Electronic Supplementary Information (ESI)

Efficient visible-light photocatalyst made from a nonpolar layered semiconductor by grafting electron-withdrawing organic molecules to its surface

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Methods

Synthesis of $BiO(HCO_2)$ (BFM). All reagents used in our experiments are of analytical grade and were used without further purification. 2 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 10 mL N,N-dimethyl formamide (DMF). Then 80mL deionized water was added under stirring. After stirring for 15 min, the obtained suspension was transferred into a 100 mL autoclave with a Teflon liner and kept at 120 ℃ for 12 h, and then cooled to room temperature naturally. The white powder was collected, washed with deionized water and ethanol three times, and dried at 60 ℃ for 12 h.

Synthesis of 4CBT@BFM. 0.67mmol BFM and 1.33mmol 4CBT-H were dispersed in 60 mL of deionized water. Subsequently, 20 mL of DMF was added into the above suspension. The mixture was constantly stirred for 15 min. Finally, the obtained suspension was transferred into a 100 mL autoclave with a Teflon liner and kept at 120 ℃ for 24 h, and then cooled to room temperature naturally. The product was collected, washed with deionized water and absolute ethanol for three times, and dried at 60 ℃ for 12 h.

4NT@BFM, 4CT@BFM, 4BT@BFM, 4HT@BFM, 4MT@BFM and 4AT@BFM (here 4NT = 4-nitrothiophenolate, 4CT = 4-chlorothiophenolate, 4BT = 4-bromothiophenolate, 4HT = thiophenolate, 4MT = 4-methylthiophenolate, 4AT = 4-aminothiophenolate) were synthesized in a similar way to 4CBT@BFM. The only difference is that a lower temperature was used for 4AT@BFM, which was prepared at 90 ℃ for 24 h. All the samples are characterized by XRD and DRS spectra (Fig. S8, S9). The XRD patterns confirm that all the samples remain the BFM crystal structure. The DRS spectra demonstrate that the absorption is extended to visible light region, after the introduction of organic molecules.

Characterization methods. The crystalline structures of the products were evaluated by XRD analysis at room temperature on a Bruker AXS D8 advanced X-ray powder diffractometer with Cu Kα radiation (λ= 1.54056 Å). The chemical composition and morphologies of the samples were determined by EDS and SEM (Hitachi S-4800 microscope), respectively. Raman spectra were recorded on LABRAM-HR800 system with laser excitation of 633 nm. UV-visible DRS analyses were carried out using a Shimadzu UV 2550 recording spectrophotometer, which was equipped with an integrating sphere and $BaSO_4$ was used as a reference. Fourier transform infrared (FT-IR) spectra were recorded using the FT-IR spectrometer (Nicolet Nexus 670). XPS analysis was characterized on a Thermo Fisher Scientific Escalab 250 spectrometer and C 1s (284.6 eV) was used to calibrate the peak positions. The PL measurements were carried out on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. The second harmonic generation (SHG) signal from the sample was selectively detected by a photomultiplier tube (PMTH-S1V1-CR131), averaged by a fast-gated integrator and boxcar averager (Stanford Research Systems), and then recorded by data acquisition software. All experiments were performed at room temperature.

Photocatalytic properties. The photocatalytic properties of the as-prepared catalysts were evaluated at room temperature using rhodamine-B (RhB) as the target molecule. In a typical process, the suspension solution that contained 100 mg catalyst and 100 mL RhB solution (20 mg L^{-1}) was stirred magnetically for 2 h in the dark to establish an adsorption-desorption equilibrium. At irradiation time intervals, 5 mL of the suspensions were collected and then centrifuged. The concentration of catalyst-free RhB solution was analyzed on a UV-vis spectrophotometer (Shimadzu UV 2550) with deionized water as a reference sample. The light source was a 300W Xe arc lamp, providing UV-Vis light. The visible light was obtained using a filter, providing visible light with $\lambda > 400$ nm. The ultraviolet light source is a 10W H-UV lamp with a certain double wavelength (185 and 254 nm).

Electrochemical measurements. The electrochemical measurements were carried out using a 263A Princeton Applied Research (PAR) potentialstat/galvanostat. The photocurrents and electrochemical impedance spectra (EIS) were measured by an electrochemical analyzer in a standard three-electrode system, with the catalyst-coated ITO glass as the working electrode, a Pt foil as a counter electrode, and a saturated Ag-AgCl electrode (saturated KCl) as the reference electrode. The light source was a 300W Xe arc lamp. The electrolyte was 0.1M LiCl acetonitrile solution.

Table S1. The apparent rate constant k_{app} for the photocatalytic degradation of RhB and photocurrent i_{photo} using samples of BFM with surface modified by 4-substitued thiophenolates $^-$S-C_6H_4 Z under visible light irradiation.

Z	$k_{app}{}^a$ (h^{-1})		$i_{photo}{}^b$($\mu A\cdot cm^{-2}$)		σ_{para}
NO_2	$\bar{k}$ =2.111 SD=0.064	k_1=2.118, k_2=2.185, k_3=2.029	$\bar{i}$ =1.951, SD=0.017	i_1=1.934, i_2=1.974, i_3=1.946	0.78
COOH	$\bar{k}$ =1.923 SD=0.026	k_1=1.910, k_2=1.960, k_3=1.900	$\bar{i}$ =1.113 SD=0.04	i_1=1.114, i_2=1.147, i_3=1.053	0.45
Cl	$\bar{k}$ =1.828 SD=0.015	k_1=1.85, k_2=1.82, k_3=1.816	$\bar{i}$ =0.915 SD=0.016	i_1=0.909, i_2=0.936, i_3=0.899	0.23
Br	$\bar{k}$ =1.756 SD=0.034	k_1=1.8, k_2=1.703, k_3=1.765	$\bar{i}$ =0.804 SD=0.017	i_1=0.828, i_2=0.790, i_3=0.795	0.23
H	$\bar{k}$ =1.160 SD=0.081	k_1=1.221, k_2=1.046, k_3=1.214	$\bar{i}$ =0.641 SD=0.021	i_1=0.652, i_2=0.660, i_3=0.611	0
CH_3	$\bar{k}$ =0.912 SD=0.012	k_1=0.927, k_2=0.897, k_3=0.911	$\bar{i}$ =0.572 SD=0.011	i_1=0.578, i_2=0.556, i_3=0.582	-0.17
NH_2	$\bar{k}$ =0.264 SD=0.034	k_1=0.217, k_2=0.293, k_3=0.282	$\bar{i}$ =0.360 SD=0.026	i_1=0.324, i_2=0.382, i_3=0.376	-0.66

^{a} k_{app} = 0.0115 $h^{-1}$for BFM.

k_1, k_2,and k_3 are the results of three different measurements, and $\bar{k}$ is their mean value, which is referred to as k_{app}. The SD is the standard deviation.

^{b} The photocurrent of BFM is not observed under visible light irradiation.

i_1, i_2, i_3 are the results of three different measurements, and $\bar{i}$ is their mean value, which is referred to as i_{photo}. The SD is the standard deviation.

Calculation of the photocatalytic rate constant:

The results of these experiments can be summarized by determining the apparent rate constants, k_{app}, of the degradation reactions, which we describe in terms of the apparent pseudo-first-order kinetics equation (1) [1,2]

$$\ln \frac{C_0}{C} = k_{app} t \tag{1}$$

where k_{app} is the rate constant (h^{-1}), C is the concentration (mgL^{-1}) of RhB in aqueous solution at time t, and C_0 is the initial concentration of RhB at $t = 0$.

Reference

(1) K. Dai, L. H. Lu, C. H. Liang, Q. Liu, G. P. Zhu, *Appl. Catal. B: Environ.*, 2014, **156-157**, 331.

(2) Y. Hong, C. G. Tian, B. J. Jiang, A. P. Wu, Q. Zhang, G. H. Tian, H. G. Fu, *J. Mater. Chem. A*, 2013, **1**, 5700.

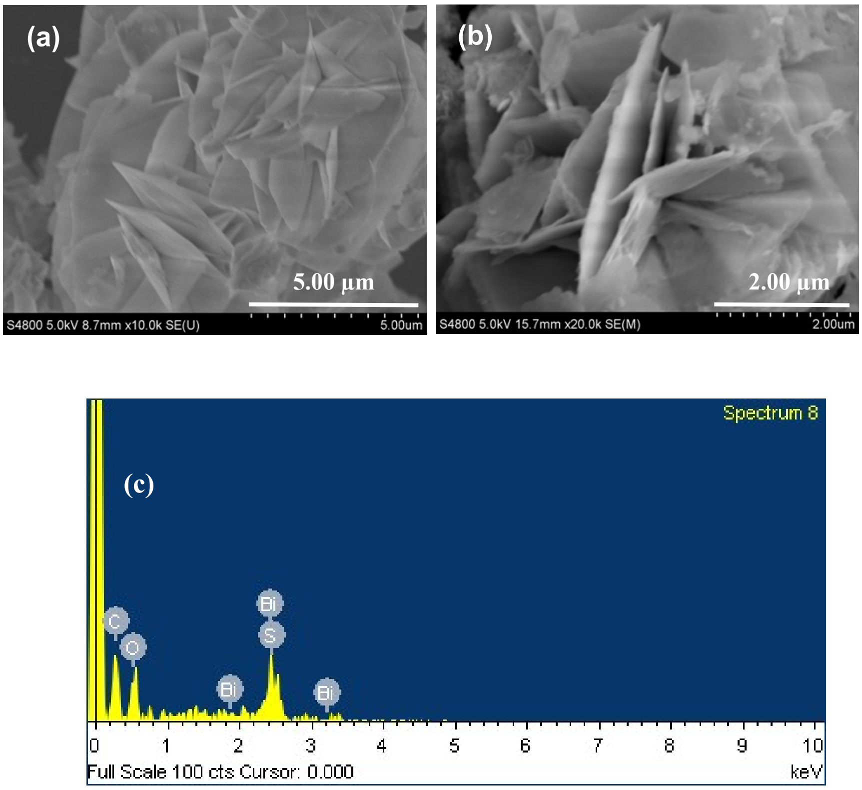

Fig. S1. SEM images of (a) BFM and (b) 4CBT@BFM; (c) EDS spectrum of 4CBT@BFM.

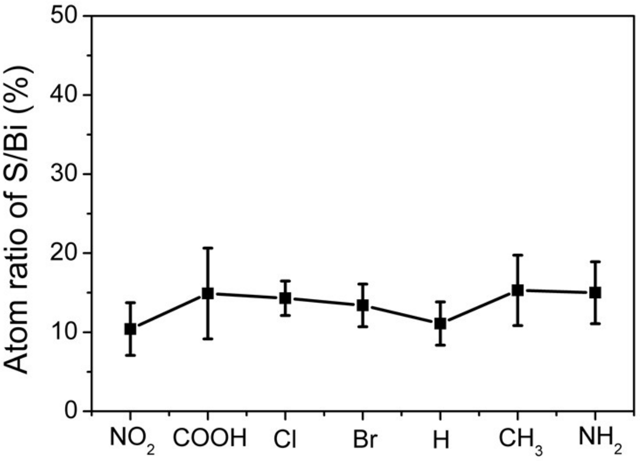

Fig. S2. The S:Bi atom ratio (in %) measured from EDS measurements for the BFM samples whose surfaces are modified by *para*-substituted thiophenolate $^{-}S\text{-}C_6H_4Z$ (Z = NO_2, COOH, Cl, Br, H, CH_3, NH_2).

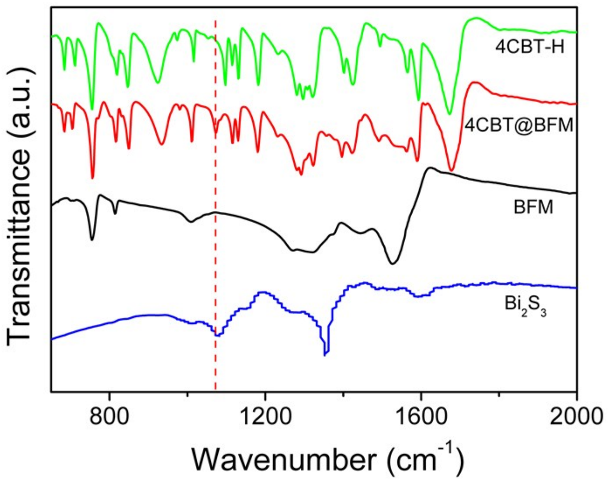

Fig. S3. FTIR spectra of BFM, 4CBT@BFM, 4CBT-H and Bi_2S_3.

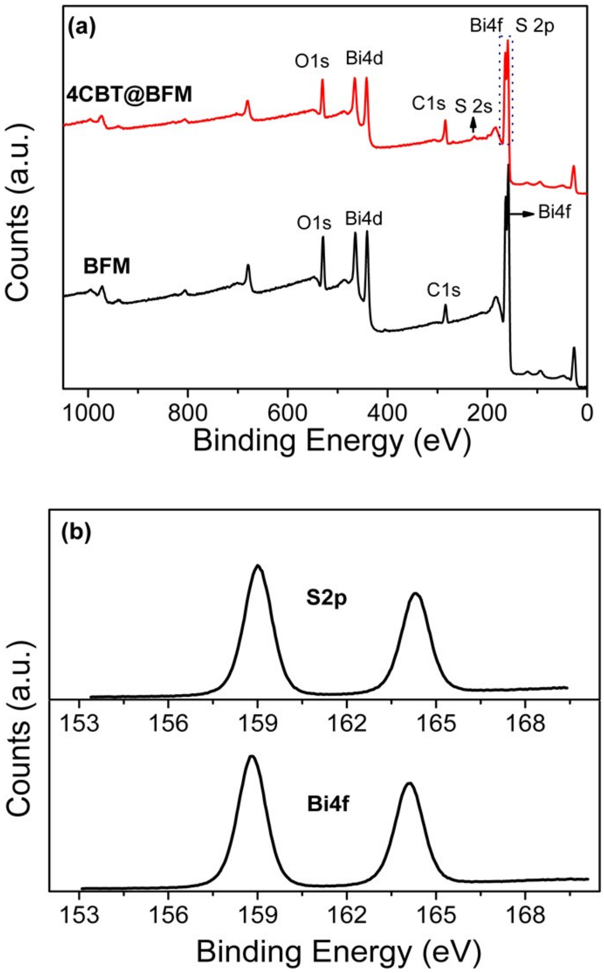

Fig. S4. (a) XPS survey spectrum of BFM and 4CBT@BFM, (b) XPS spectrum of the S 2p and Bi 4f state of 4CBT@BFM in the dashed frame of (a).

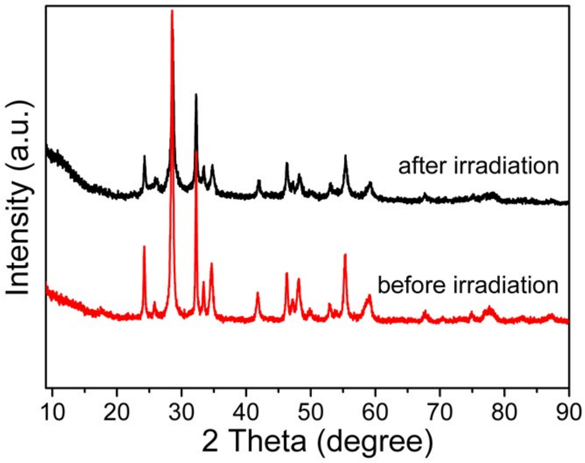

Fig. S5. XRD patterns of 4CBT@BFM before and after 2 h of UV-visble light irradiation.

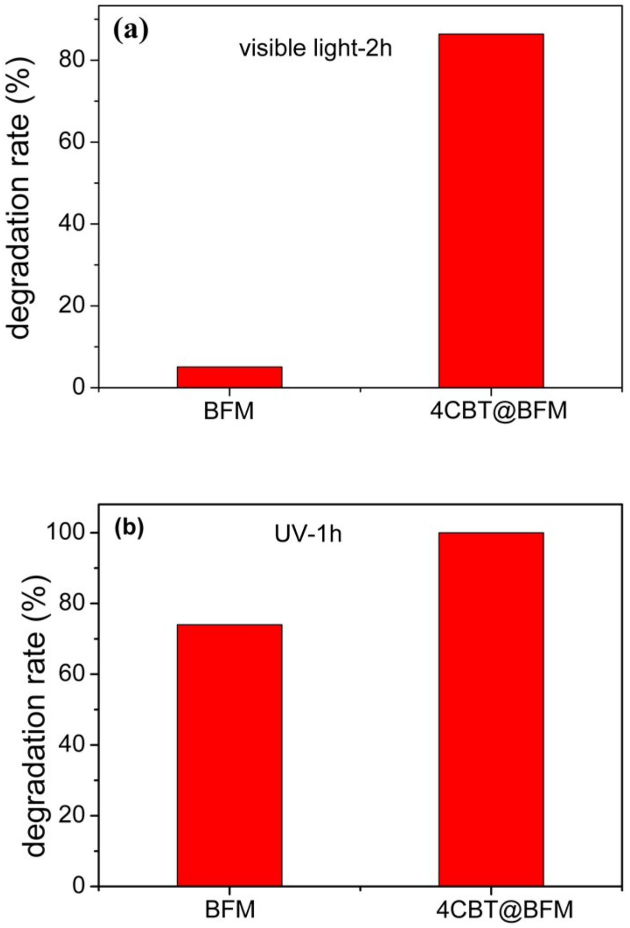

Fig. S6. Photocatalytic degradation of RhB over 4CBT@BFM under (a) visible and (b) UV light irradiation.

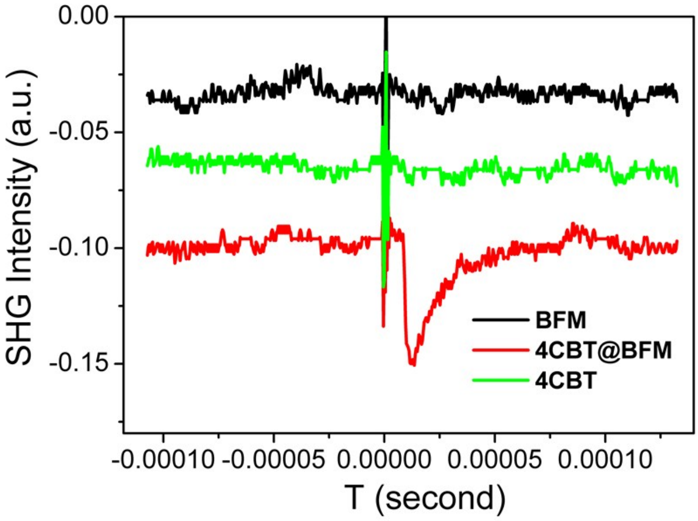

Fig. S7. SHG spectra of BFM, 4CBT-H, and 4CBT@BFM.

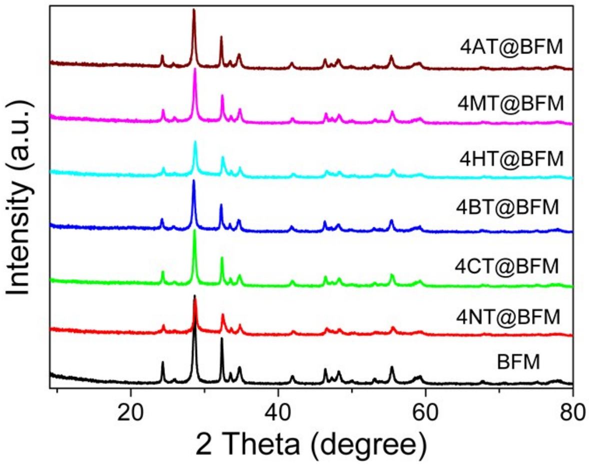

Fig. S8. XRD patterns of the thiophenolate@ BFM samples.

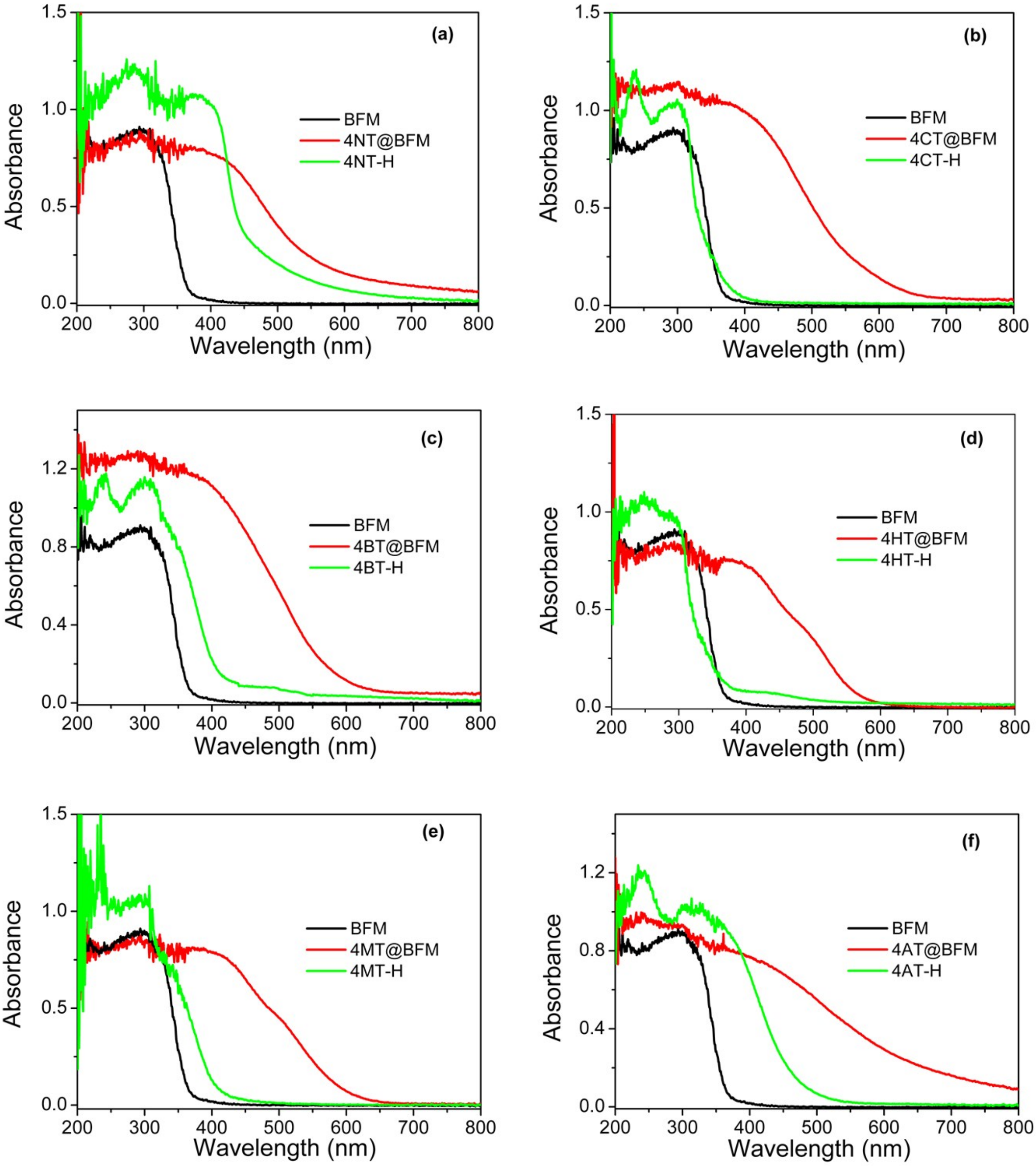

Fig. S9. DRS spectra of various thiophenolate@BFM samples.