Supporting information for

Fabrication of MoS_2/BiOBr heterojunctions on carbon fibers as weaveable photocatalyst for tetracycline hydrochloride degradation and Cr(VI) reduction under visible light†

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1. Experimental section

1.1 Materials and chemicals

All reagents were analytical grade and used without further purification. Absolute ethanol (CH_3CH_2OH), acetone (CH_3COCH_3), nitric acid (HNO_3), hydrochloric acid (HCl), sodium hydroxide (NaOH), thiourea (CH_4N_2S), sodium molybdate ($Na_2MoO_4\cdot2H_2O$) and oxalic acid ($C_2H_2O_4$), bismuth nitrate pentahydrate ($Bi(NO_3)_3\cdot5H_2O$), potassium bromide (KBr), N,N-dimethylacetamide (DMAC) p-Benzoquinone (BQ), silver nitrate ($AgNO_3$), isopropyl alcohol (IPA), ammonium oxalate (AO), sodium sulphate (Na_2SO_4) and potassium dichromate ($K_2Cr_2O_7$) were purchased from Sinopharm Chemical Reagent Co., Ltd (P. R. China). Tetracycline Hydrochloride (TCH) was purchased from Sangon Biotech (Shanghai) Co., Ltd. The carbon fibers (CFs) were purchased from TOHO (UTS50-12K) and were ultrasonically washed in a mixture solution (deionized water, ethanol and acetone; v/v/v, 1:1:1) for 30 min to

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wash off the oil on the surface.

1.2 Characterization

The morphology and size of the resulting represented sample were investigated by using a field emission-scanning electron microscopy (FE-SEM, Hitachi S-4800) and a field emission-transmission electron microscopy (FE-TEM, Hitachi JEM-2100F). The elemental composition and distribution were also investigated by using energy dispersive X-ray spectroscopy (EDS) on a Bruker Quantax 400 EDS system during SEM characterization. The crystal phase and structure of the prepared samples were examined by X-ray diffraction (XRD, */D/max-2550VB+/PC) and Fourier transform infrared (FT-IR, NEXUS-670).The chemical states and surface elemental compositions of the as-materials were characterized on an X-ray photoelectron spectroscopy (XPS, Escalab 250Xi). When we measured the UV-vis diffuse reflection spectra of fiber-based samples, plenty of fiber-based samples were adhered tightly on sample stage by the double-sided adhesive tape, resulting in the formation of fiber-based texture/film. Their optical diffuse reflectance spectra were conducted on a UV-vis-NIR scanning spectrophotometer (UV3600, Shimadzu) using an integrating sphere accessory. Liquid chromatography-mass (LC-MS) spectrometry (6230, Agilent) was used to monitor the intermediate products during the degradation of TCH by CFs/MoS_2/BiOBr.

1.3 Mott-Schottky and photoelectrochemical tests

All the tests were performed on a CHI660E Electrochemical Workstation (Chenhua Instruments Co., Shanghai, China). The Mott-Schottky measurement used a standard three-electrode configuration with Ag/AgCl electrode. Besides, o.1 M Na_2SO_4 aqueous solution was used as the electrolyte. The flat band potentials of semiconductors were determined by Mott-

Schottky relation. And a standard self-made three-electrode electrochemical system was applied to study the photoelectrochemical behaviors of CF/MoS_2/BiOBr, CF/MoS_2 and CF/BiOBr cloths. An aqueous Na_2SO_4 solution, a Pt sheet and saturated calomel electrode (SCE) were used as electrodes in the system. The current-time (I-t) curves were acquired with an on-off irradiation cycle interval of 50 s at a 0.3 V external voltage. Electrochemical impedance spectroscopy (EIS) was measured with an amplitude of 0.3 V and a frequency range from 100 kHz to 0.01 Hz.

The GGA with the PBE was adopted to estimate the electronic structures and density of states (DOS) using CASTEP code.

1.4 Photocatalytic activity

Flexible bundles (CFs, CFs/MoS_2, CFs/BiOBr and CFs/MoS_2/BiOBr) were reorganized and woven to cloths (area: 5×5 cm^2, weight: 0.15 g) as photocatalysts. The photocatalytic oxidation and reduction abilities of different cloths were investigated by removing TCH and Cr^{6+}. Typically, the cloth was floated in 50 mL of the aqueous solution containing TCH (20 mg L^{-1}) or Cr^{6+} (20 mg L^{-1}). Before the photocatalytic reaction, the solution was stirred for 60 min with the floating cloth in dark to ensure an adsorption-dissolution equilibrium. Then, the reaction system was transferred to stirrer below a 300 W xenon lamp ($\lambda > 420$ nm). During the illumination, 1 mL solution was sampled at the intervals of 10 min and then analyzed by a U-2910 UV-vis spectrophotometer (Hitachi, Japan) at detection wavelength of 357 nm (TCH). The typical 1,5-diphenylcarbazide colorimetric method was applied to determine the Cr^{6+} concentration in the supernatant using a UV-vis spectrophotometer. Typically, 1 mL reduced Cr^{6+} solution and 9 mL 0.2 M H_2SO_4 solution were injected into a 10 mL volumetric flask, respectively. Then, sufficient 1,5-diphenylcarbazide solution was injected into the flask which was shaken for uniformity. 1,5-Diphenylcarbazide will combine with Cr^{6+} to form a purple complex, which could be detected using a UV-vis spectrophotometer at 540 nm.

The pH effect tests were carried out under the similar conditions with different pH values, which were adjusted to be around 3, 5, 7, 9 and 11, respectively, by dilute HCl and NaOH solution.

The total organic carbon (TOC) test was carried out by degrading a high concentration of TCH solution (50 mg L^{-1}, 300 mL) to evaluate the removal effect of organic pollutants by studying the change of TOC concentration during photocatalytic degradation. During the photocatalytic process, 20 mL of solution was collected at the intervals of 1 h and analyzed by Total Organic Carbon (TOC) analyzer (TOC-VCPH, Shimadzu).

The experiment of main active species was carried out by adding free radical trapping agents (1.0 mmol isopropanol (IPA), 1.0 mmol $AgNO_3$, 1.0 mmol ammonium oxalate (AO) or 0.2 mmol benzoquinone (BQ)) into TCH solution (20 mg L^{-1}, 50 mL) before the photocatalytic tests. During the photocatalytic process, 1 mL of solution was collected at the intervals of 10 min and analyzed. The quantitation of $\cdot O_2^-$ was realized via detecting the concentration change of nitrotetrazolium blue chloride (NBT) solution (20 μmol/L, 50 mL) with different photocatalysts (CFs/MoS_2, CFs/BiOBr and CFs/MoS_2/BiOBr, 0.15g). During the photocatalytic process, 1 mL of solution was collected at the intervals of 20 min and analyzed by a U-2910 UV-vis spectrophotometer (Hitachi, Japan). The yield of $\cdot O_2^-$ is about 4 times the consumption of NBT.

The stability and reusability of CFs/MoS_2/BiOBr are very important for its practical application. As-prepared CFs/MoS_2/BiOBr cloth was applied to wipe off TCH (20 mg L^{-1}, 50 mL) or Cr^{6+} (20 mg L^{-1}, 50 mL) and easily taken out, washed, dried, and then re-used. The degradation of TCH by CFs/MoS_2/BiOBr was monitored for four cycles (each cycle lasts 2 h). During the photocatalytic process, 1 mL of solution was collected at the intervals of 30 min and analyzed.

2 Figures

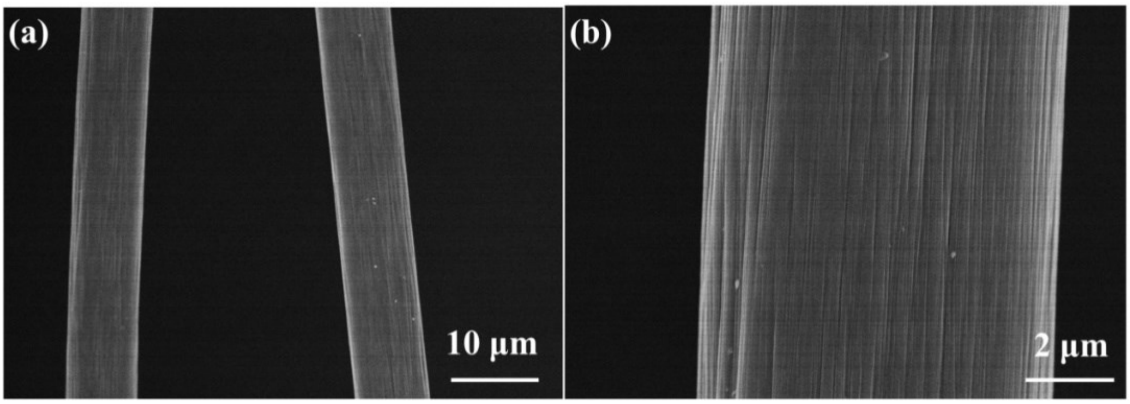

Fig. S1 SEM images of CF bundles (a) and single CF fiber (b).

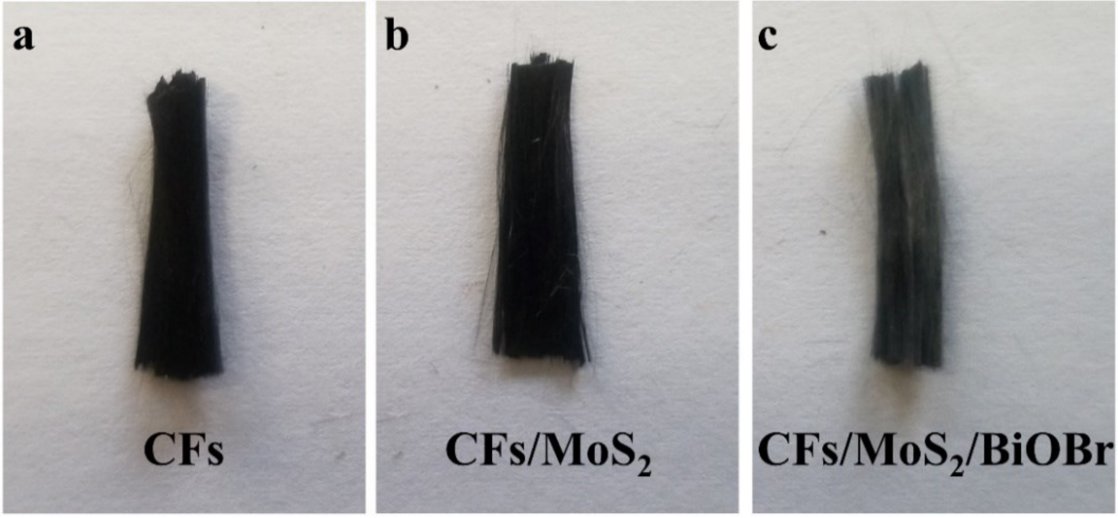

Fig. S2 Photos of CFs (a), CFs/MoS_2 (b), and CFs/MoS_2/BiOBr (c) bundles.

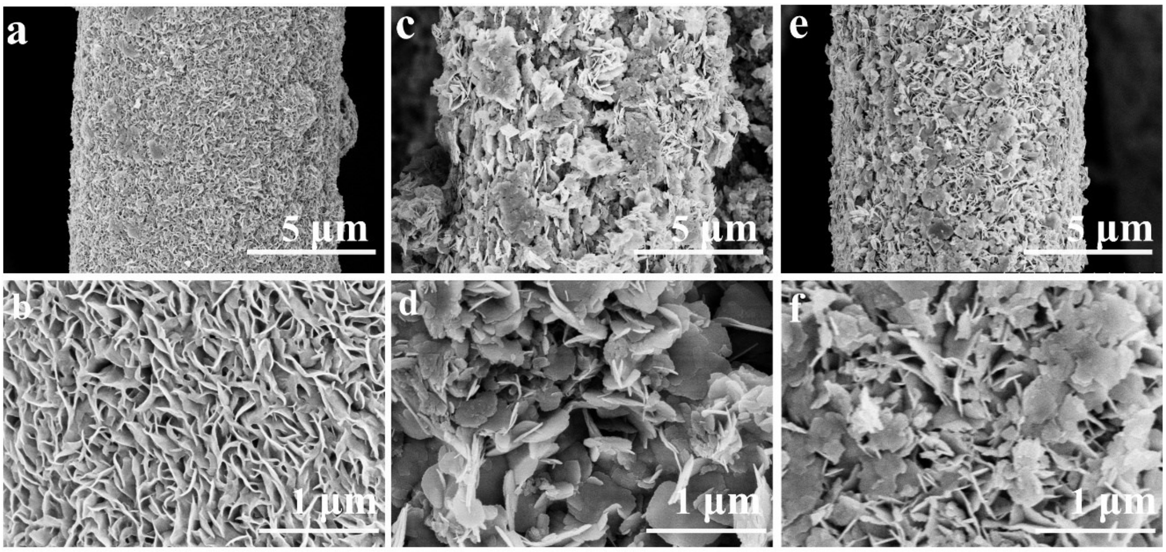

Fig. S3 SEM images of CFs/MoS_2 (a, b), CFs/BiOBr (c, d), and CFs/MoS_2/BiOBr (e, f).

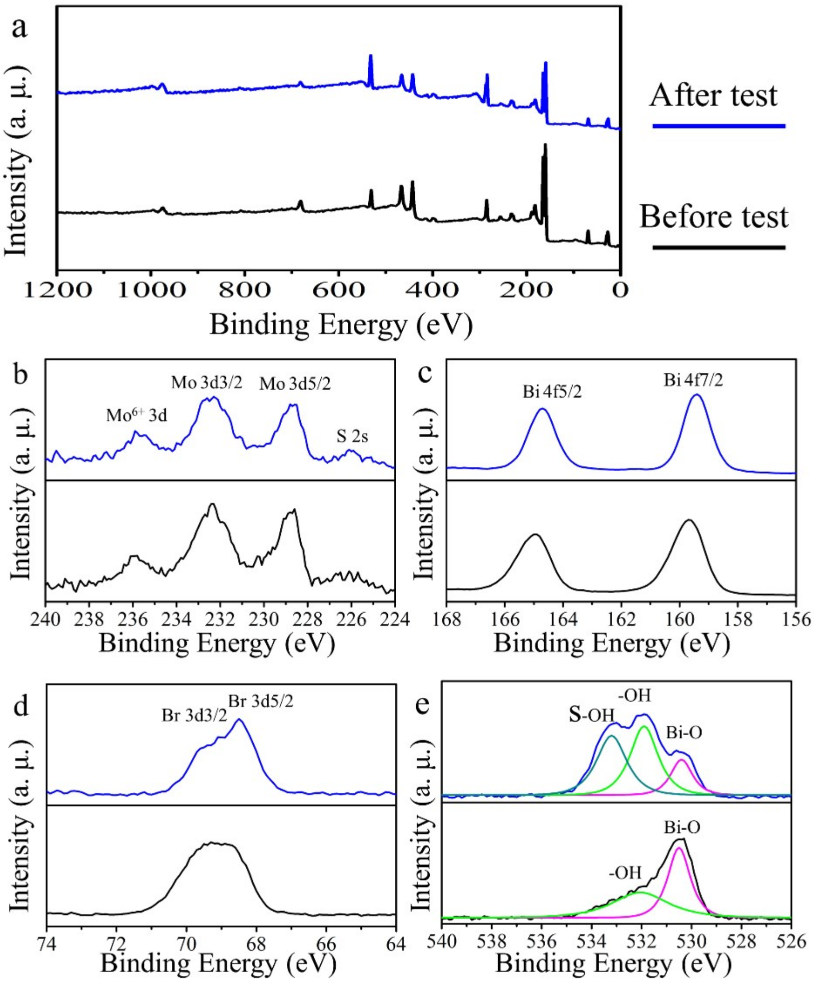

Fig. S4 XPS spectra of CFs/MoS_2/BiOBr before and after photoelectrochemical test: full survey spectra (a), Mo 3d (b), Bi 4f (c), Br 3d (d) and O 1s(e).

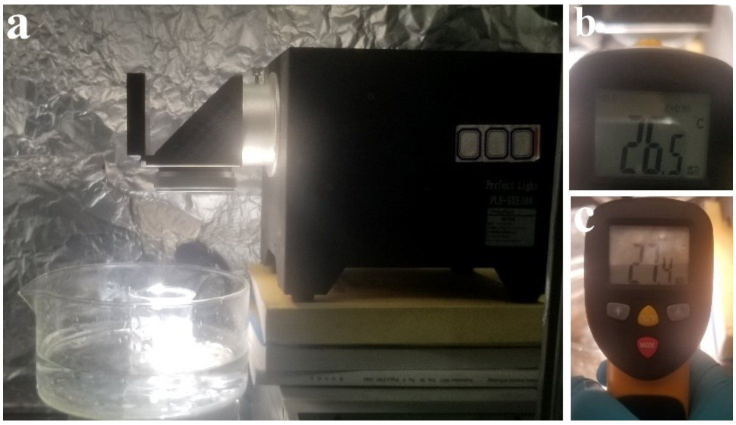

Fig. S5 Photos of the reaction system surrounded by cold water (a), the temperatures of the solution surface before (b) and after (c) the photocatalytic reaction.

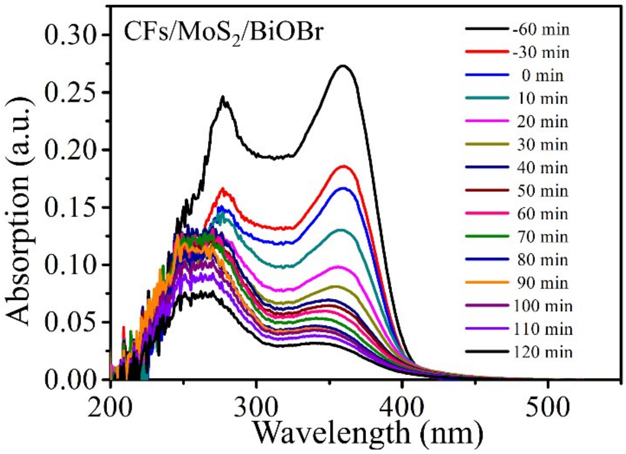

Fig. S6 Temporal evolution of UV–Vis spectrum of TCH solution degraded by CFs/MoS_2/BiOBr cloth.

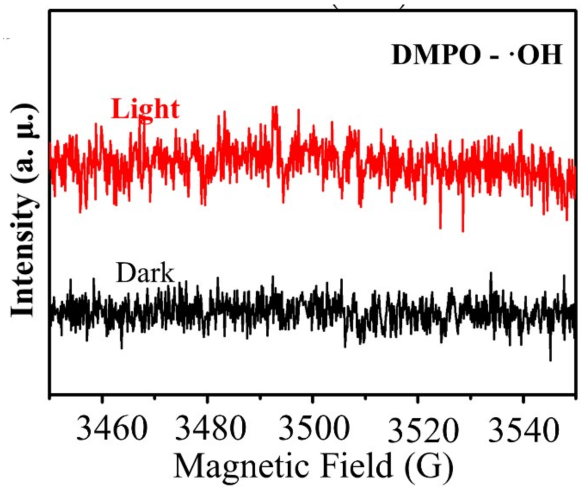

Fig. S7 ESR spectra of CFs/MoS_2/BiOBr in the aqueous dispersion for DMPO− ·OH with and without visible-light irradiation.

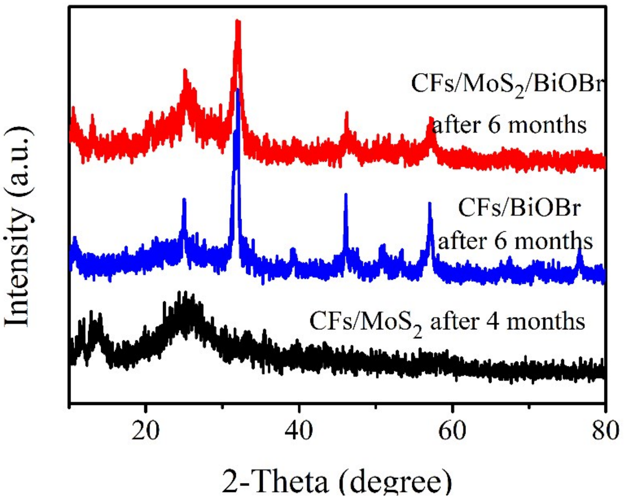

Fig. S8 XRD patterns of CFs/MoS_2, CFs/BiOBr and CFs/MoS_2/BiOBr placed for several months.

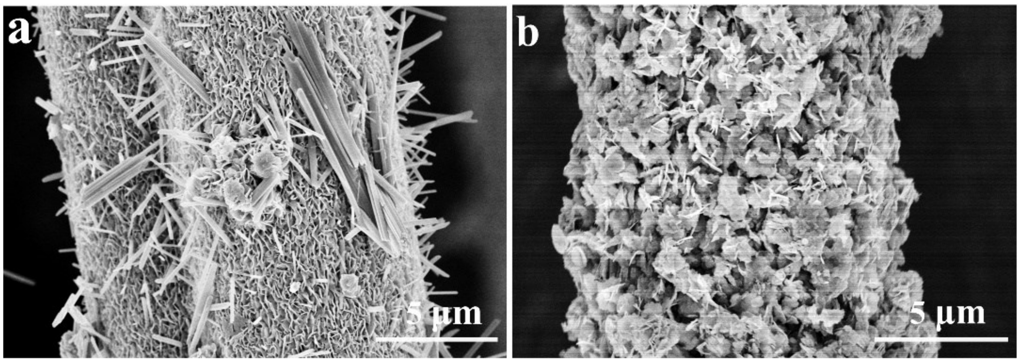

Fig. S9 SEM images of CFs/MoS_2 placed for 4 months (a), and CFs/MoS_2/BiOBr placed for 6 months (b).

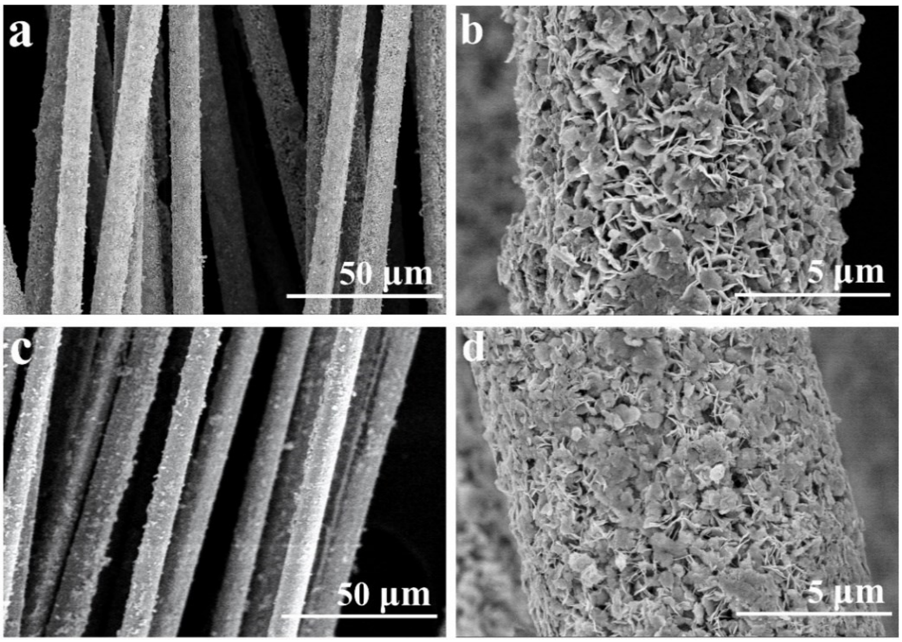

Fig. S10 SEM images of CFs/MoS_2/BiOBr after the removal of TCH (a, b), and Cr^{6+} (c, d).