

Supporting Information

Organohalide Precursors for the Continuous Production of Photocatalytic Bismuth Oxyhalide Nanoplates

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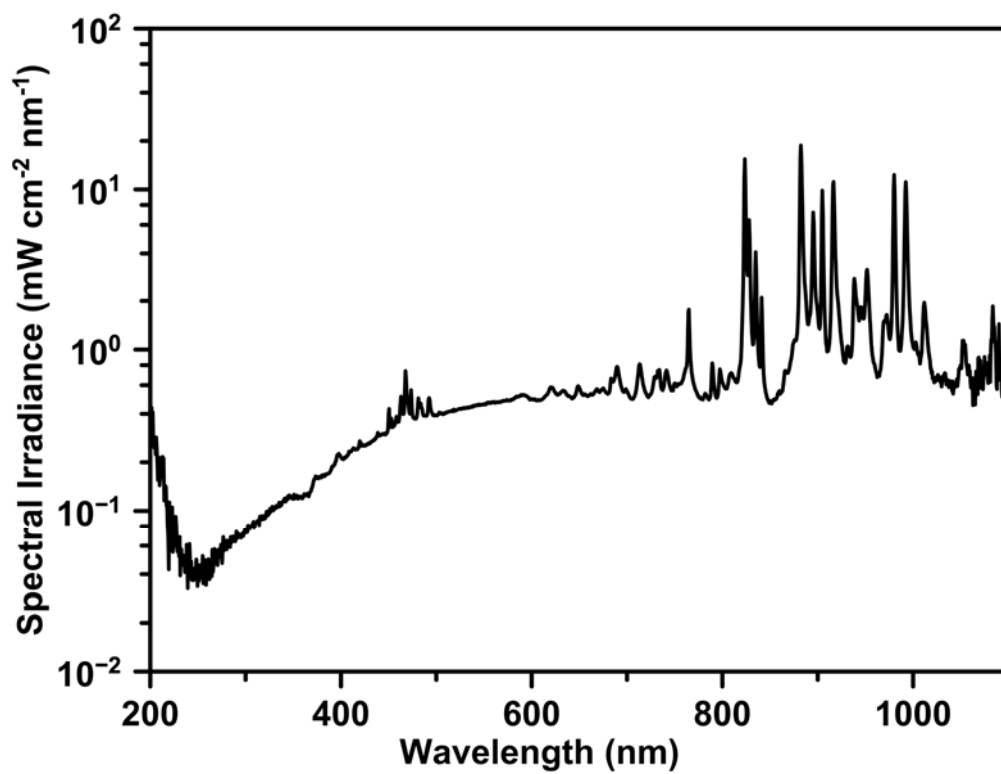


Figure S1. Spectral irradiance of the Xe lamp used in photocatalytic experiments.

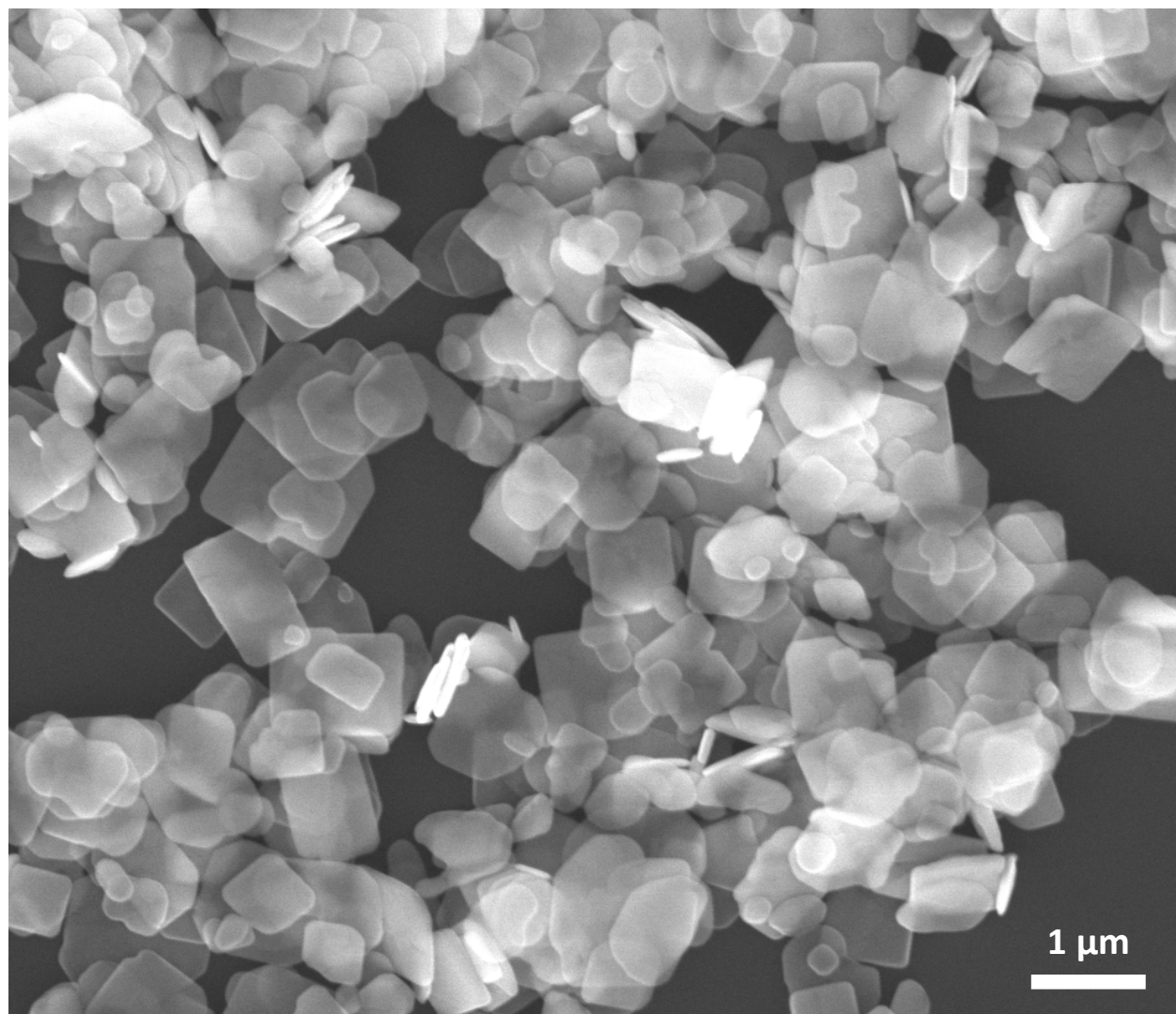


Figure S2. Large field of view SEM image of BiOBr nanoplates.

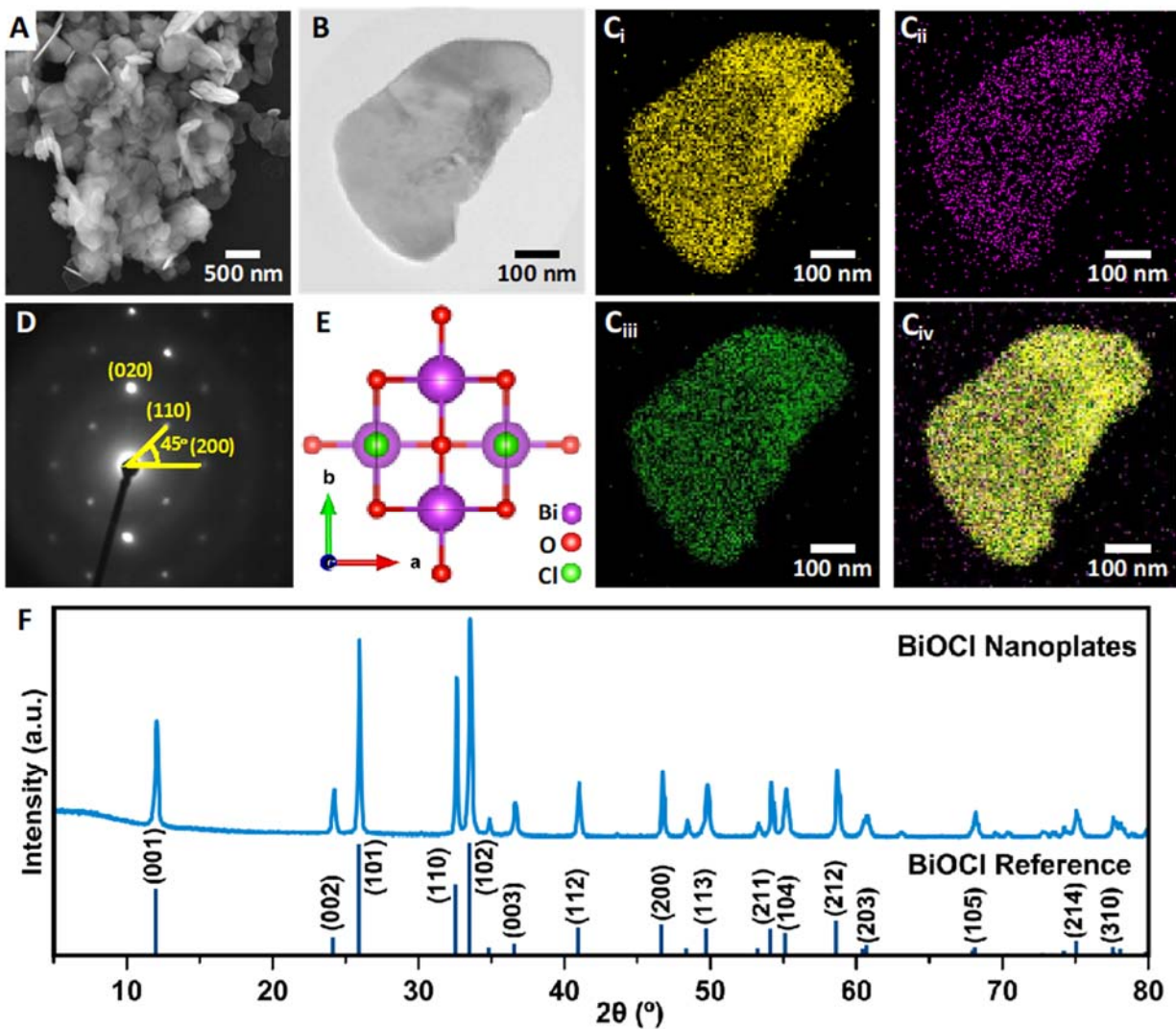


Figure S3. (A) SEM image of BiOCl nanoplates. (B) TEM image of a BiOCl nanoplate. (C) STEM-EDS elemental mapping of (B) shows presence of (C_i) bismuth (yellow), (C_{ii}) oxygen (magenta), (C_{iii}) chlorine (green), and (C_{iv}) combined bismuth, oxygen, and chlorine signals. (D) SAED pattern of (B) with reflections indexed. (E) Depiction of BiOCl crystal structure (P4/nmm, #129) viewed down the [001] direction. (F) pXRD pattern of BiOCl with reference pattern (JCPDS 85-0861).

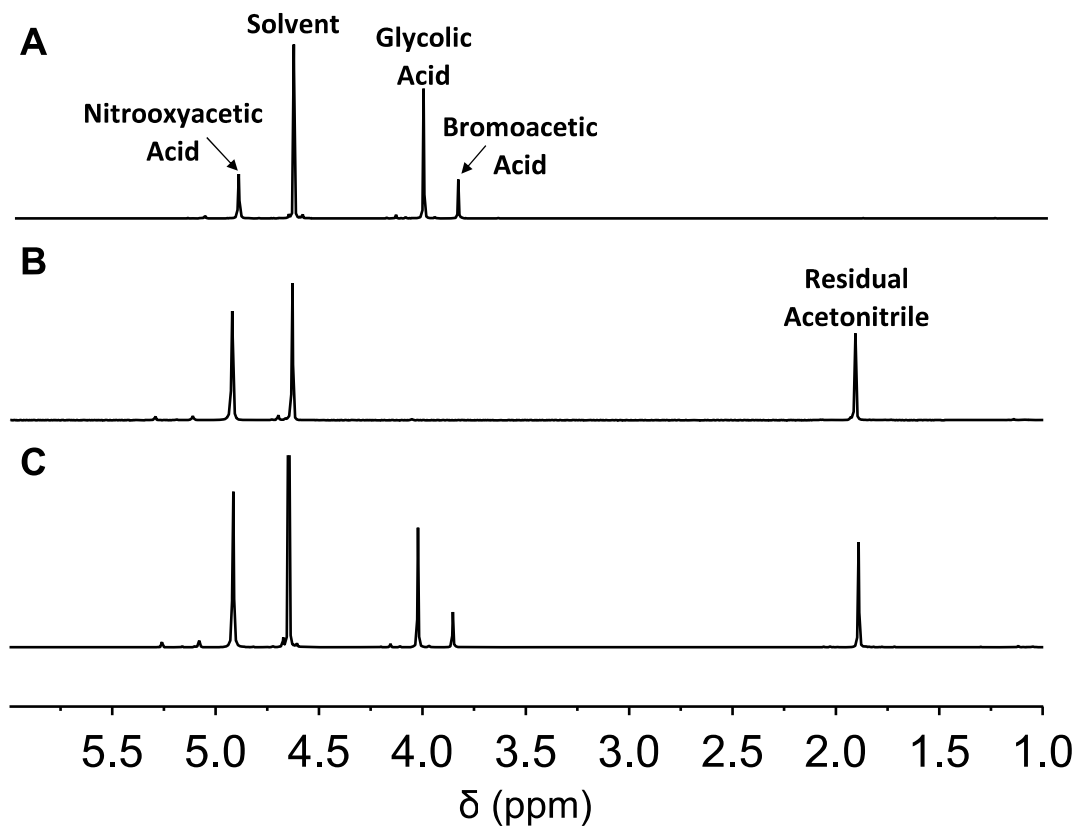


Figure S4. ^1H NMR of (A) bromoacetic acid and AgNO_3 in D_2O after heating at $100\text{ }^\circ\text{C}$ for 90 minutes, (B) nitrooxyacetic acid synthesized by a literature method¹ in D_2O , and (C) sample in “A” spiked with additional nitrooxyacetic acid “B.”

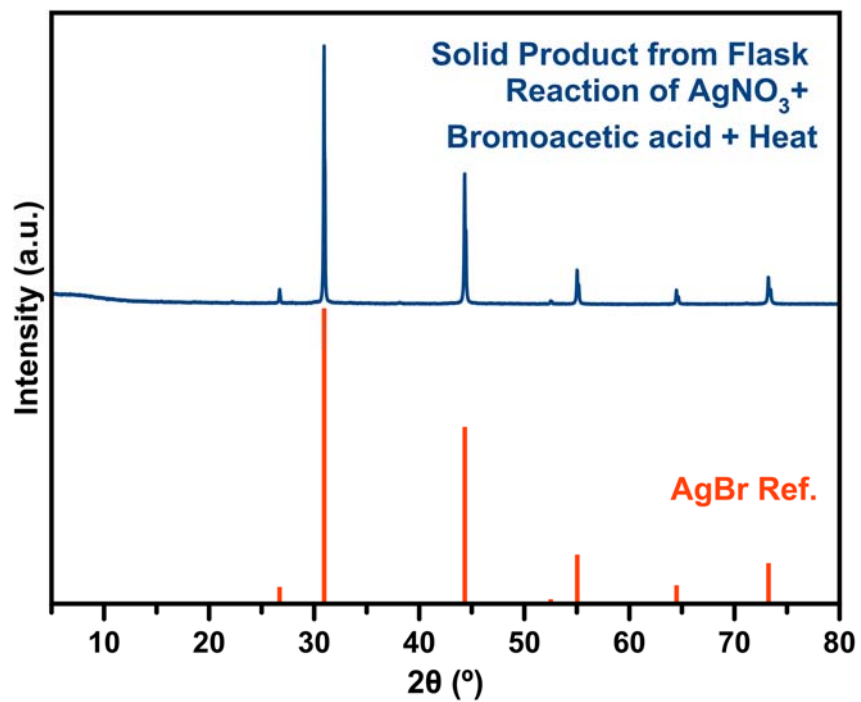


Figure S5. pXRD pattern of the solid product produced in the flask reaction of AgNO₃, bromoacetic acid, and heat. XRD reference pattern is given for AgBr: JCPDS 79-0149.

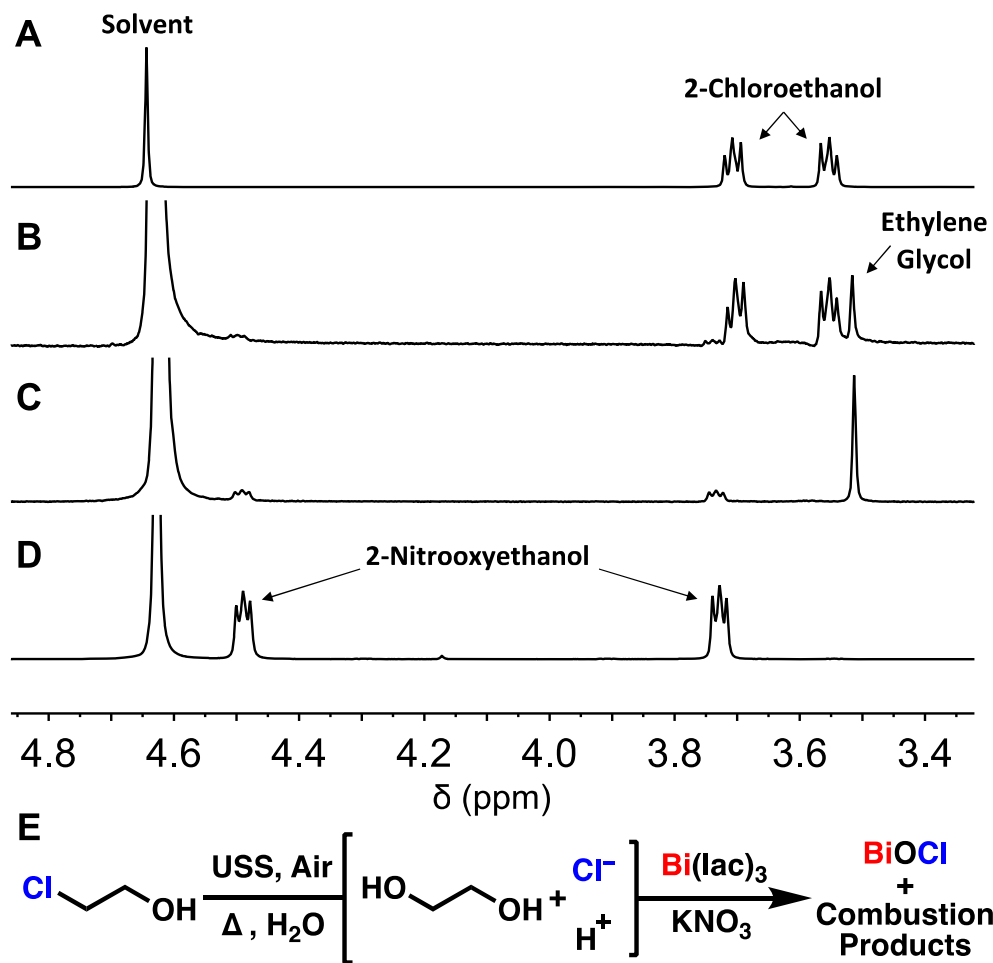


Figure S6. ^1H NMR of 2-chloroethanol and AgNO_3 in D_2O (A) without heating, (B) after heating at $100\text{ }^\circ\text{C}$ for 90 minutes, (C) after heating at $100\text{ }^\circ\text{C}$ for 6 hours, and (D) the side product 2-nitrooxyethanol synthesized by a literature method² in D_2O . (E) Proposed BiOCl production scheme.

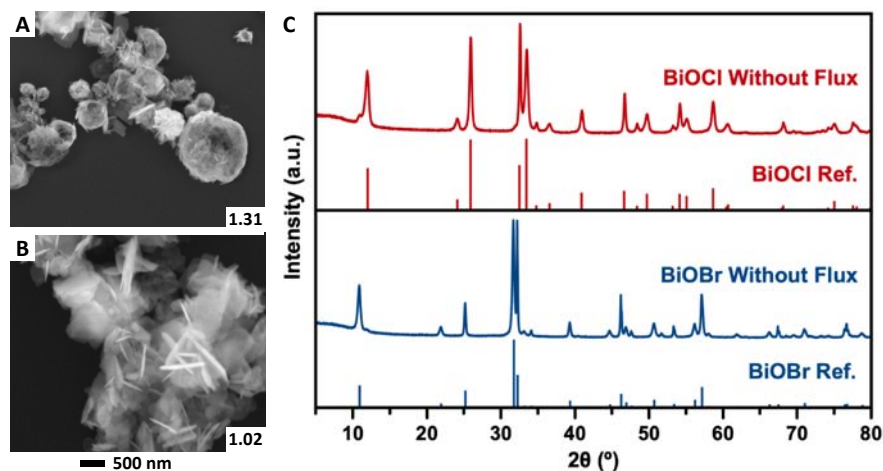


Figure S7. SEM images of (A) BiOCl and (B) BiOBr products synthesized without flux with their (C) corresponding pXRD patterns. The inset in the lower right corner of the SEM images represents the Bi/X ratio determined by SEM-EDS. The scale bar applies to both SEM images. XRD reference patterns are given for BiOCl: JCPDS 85-0861 and BiOBr: JCPDS 73-2061.

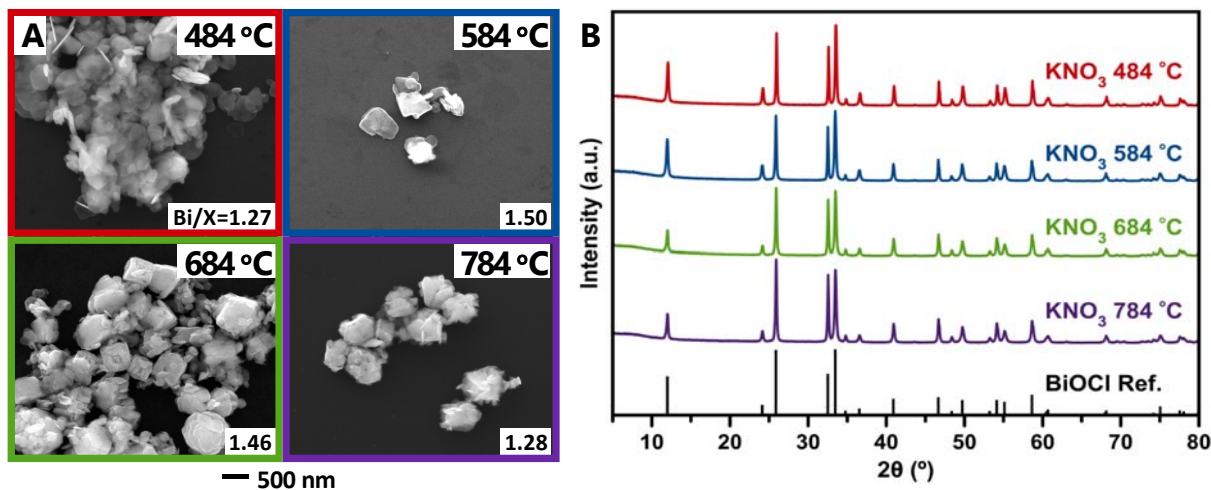


Figure S8. (A) SEM images and (B) pXRD patterns of BiOCl products synthesized with KNO₃ flux at various temperatures. The inset in the lower right corner of the SEM image represents the Bi/Cl ratio determined by SEM-EDS. The scale bar applies to all SEM images. XRD reference patterns is given for BiOCl: JCPDS 85-0861.

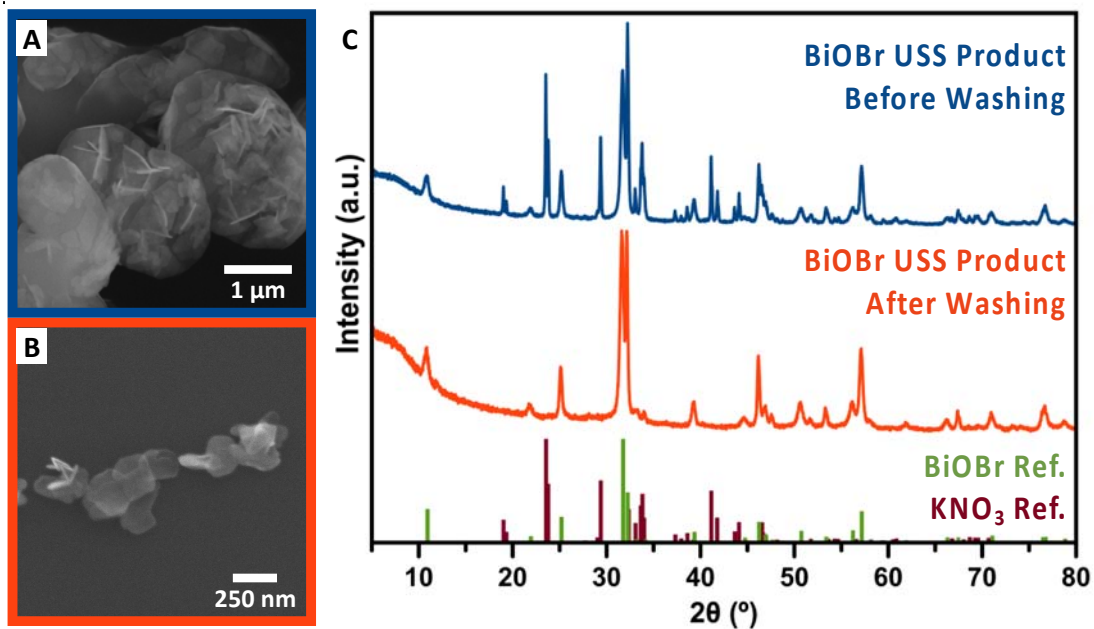


Figure S9. SEM images of BiOBr products exiting the USS reactor (A) before washing and (B) after washing with water with (C) their corresponding pXRD patterns. XRD reference patterns are given for BiOBr: JCPDS 73-2061 and KNO_3 : JCPDS 72-3826.

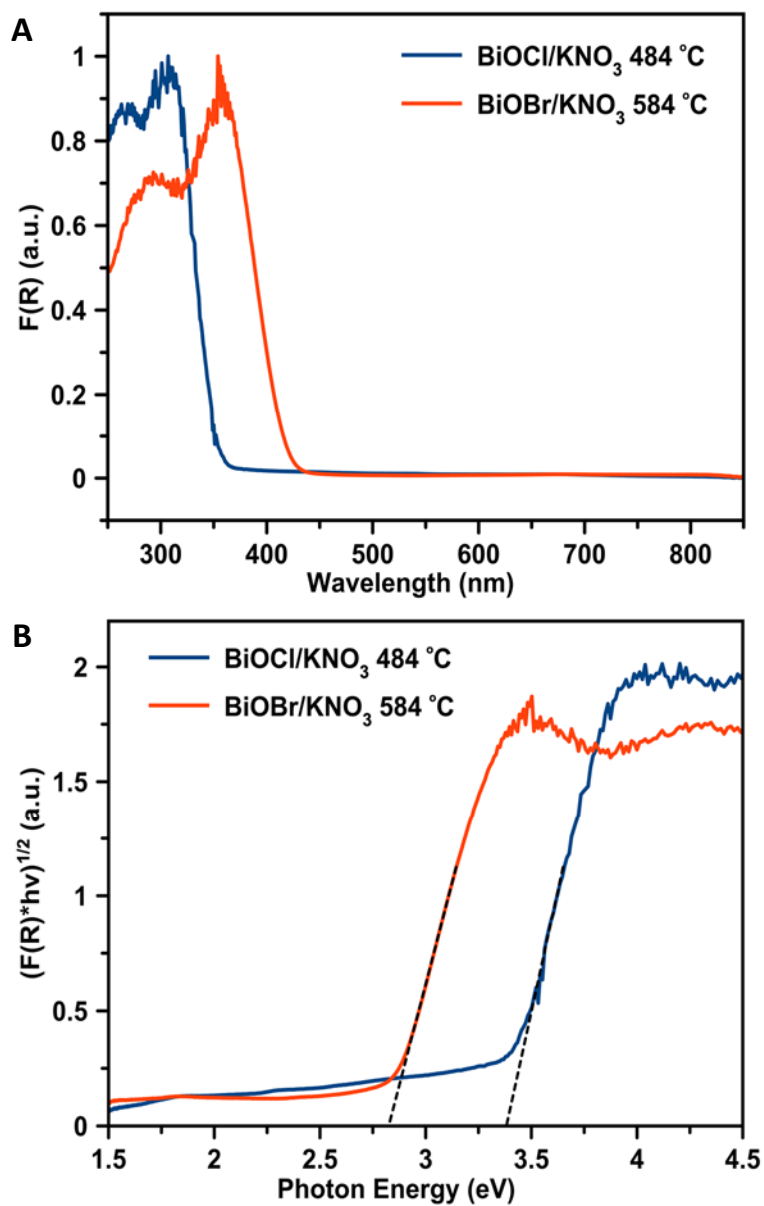


Figure S10. (A) UV-Visible DRS spectra and (B) Tauc plot of for BiOBr and BiOCl showing calculated indirect band gaps of 2.83 eV for BiOBr (orange) and 3.38 eV for BiOCl (blue).

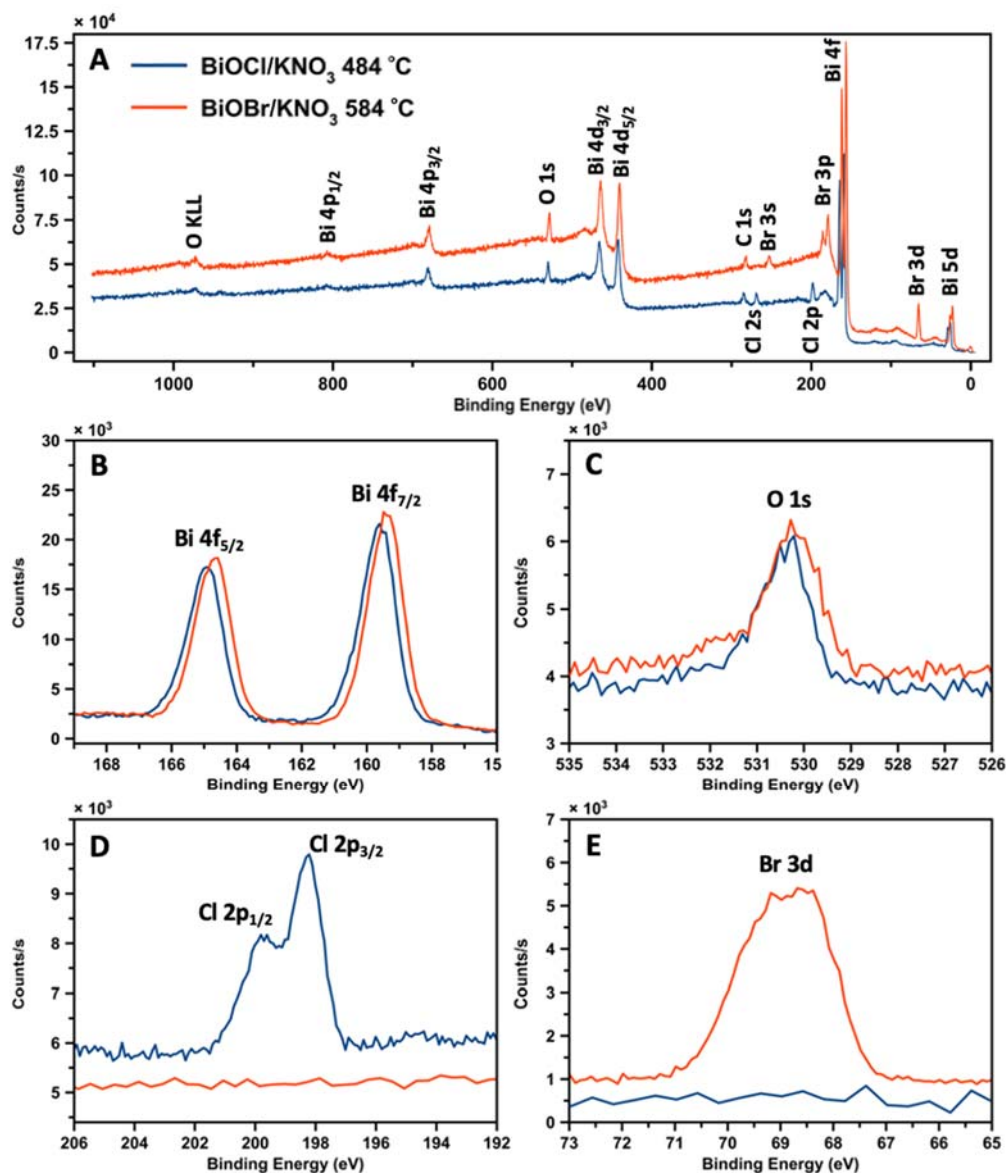


Figure S11. (A) Survey XPS spectra of BiOBr (orange) and BiOCl (blue) samples. High resolution XPS spectra of (B) Bi 4f, (C) O 1s, (D) Cl 2p, and (E) Br 3d regions.

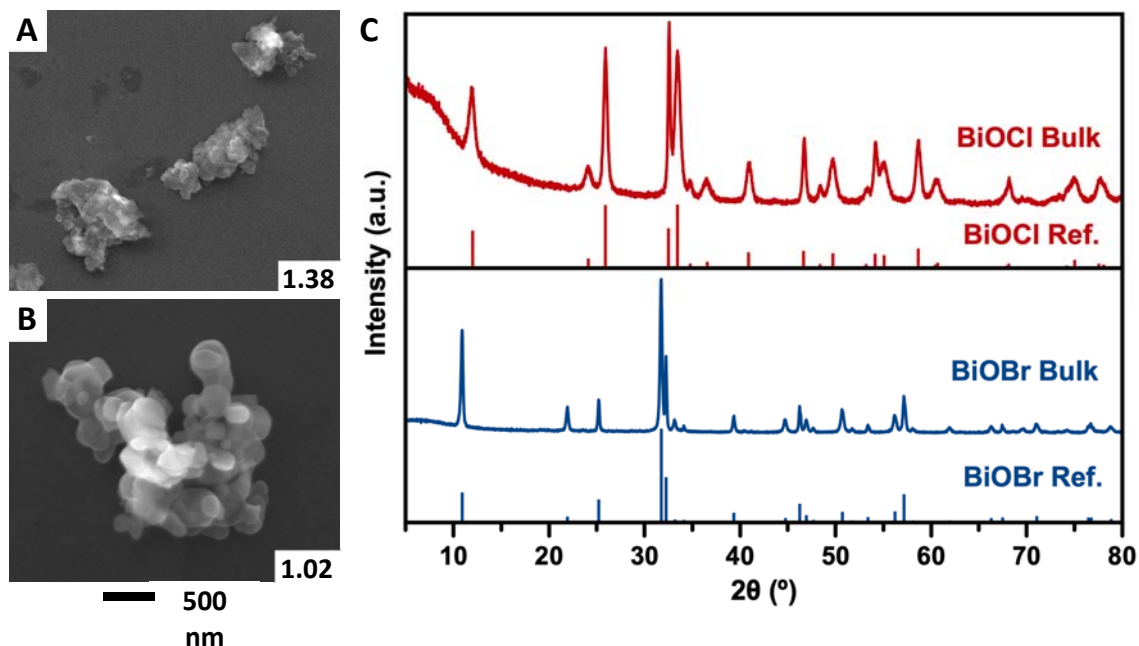


Figure S12. SEM images of bulk (A) BiOCl and (B) BiOBr products synthesized via a precipitation route with their (C) corresponding pXRD patterns. The inset in the lower right corner of the SEM images represents the Bi/X ratio determined by SEM-EDS. The scale bar applies to both SEM images. XRD reference patterns are given for BiOCl: JCPDS 85-0861 and BiOBr: JCPDS 73-2061.

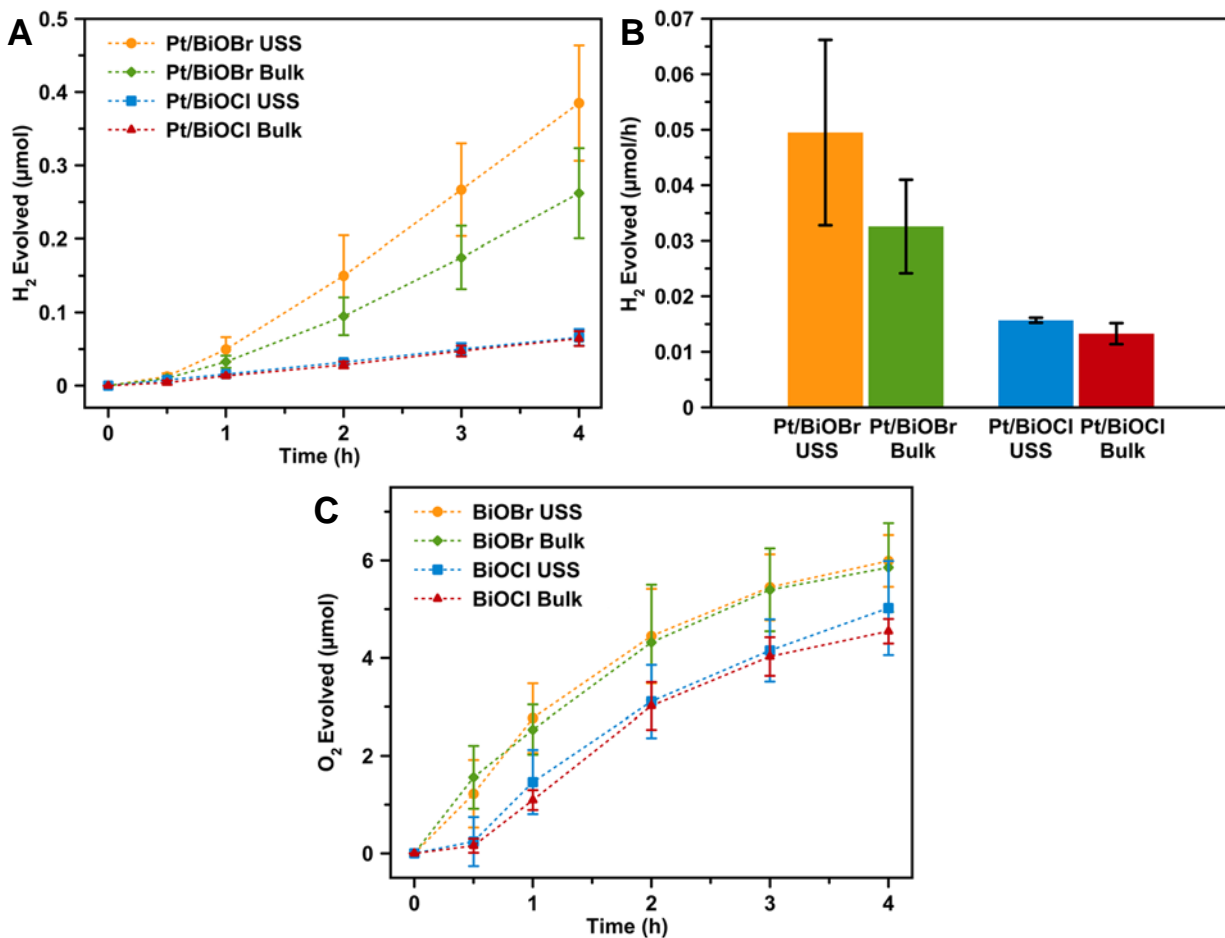


Figure S13. (A) Time-courses of photocatalytic HER on the Pt/BiOX USS samples compared to Pt/BiOX synthesized by a bulk precipitation route. (B) The hydrogen evolution rate for these samples after 1 hour. Graphs shows the average of a minimum 3 experiments with standard deviations. (C) Time-courses of photocatalytic OER on the BiOX USS samples compared to BiOX synthesized by bulk precipitation from Figure 4 with standard deviations included. Reaction conditions: HER: 10 mg 1wt% Pt-loaded sample in 10 mL 10% v/v MeOH/H₂O, 300 W Xe Lamp (full arc). OER: 10 mg sample in 10 mL 5 mM Fe(NO₃)₃ (previously adjusted to pH 2.4 with HNO₃ to prevent Fe(OH)₃ precipitation), 300 W Xe Lamp (full arc).

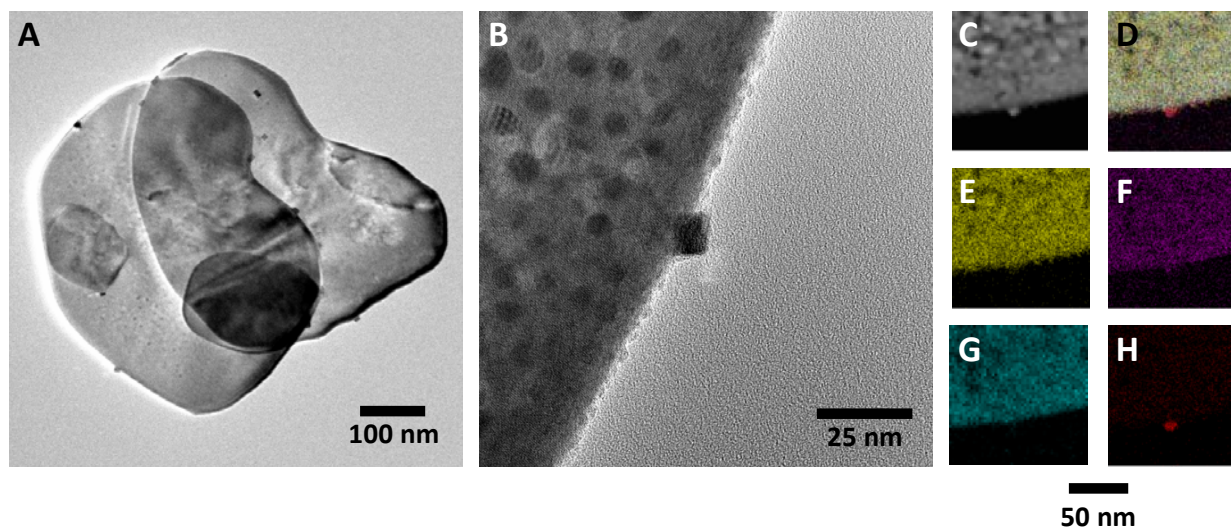


Figure S14. Characterization of BiOBr particles prepared by USS loaded with 1 wt% Pt. (A) TEM image of the Pt/BiOBr particles; (B) higher magnification of a Pt nanoparticle on BiOBr; STEM-EDS (C) electron image and (D) mixed elemental mapping of (C) highlighting (E) bismuth (yellow), (F) oxygen (magenta), (G) bromine (cyan), and (H) platinum (red). 50 nm scale bar at bottom right applies images C-H.

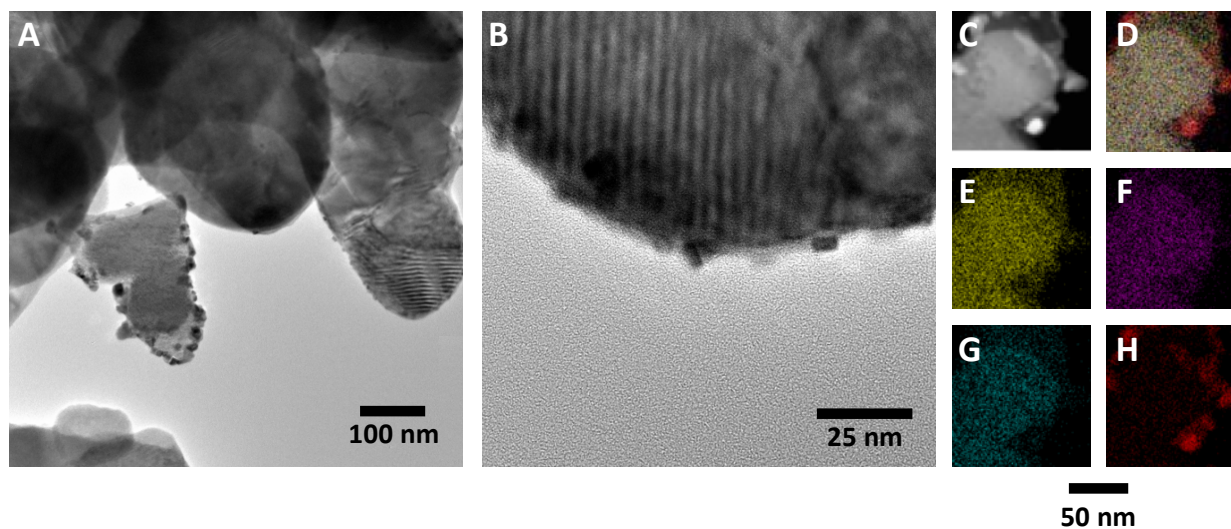


Figure S15. Characterization of BiOBr particles prepared by bulk precipitation loaded with 1 wt% Pt. (A) TEM image of the Pt/BiOBr particles; (B) higher magnification of Pt nanoparticles on BiOBr; STEM-EDS (C) electron image and (D) mixed elemental mapping of (C) highlighting (E) bismuth (yellow), (F) oxygen (magenta), (G) bromine (cyan), and (H) platinum (red). 50 nm scale bar at bottom right applies images C-H.

Table S1. Bi:X elemental composition ratio for BiOX samples determined by SEM-EDS and XPS.

Bi:X Ratio	SEM-EDS	XPS
BiOBr USS	1.07	1.69
BiOCl USS	1.27	1.90

Ferrioxalate Actinometry Details:

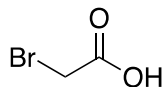
Ferrioxalate actinometry was performed to find the rate of incident photons on the reactor using a modified literature procedure.³ $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ was first synthesized by combining $K_2C_2O_4$ (1.50 M in water, 30.0 mL, 0.0450 mmol, 4.50 equiv.) and $FeCl_3$ (1.00 M in water, 10.0 mL, 0.0100 mmol, 1.00 equiv.). The green precipitate was recrystallized three times with warm water, dried at 45 °C, and kept in the dark. A $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ solution (0.0120 M in 0.0500 M H_2SO_4 , 10.0 mL, 0.120 mmol) was irradiated for 5 seconds using the same quartz reactor and 300 W Xe lamp as used for the photocatalysis experiments. An aliquot of the irradiated solution (1.5 mL) was combined with a phenanthroline buffer solution (0.10 wt% 1,10-phenanthroline and 25 wt% sodium acetate in 0.50 M H_2SO_4 , 1.0 mL) and diluted to 10 mL with water. The solution was kept in the dark for one hour before its absorbance was measured at 510 nm and compared to an unirradiated sample treated similarly as a blank. The rate of incident photons can then be calculated by the following equation, assuming all incident photons were absorbed:

$$\frac{\text{moles of photons}}{s} = \frac{V_1 \times V_3 \times \Delta A_{510 \text{ nm}}}{1000 \times V_2 \times \epsilon_{510 \text{ nm}} \times l \times \Phi \times t}$$

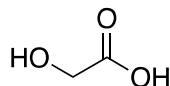
where V_1 is the irradiated volume, V_2 is the volume of the aliquot of the irradiated solution, V_3 is total volume after complexation with phenanthroline (all in mL), $\Delta A_{510 \text{ nm}}$ is the change in absorbance at 510 nm between the irradiated solution and the blank, $\epsilon_{510 \text{ nm}}$ is the molar absorptivity of ferroin ($\frac{11,100 \text{ L}}{\text{mol} \times \text{cm}}$), l is the optical path length of the spectrophotometer cuvette (in cm), Φ is the quantum yield of ferrous ion production (a value of 1.12 was used), and t is the time in seconds.

NMR Characterization:

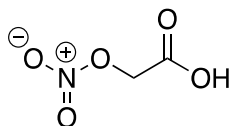
General Considerations: ^1H Nuclear Magnetic Resonance (NMR) spectra were recorded at room temperature on a Varian I400 (400 MHz) or Varian VXR400 (400 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard (D_2O : δ 4.79 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet), and integration. “O-H” protons not observed due to rapid hydrogen/deuterium exchange with D_2O .



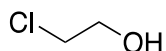
Bromoacetic acid: The title compound was purchased from Alfa Aesar and used as received. ^1H NMR (400 MHz, D_2O): δ 3.87 (s, 2H).



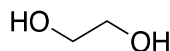
Glycolic acid: The title compound was purchased from Oakwood Chemicals and used as received. ^1H NMR (400 MHz, D_2O): δ 4.03 (s, 2H).



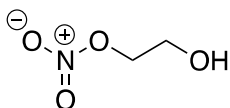
Nitrooxyacetic acid: The title compound was synthesized in accordance with literature procedure.¹ ^1H NMR (400 MHz, D_2O): δ 4.92 (s, 2H).



2-Chloroethanol: The title compound was purchased from Alfa Aesar and used as received. ^1H NMR (400 MHz, D_2O): δ 3.69 (t, 2H), 3.53 (t, 2H).



Ethylene Glycol: The title compound was purchased from Macron Fine Chemicals and used as received. ^1H NMR (400 MHz, D_2O): δ 3.46 (s, 4H).



2-Nitrooxyethanol: The title compound was synthesized in accordance with literature procedure.² ^1H NMR (400 MHz, D_2O): δ 4.49 (t, 2H), 3.73 (t, 2H).

References:

1. Hu, C.; Cun, X.; Ruan, S.; Liu, R.; Xiao, W.; Yang, X.; Yang, Y.; Yang, C.; Gao, H. Enzyme-Triggered Size Shrink and Laser-Enhanced NO Release Nanoparticles for Deep Tumor Penetration and Combination Therapy. *Biomaterials* **2018**, *168*, 64-75.
2. Ziakas, G. N.; Rekka, E. A.; Gavalas, A. M.; Eleftheriou, P. T.; Tsiakitzis, K. C.; Kourounakis, P. N. Nitric Oxide Releasing Derivatives of Tolfenamic Acid with Anti-Inflammatory Activity and Safe Gastrointestinal. *Profile. Bioorg. Med. Chem.* **2005**, *13*, 6485-6492.
3. Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. Chemical Actinometry (IUPAC Technical Report). *Pure Appl. Chem.* **2004**, *76*, 2105-2146.