

Supporting Information

Boosting photocatalytic CO₂ reduction over S-scheme CTF-Bi-BiOBr using pre-oxidized dissolved effluent organic matter as electron donors

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Characterization and photoelectrochemical measurements

1. Materials characterization

The surface morphology and microstructure of the materials were analyzed by the scanning electron microscopy (SEM, FEI Nova Nano SEM 230) and high-resolution transmission electron microscopy (HRTEM, FEI TECNAI G2 F20). The crystal structures of the samples were measured by powder X-ray diffraction (PXRD) on a Rigaku MiniFlex 600 X-ray diffractometer with Ni-filtered Cu K α irradiation ($\alpha = 1.5406 \text{ \AA}$) and the range of measurement condition was set from 5° to 80° . The Brunauer-Emmett-Teller (BET) specific surface areas of the samples were obtained by an ASAP 2020 apparatus (Micromeritics Instrument Corp.). The functional groups were analyzed by Fourier transform infrared (FT-IR) spectrum in an analytical instrument of Thermo Scientific Nicolet iS10 spectrometer using KBr pellets at a resolution of 4 cm^{-1} . X-ray photoelectron spectroscopy (XPS, PHI Quantum 2000) equipped with a monochromatic Al K α was measured in order to analyze the elemental composition and particular surface chemical state of the samples. All binding energies were referenced to the C 1s peak (284.6 eV) from the air contamination carbon. In order to explore the optical character, the solid-state UV-vis diffuse reflectance spectra (UV-vis DRS) were conducted by a Varian Cary 500 Scan UV-vis-NIR spectrophotometer, and barium sulfate was used as a referent. The photoluminescence (PL) spectra were performed in a spectrophotometer (G9800A, Agilent, America) with excitation wavelength at 420 nm. All the tests were performed under the room temperature.

2. Photoelectrochemical measurements

The photoelectrochemical measurements including the transient photocurrent tests, Mott-Schottky analyses, and electrochemical impedance spectroscopy (EIS) were carried out by an electrochemical workstation (CHI 650E, Shanghai Chenhua Instrument Co. Ltd. China) with a standard three-electrode system (a platinum plate electrode, an Ag/AgCl electrode and a working electrode) in a $0.2 \text{ M Na}_2\text{SO}_4$ electrolyte

solution. The working electrode fabrication was as follows: 5 mg photocatalyst powder was dispersed into the mixture of 400 μL ethanol and 50 μL nafion solution under sonication for 4 h. 10 μL of the obtained suspension was dipped onto a piece of fluoride-tin oxide (FTO) glass substrate with a designed area of $0.5 \times 0.5 \text{ cm}^2$ and the residual parts of the FTO glass were coated with epoxy. Finally, the as-prepared working electrode was dried under room temperature. The transient photocurrent analyses were characterized by an electrochemical workstation (CHI 650E) equipped with a conventional three-electrode cell, and 0.2 M Na_2SO_4 aqueous solution was used as an electrolyte. Moreover, a 300 W Xe lamp (PLS-SXE300C) with a 420 nm cut-off filter was used as the visible-light source. The Mott-Schottky analyses, and EIS were carried out by CHI 650E electrochemical workstation. Besides, the mixture of 10 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.1 M KCl and 0.2 M Na_2SO_4 aqueous solution were used as the electrolyte, respectively. All the measurements were repeated at least three times in the same condition.

3. dE_jOM characterization

The concentration of wastewater was identified by TOC measurement (TOC-L CPH, Shimadzu, Japan). To further explore the specific effects of untreated sewage and oxidized sewage on photocatalytic CO_2 reduction, a series of sewage characterizations including Fourier transform infrared (FT-IR) spectrum, X-ray photoelectron spectroscopy (XPS), UV-vis spectrophotometer, and fluorescence 3D electron microscopy studies were carried out in a new type of model designed to infer the possible characteristics of effluents and intermediates.

The Fourier transform infrared (FT-IR) spectrum and X-ray photoelectron spectroscopy (XPS) were measured to identify the elemental constitute and functional groups. The sewage samples were freeze-dried in advance, and the measurement conditions were the same as photocatalysts characterization. The UV-vis absorption spectra were measured to obtain the spectral slope ratio (S_R) which was calculated as the slope in wavelength of 275-295 nm divided by slope in wavelength of 350-400 nm.

The 3D excitation-emission-matrix (EEM) spectra were conducted in condition that the excitation wavelength was 250-400 nm in 5 nm intervals and the emission wavelength was 300-500 nm in 5 nm intervals. The emission and excitation slits were set at 10 nm, and the scanning speed was controlled in 12000 nm/min. The acquired data was further analyzed by matlab 12.0. Parallel factor analysis (PARAFAC) method.

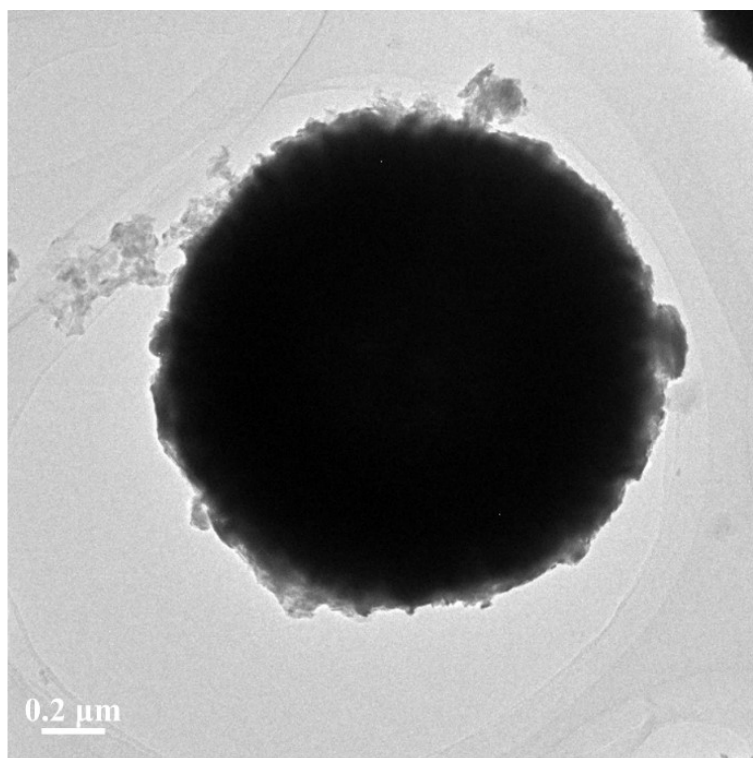


Fig. S1. TEM image of 20% CTF-1-Bi-BiOBr.

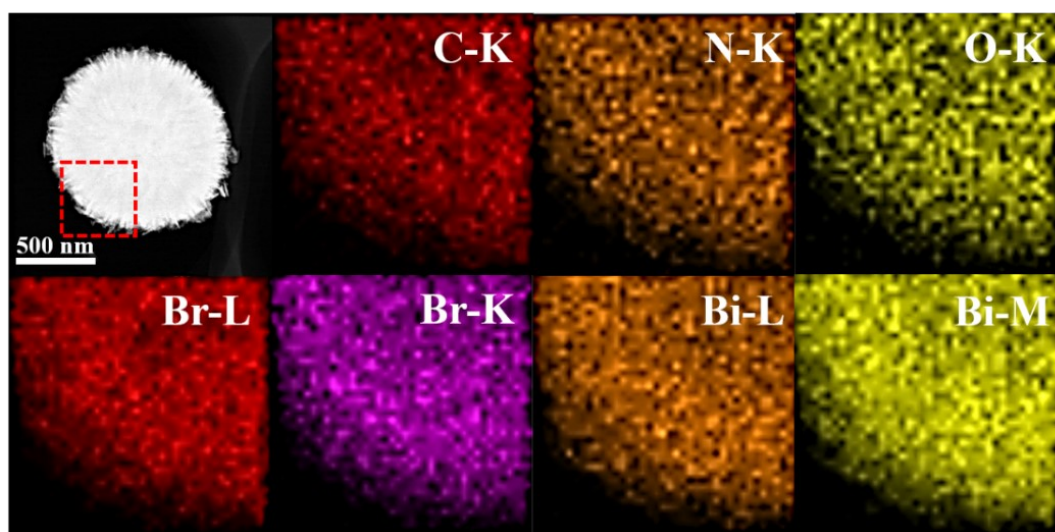


Fig. S2. Energy dispersive X-ray (EDX) mappings of 20% CTF-1-Bi-BiOBr.

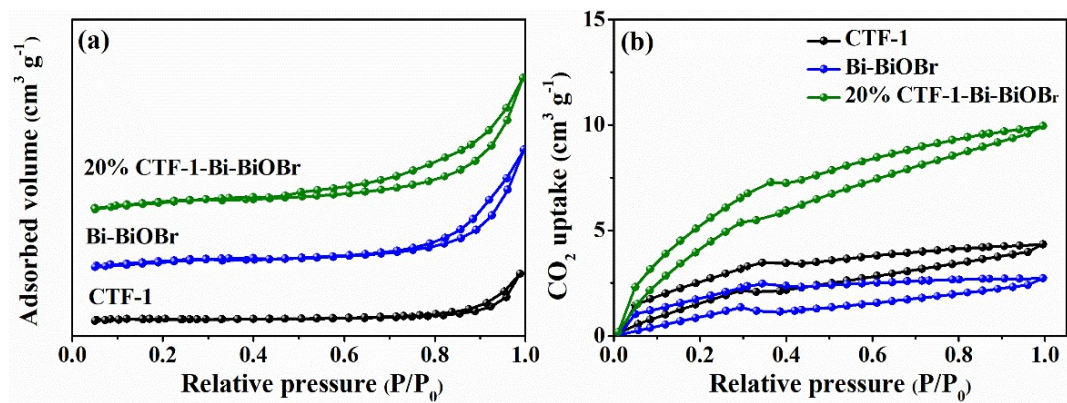


Fig. S3. (a) BET and (b) CO₂ adsorption curves of CTF-1, Bi-BiOBr and 20% CTF-1-Bi-BiOBr.

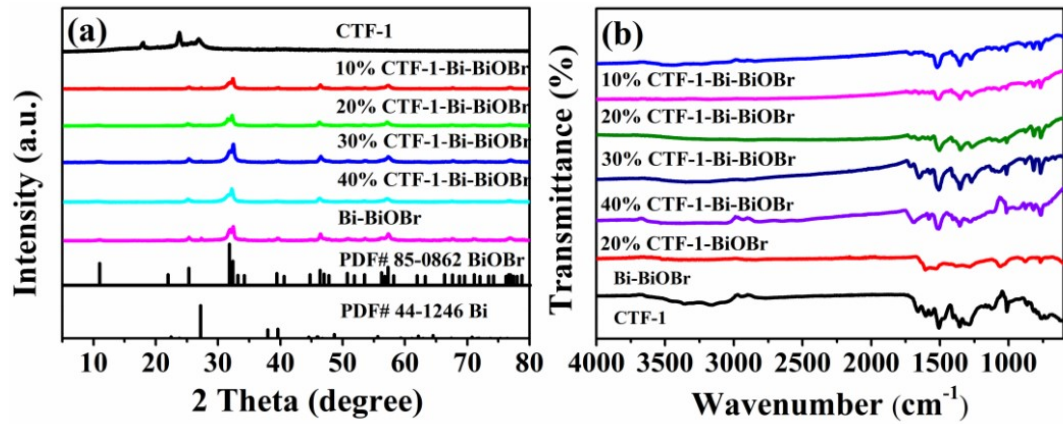


Fig. S4. (a) XRD patterns and (b) FT-IR spectra of CTF-1, Bi-BiOBr, and CTF-1-Bi-BiOBr composites.

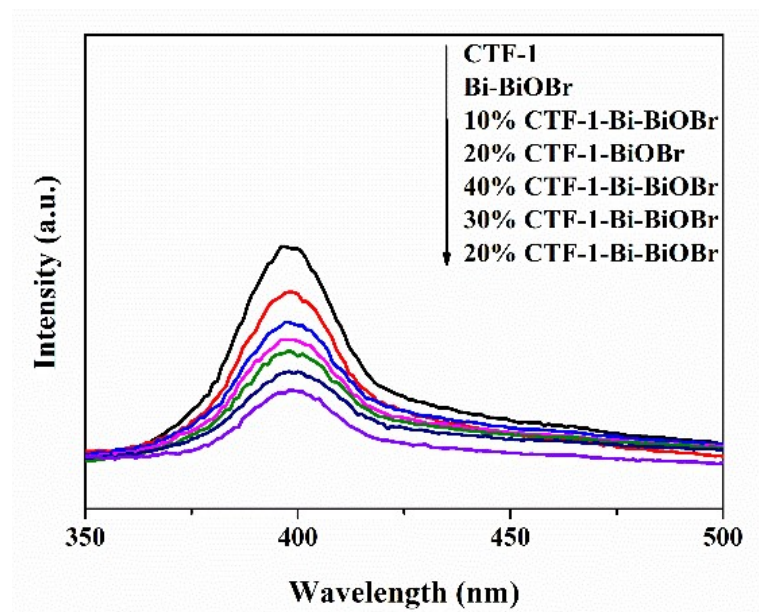


Fig. S5. PL spectra of CTF-1, Bi-BiOBr, 20% CTF-1-BiOBr and CTF-1-Bi-BiOBr composites.

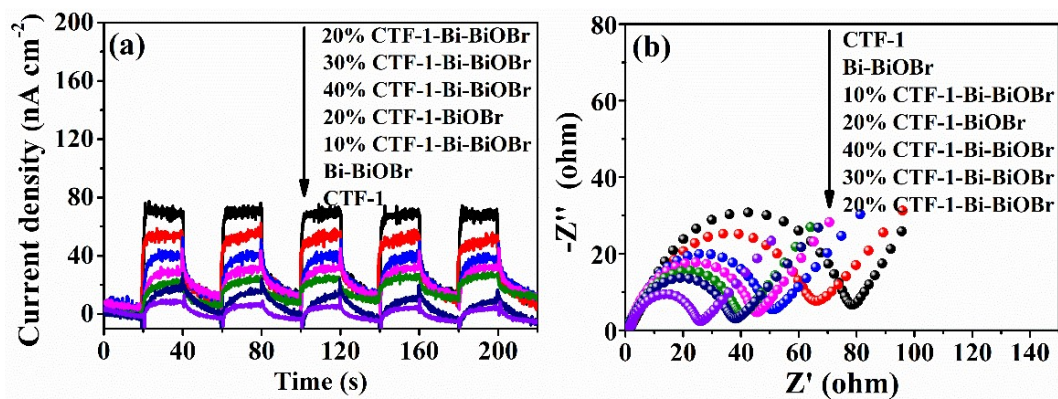


Fig. S6. (a) The transient photocurrent responses and (b) the EIS plots of CTF-1, BiOBr, 20% CTF-1-BiOBr and CTF-1-Bi-BiOBr composites.

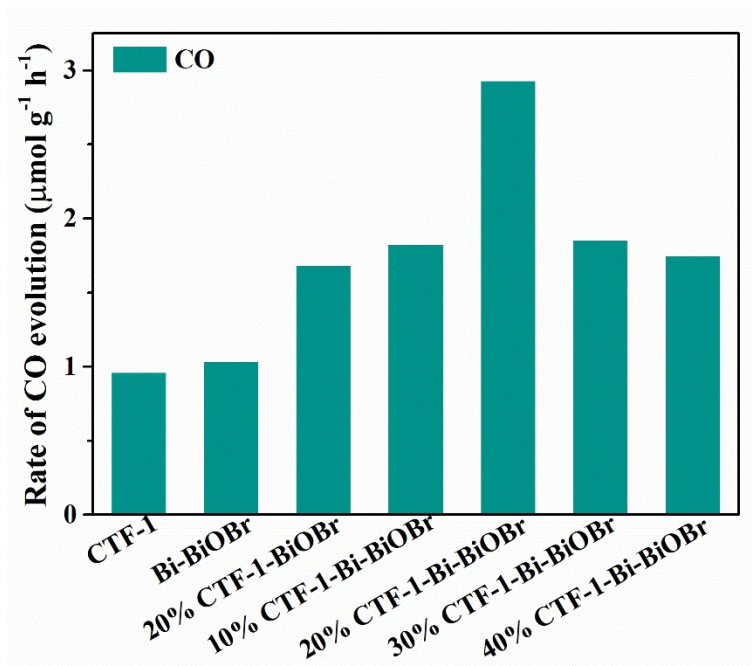


Fig. S7. Photocatalytic anoxic CO_2 reduction activities in the presence of different as-prepared samples and pre-oxidized 4 h dE_rOM .

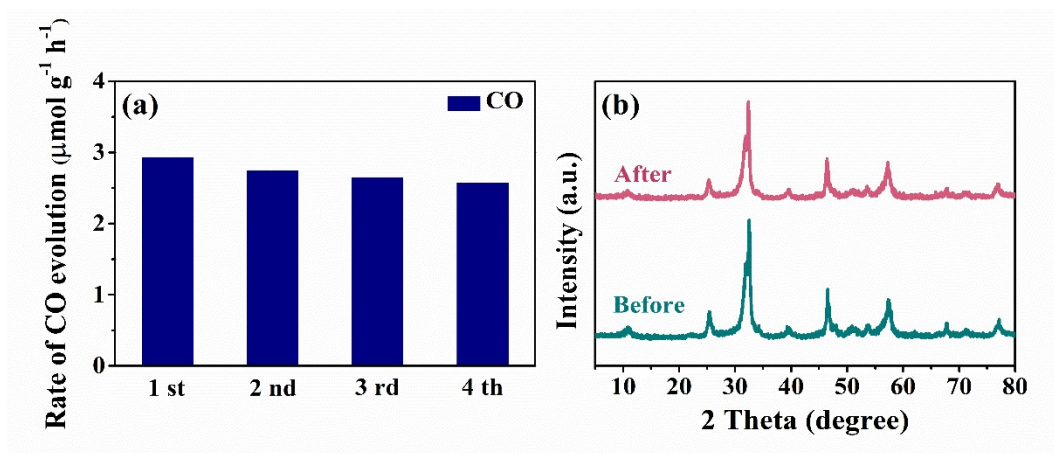


Fig. S8. (a) The photocatalytic CO_2 reduction stability tests of 20% CTF-1-Bi-BiOBr and (b) XRD patterns of 20% CTF-1-Bi-BiOBr before and after reactions.

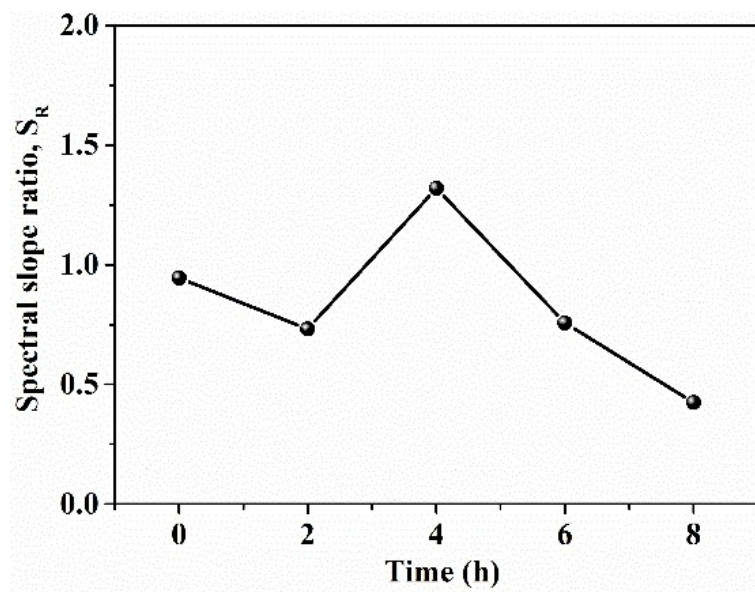


Fig. S9. Variation of the spectral slope ratio, S_R , under different pre-oxidized time.

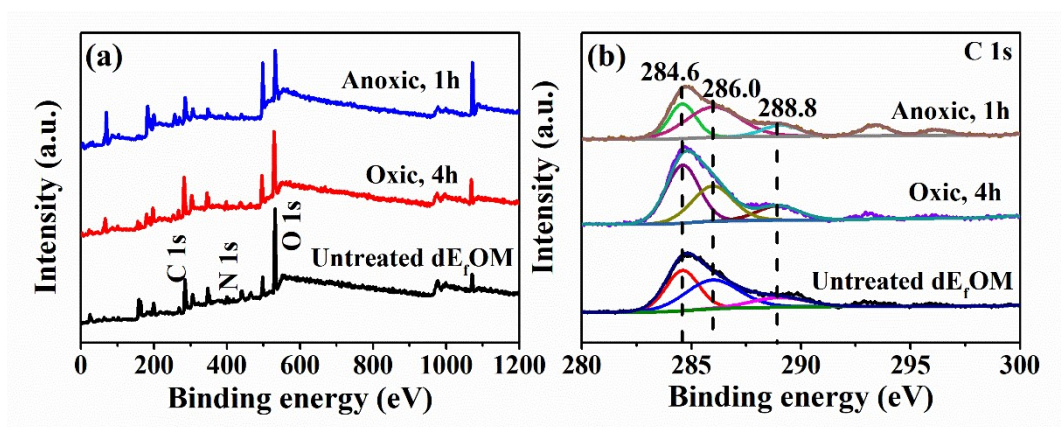


Fig. S10. (a) XPS and (b) C 1s high-resolution spectra of untreated dE_fOM, pre-oxidized sewage for 4 h and anoxic photocatalytic treated sewage for 1 h (using the pre-oxidized dE_fOM for 4 h as sacrificial reagent).

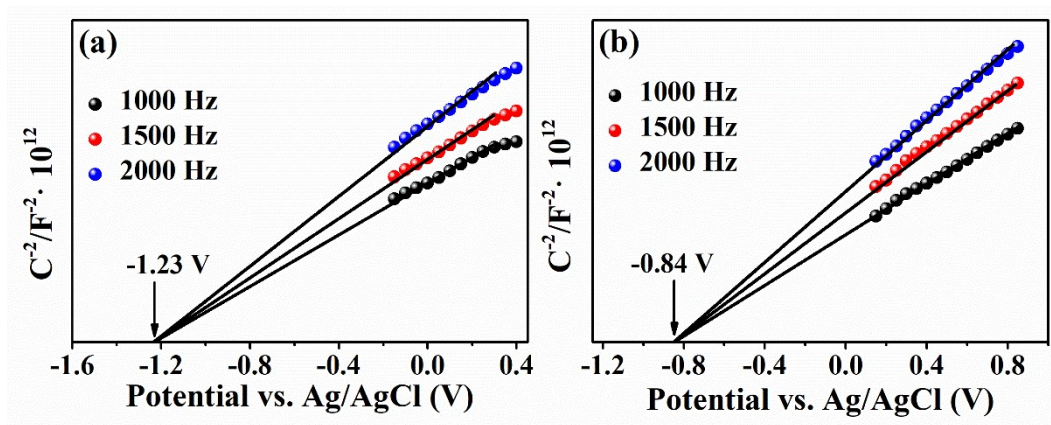


Fig. S11. Mott-Schottky plots for (a) CTF-1 and (b) BiOBr.

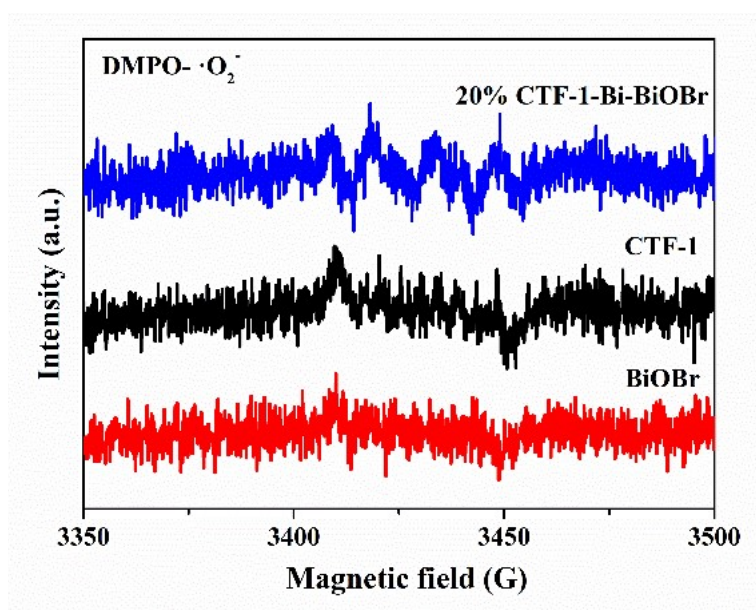


Fig. S12. DPMO spin-trapping ESR spectra for CTF-1, BiOBr and 20% CTF-1-Bi-BiOBr in methanol dispersion for DMPO- $\cdot\text{O}_2^-$.

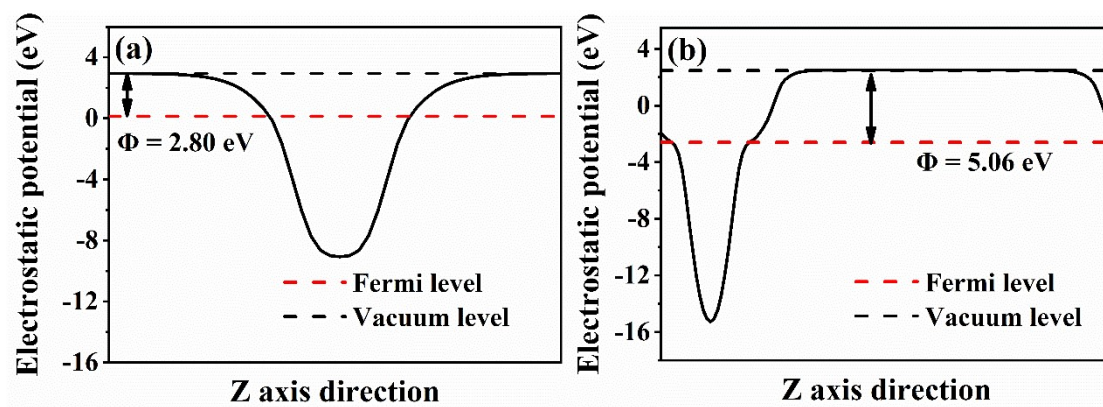


Fig. S13. The calculated work function of the (a) CTF-1 and (b) the (110) plane of BiOBr.

Table S1 BET surface area and pore volume of CTF-1, Bi-BiOBr and 20% CTF-1-Bi-BiOBr.

Sample	BET surface area (m² g⁻¹)	Pore volume (cm³ g⁻¹)
CTF-1	9.3	0.04
Bi-BiOBr	25.6	0.09
20% CTF-1-Bi-BiOBr	38.1	0.11

Table S2 Main assignments of the sewage FT-IR spectra.

Wavenumber (cm⁻¹)	Assignments
700	Out-plane bending vibration of aromatic hydrocarbon (C-H)
832	Out-plane bending vibration of C-H of olefin
870	Out-plane bending vibration of amine (N-H)
1070	Aliphatic OH
1380	C-O bond of carboxylic acids
1647	C=O stretching of carboxylate (COO ⁻)

Table S3 Comparisons of atomic concentration ratios and functional groups with respect to total carbon during the consecutive oxic-anoxic treatment.

Samples	chemical functions (molar ratio with respect to total carbon, %)		
	284.6 eV C-C/C-H	286.0 eV C-O	288.8 eV O=C-OH O=C-OR
Untreated dE _f OM	38.18	55.24	6.59
Oxic,4 h	24.39	60.30	15.31
Oxic,4 h+Anoxic,1 h	27.09	47.92	11.96