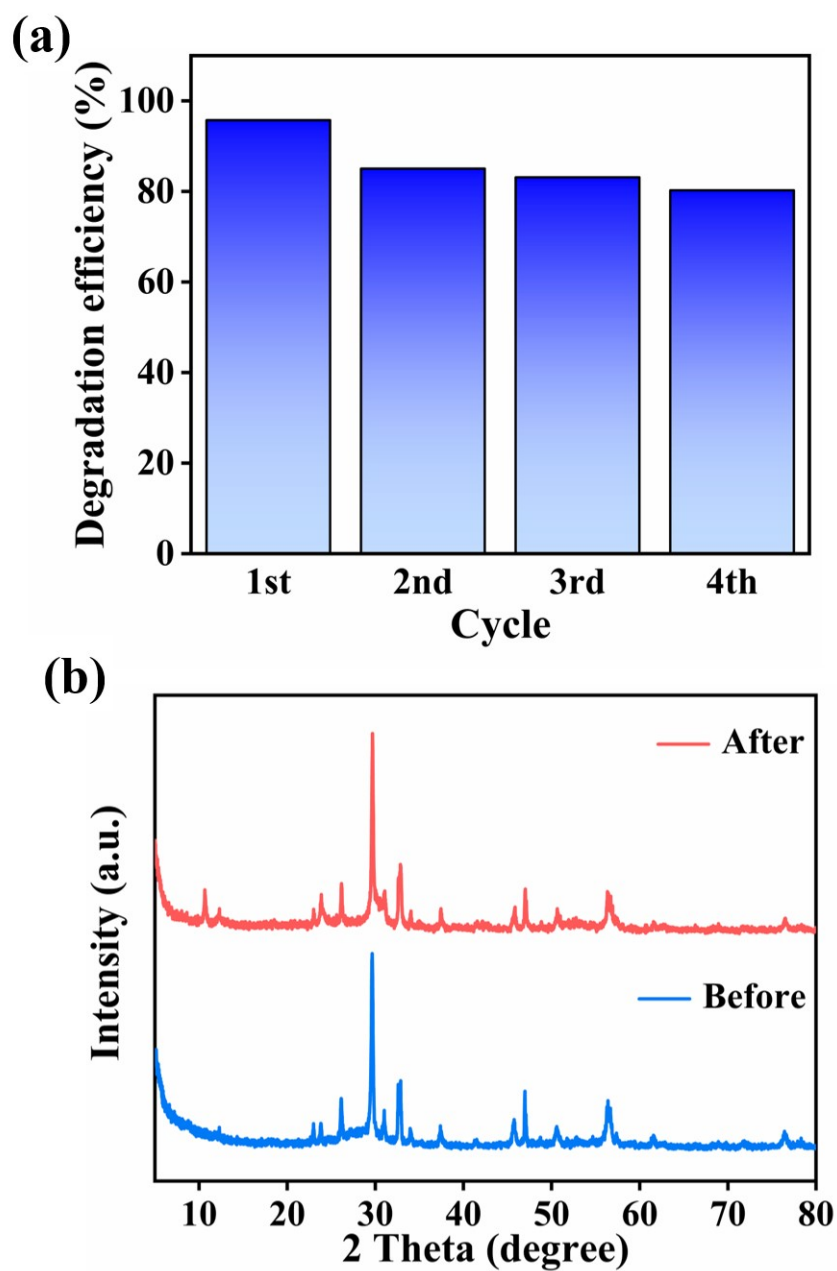| Items | BTOB | L-BTOB | M-BTOB | H-BTOB | OFX |
|---|---|---|---|---|---|
| BET Surface Area $(m^2 \cdot g^{-1})$ | 4.93 | 6.89 | 33.10 | 40.12 | Not appliable |
| BJH Adsorption cumulative volume $(cm^3 \cdot g^{-1})$ | 0.059 | 0.120 | 0.172 | 0.124 | Not appliable |
| BJH Adsorption average pore width (nm) | 37.15 | 33.72 | 15.96 | 10.51 | Not appliable |
| Zeta Potential (mV) | -11.2 | -0.437 | 11.6 | -0.272 | -13.2 |

*4.5 Cyclicing test*



**Fig. S6** The degradation of OFX (a) The cycling test of M-BTOB; (b) the XRD pattern of M-

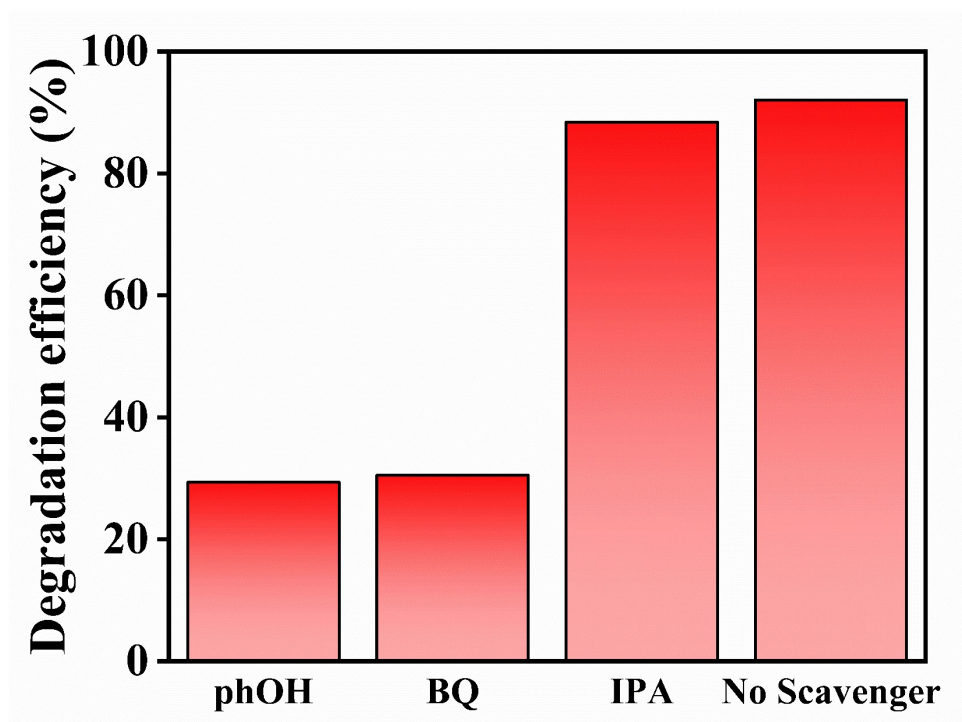BTOB before and after the photocatalytic reaction.

**Fig. S7** The active species test of M-BTOB.

**Notes:** The effects of different scavengers over M-BTOB were tested and BQ, phOH, and IPA were selected as quenching agents for $\cdot O_2^-$, $h^+$, $\cdot OH$, respectivelly.
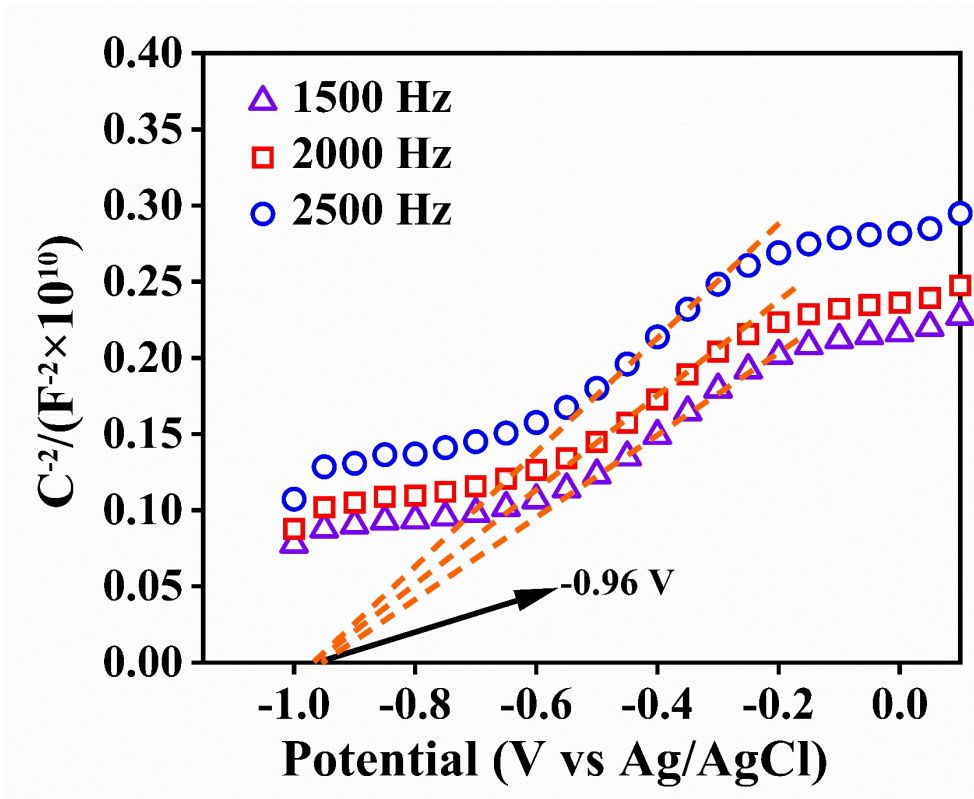
*4.7 The VB and CB of BTOB*



**Fig. S8** The Mott-Schottky curves BTOB.

**Notes:** The Mott-Schottky measurement (Fig. S8) was implemented to confirm the flat band potential positions of samples. It can be seen from the slope that the BTOB belonged to N-type semiconductor and the flat band potential ($E_{fb}$) of N-type semiconductors could be determined by the following equations:

$$\frac{1}{C^2} = \frac{2}{e\varepsilon\varepsilon_0 N_D}(E - E_{fb} - \frac{KT}{e})$$

(C: the capacitance of the space charge layer; e: the elementary charge, $\varepsilon_0$: the permittivity of the vacuum; $\varepsilon$: the permittivity of the semiconductor; ND: the donor density; E: the applied potential; K: the Boltzmann constant; T: the thermodynamic temperature.)

Based on Fig. S8, the E values of BTOB is -0.96V (vs Ag/AgCl) and according to the KT/e = 0.0257, $E_{NHE} = E_{Ag/AgCl} + 0.197$ V. Thus, the $E_{fb}$ of BTOB is -0.79 V (vs NHE), respectively. In general, the conduction band bottom position ($E_{CB}$) of an n-type semiconductor is approximately 0.1 V negative than $E_{fb}$, therefore, the $E_{CB}$ of BTOB is -0.89 V (vs NHE), Meanwhile, the valence band potential ($E_{VB}$) of BTOB was also calculated at 1.61 eV by using the formula $E_g = E_{VB} - E_{CB}$.

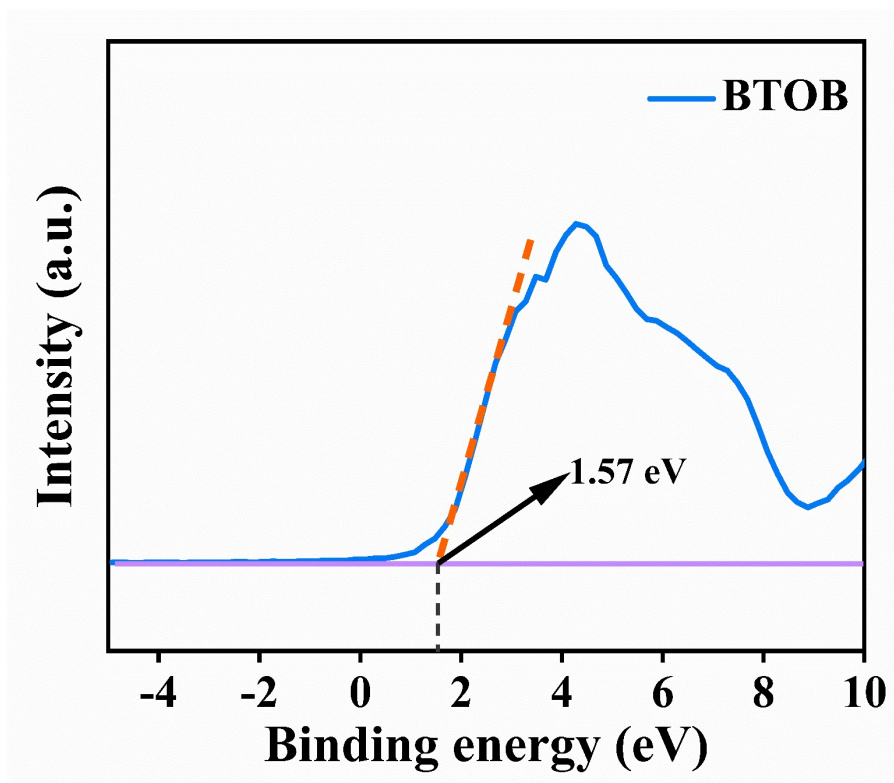*4.8 Fermi energy level of BTOB analysis*



**Fig. S9** The VB-XPS spectrum of BTOB.

**Notes:** The VB-XPS test is in Fig.S9 which shows that $E_{VB}$ of BTOB is 1.57 eV below $E_f$.
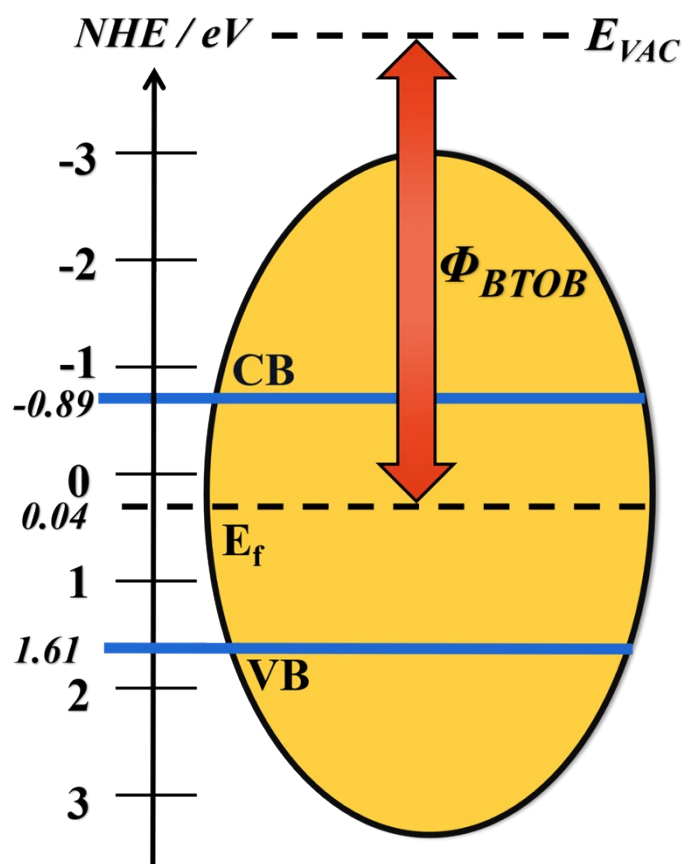
*4.9 Band position of BTOB*



**Fig. S10** The energy band structure diagrammatic sketch of BTOB.