Supplementary Materials

Visible-light-driven BiOBr-TiO_2-attapulgite photocatalyst with excellent photocatalytic activity for multiple xanthates

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Supporting Text I

3. Materials and Methods

3.1 Materials and chemicals

Attapulgite was purchased from Changzhou Dingbang mineral products technology Co., Ltd. Sulfuric acid (H_2SO_4), bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), hydrogen peroxide (H_2O_2), ammonium hydroxide ($NH_3{\cdot}H_2O$), and potassium bromide (KBr) were purchased from Sinopharm Chemical Reagent Co., Ltd. In addition, Shanghai Macklin Biochemical Co., Ltd supported ammonium hexafluorotitanate ($(NH_4)_2TiF_6$). Wuhan Huaxiang Kejie Biotechnology Co., Ltd provided sodium ethyl xanthate (SEX), sodium butyl xanthate (SBX), sodium isoamyl xanthate (SIAX), and sodium isopropyl xanthate (SIPX). The attapulgite was supported by Changzhou Dingbang mineral products technology Co. LTD.

3.2 Microstructure characterization

The crystal phase structure of the samples was observed by X-ray diffraction (XRD, XRD-7000). The morphology of the samples was confirmed by using scanning electron microscope (SEM, Hitachi S-4800) and transmission electron microscope (TEM, JEM-F200). The surface area of the samples was investigated by Brunauer–Emmett–Teller (BET, Quadrasorb SI). The thermogravimetric and differential scanning calorimetry (TG-DSC) analysis was investigated by using an analyzer (STA-8000). An X-ray photoelectron spectroscope (XPS, NexsaG2, thermo scientific) was used to investigate the compositions and valence state of the elements of the obtained composites. Liquid chromatography-mass spectrometry (LC-MS, Agilent 1290 Infinity & Agilent G6125B) was applied to measure the mass/charge ratio (m/z) to determine the intermediate products.

3.3. Preparation of BiOBr-TiO$_2$-Attapulgite composites

This study aimed to synthesize BTA composites using hydrothermal and water-bath methods. Firstly, 5wt% H_2SO_4 solution was employed to activate the attapulgite and eliminate impurities. And then, TiO$_2$-attapulgite (TA) was synthesized through a hydrothermal method, where a mixture of 50 mL of deionized water, 1.5 g of $(NH_4)_2TiF_6$, 4.8 mL of H_2O_2, and 0.1 g of acid-treated attapulgite was stirred at room temperature for 30 min after adjusting the pH to 8 with an ammonia solution. The resulting precursor solution was treated by a hydrothermal reaction at 160 °C for 12 h. Subsequently, the obtained powders underwent repeated washing and drying before being sintered at 400 °C to obtain anatase TA.

Next, BiOBr-TiO$_2$-attapulgite (BTA) were synthesized using the water-bath method. A mixture of 0.093 g of TA and $Bi(NO_3)_3 \cdot 5H_2O$ was stirred and ultrasonicated briefly. Then, a KBr solution was dropwise added to maintain a Br:Bi molar ratio of 1:1. After allowing the mixture to react for 2 h at 50 °C, it was washed, dried, and finally subjected to heat treatment at 300 °C to obtain the BTA composites. Similar methods were utilized to synthesize B, T, and BT samples.

3.4. Measurement of photocatalytic activity

The photocatalytic instrument used in this study was a PL-03 infrastructure provided by Beijing Precise Technology Co., Ltd. It consists of a circulating cooling system, eight 50 mL quartz tubes, a 400 W xenon lamp, and optical filters. To ensure that the catalytic reaction was not affected by thermal catalysis, the cooling water system maintained a reaction temperature below 20 °C. The xenon lamp was served as the visible light source, while the optical filter was used to eliminate ultraviolet light, ensuring that only visible light was emitted. The quartz tubes were used to load different concentrations of the xanthate solution and photocatalysts. Prior to the initiation of the photocatalytic reaction, a 30-min period of dark adsorption was conducted to achieve an adsorption-desorption dynamic equilibrium between the xanthate solution and the photocatalyst using agitation and magnetic stirring. During the dark adsorption and photocatalytic reaction stages, 5 mL of solution was rapidly sampled, and the photocatalyst was filtered to obtain a clear solution using a filter head. Subsequently, the clear solution was analyzed for characteristic peaks using a UV-visible spectrophotometer. The maximum peak of the SEX solution was observed at 301 nm. The relationship between absorbance (A) and mass concentration (C) is shown in Figure S3. As can be observed from the figure, the equation of the standard curve is A = 0.0103 + 0.10032C, R^2=0.9988. Therefore, based on the measured absorbance values, the residual concentration of SEX can be determined. The degradation rate (D) can be calculated using the Lambert-Beer law as follows:

$$D = \frac{C_0 - C_t}{C_0} \times 100\% \qquad （1）$$

First-order kinetics can be employed to determine the degradation rate of SEX, which can be calculated utilizing the following formula:

$$\ln\left(\frac{C_0}{C_t}\right) = kt \qquad (2)$$

Here, C_0 and C_t were the concentrations of SEX solutions at reaction times of 0 and t, respectively. k was the degradation rate constant.

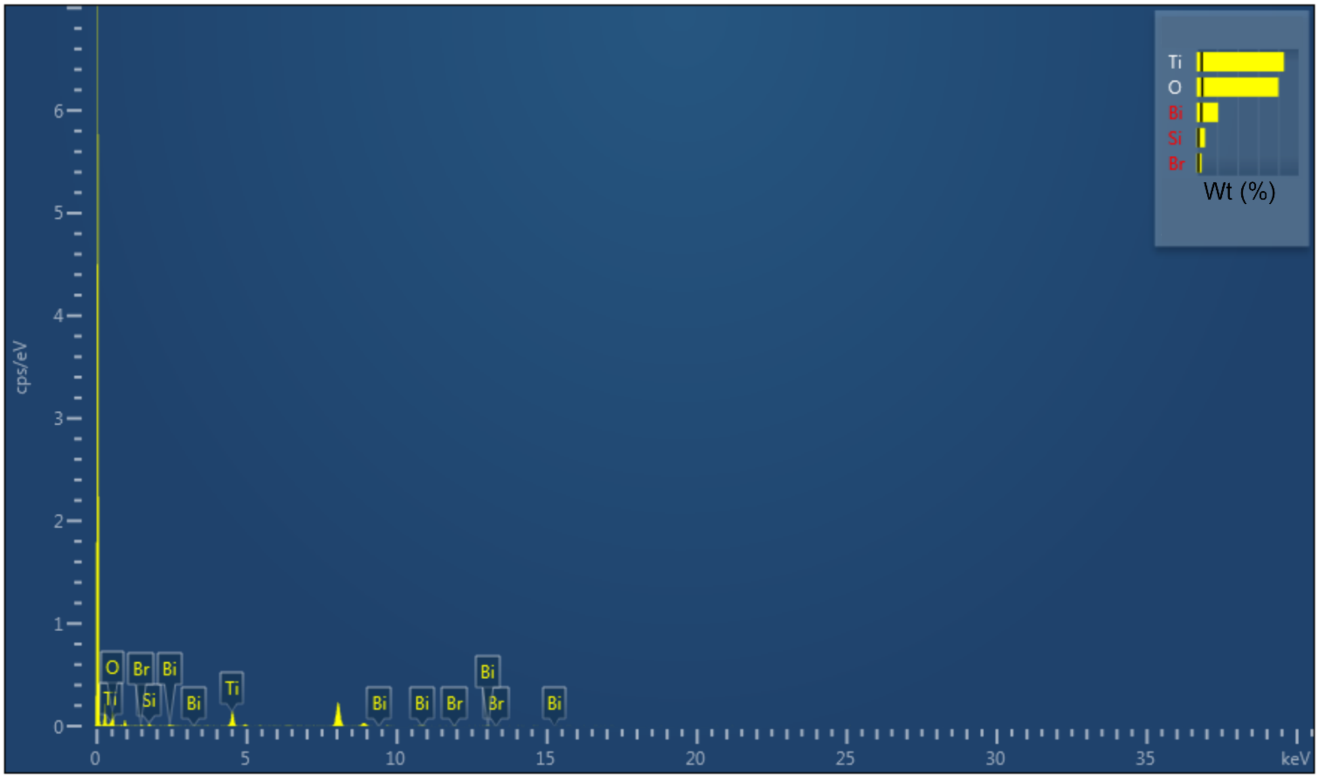


Figure S1. EDS spectra of BTA composites.

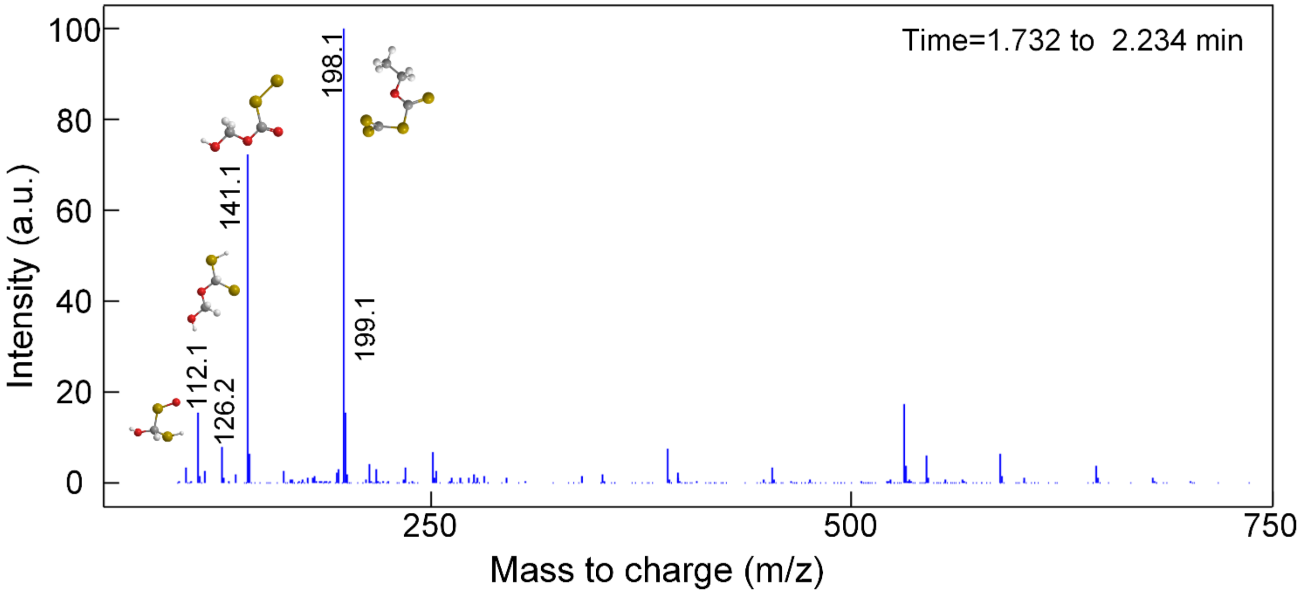


Figure S2. LC-MS pattern of SEX after a 5-min photocatalytic reaction.

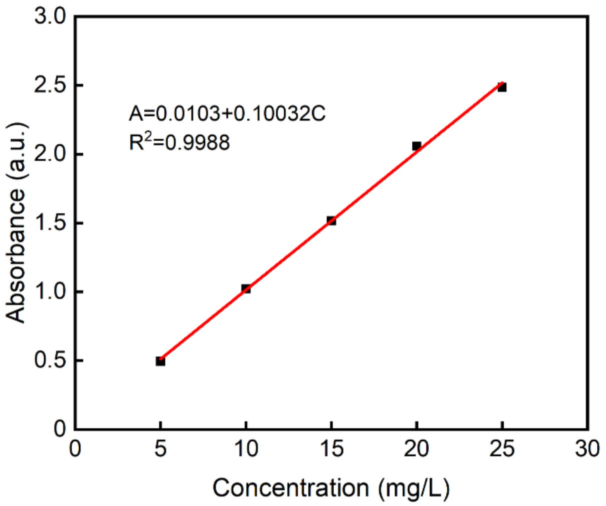
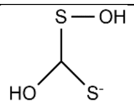
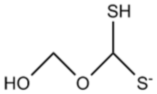
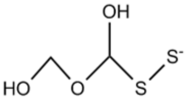
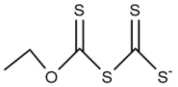


Figure S3. Absorbance standard curve of SEX solution.

Table. S1 BET specific surface area of different composites.

Sample	S_{BET} (m^2/g)
BT	29.25
BTA	57.77

Table. S2 Chemical structures and m/z values of possible degradation intermediates of SEX.

Substance	Molecular structure	Molecular weight	m/z
$CH_3O_2S_2^-$		111	112.1
$C_2H_5O_2S_2^-$		125	126.2
$C_2H_5O_2S_2^-$		141	141.1
$C_4H_5OS_4^-$		197	198.1& 199.1