

ELECTRONIC SUPPLEMENTARY INFORMATION

Hierarchical BiOI nanostructures supported on a metal organic
framework as an efficient photocatalyst for degradation of
organic pollutants in water

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1. Preparations of photocatalysts

All the chemicals and reagents such as bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), potassium iodide (KI), 1,4-benzenedicarboxylic acid, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, DMF, CH_3CN , ethylene glycol purchased from Daejung Chemicals, South Korea and were of analytical grade and used as without further purification. Deionized water (DI) was used throughout the experiment.

1.1 Preparation of MIL-88B (Fe) 3D structure

MIL-88B (Fe) 3D structure were prepared according to the modified of the earlier method.¹ In briefly, 30 mg of 1,4-benzenedicarboxylic acid (1,4-BDC) and 80 mg of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was mixed in 4 mL of DMF and then added 4 mL of CH_3CN . After that the resulting mixture was put in an oil bath for 45 min, which temperature is 120 °C. Finally, the 3D Fe-MIL-88B (MOF) were produced which were isolated by cooling the reaction mixture solution to room temperature. The product was separated and subsequently washed with fresh DMF and methanol via centrifugation and redispersion cycles. Every time successive supernatant was decanted and replaced with fresh solvent and then dried at 80 °C for 6 hours.

1.2 Preparation of BiOI and BiOI/MIL-88B (Fe) photocatalysts

In a typical synthesis, different amounts (1, 2, and 3 wt %) of the as-prepared MIL-88B(Fe) was ultrasonically dispersed into 20 mL ethylene glycol (EG) and 1 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ dissolved in it. Afterwards, 1 mmol of KI was dissolved in 20 mL deionized water and then added dropwise into the above Fe-MIL-88B and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ suspension

under magnetic stirring condition. Then, the suspension was stirred for 15 min at room temperature. The precipitate MOF then separated, washed with deionized water several times and then dried at 80 °C for 8 hours. Similarly, BiOI was synthesized under the same conditions except adding MOF.

2. Characterization of the photocatalysts

The surface morphologies and elemental analysis were evaluated using a HITACHI S-4800 field emission scanning electron microscope (FESEM) equipped with an energy-dispersive spectrometer (EDS, Inca 400, Oxford Instruments). The crystal structure of these samples was characterized by X-ray diffraction spectroscopy (XRD) through a Bruker D8 Advanced X-ray diffractometer with Cu K α radiation as the X-ray source. X-ray photoelectron spectroscopy (XPS) measurements were carried out to evaluate the chemical status and element composition of the samples with a monochromated Al K α X-ray source ($h\nu = 1486.6$ eV) at an energy of 15 kV/150 W. The UV-visible diffuse-reflectance spectrum was recorded using a UV-3600 UV-VIS-NIR spectrophotometer (UV-1650PC, Shimadzu, Japan). The Photoluminescence (PL) spectra of the photocatalysts were collected at room temperature using a Hitachi F-7000 fluorescence spectrometer. The electron spin resonance (ESR) was performed using a JES-FA100 (JEOL) spectrometer at room temperature.

3. Photocatalytic experiments

Photocatalytic performance of different photocatalysts such as BiOI and BiOI/MOF composites were explored by the degradation of RhB, phenol and ciprofloxacin (CIP) (Daejung Chemicals, South Korea), (10 mg/L) in aqueous solution under solar simulator (Model 10500 Low Cost Solar Simulator with a Model 10513 90° Uniform Illumination Accessory) equipped with an AM 1.5G filter and 150W Xe lamp as the light source (ABET technologies). Visible light photocatalytic activity was measured under the same photocatalytic experimental conditions except the irradiation source, here 150 W Xe lamp with 425 nm band pass filter having optical density greater than 4 in the rejection band and slope factor less than 1 %, were used as light sources, instead of the solar simulator. The output light intensity was measured using 15151 low-cost calibrated Si reference cell (ABET technologies). The liquid level is ~16 cm far from the window of lamp and the illuminated area is 21.24 cm². For catalytic reactions 30 mg of as-synthesized photocatalyst was dispersed in 100 mL RhB, phenol and CIP solution in a 150 mL Pyrex conical flask. Before irradiation, the photocatalyst suspension was magnetically stirred at room temperature in the dark up to 90 min to attain adsorption-desorption equilibrium. After adsorption-desorption equilibrium, the solar simulator was turned on and during irradiation, 2.0 mL suspension was withdrawn at regular 10 min time intervals and centrifuged to remove the photocatalyst and then the solution concentration was analyzed at their characteristic maximum absorption wavelength with a UV-Vis spectrophotometer (UV-1650PC, Shimadzu, Japan) at room temperature. The characteristic maximum absorption wavelength of RhB, phenol and CIP were 553.8, 269.9 and 276 nm, respectively. The visible light photocatalytic activity of the BiOI/MOF composite was tested through the degradation of colorless phenol and CIP. For the recycling experiment, previously

used BiOI/MOF photocatalyst was centrifuged out from the solution, washed and dried for 8 h at 80 °C and then reused the same concentration RhB degradation.

4. Active species and •OH radical experiments

To examine the effect of reactive species including holes, $\bullet\text{O}_2^-$, and $\bullet\text{OH}$; ethylenediaminetetraacetic acid (EDTA), benzoquinone (BQ), and t-butyl alcohol (TBA) were added during the photocatalytic process. To measure the amount of $\bullet\text{OH}$ producing from BiOI and BiOI/MIL-88B (Fe) photocatalyst, terephthalic acid (TA) (5×10^{-4} M in a 2×10^{-3} M NaOH solution) was used as a probe molecule. TA could react with $\bullet\text{OH}$ radicals to produce high fluorescent 2-hydroxy terephthalic acid (TAOH) photoluminescence signal at around 425 nm and measured by a Hitachi F-7000 fluorescence spectrometer. To determine the amount of $\bullet\text{O}_2^-$ generated from BiOI and BiOI/MIL-88B (Fe) photocatalysts, NBT (2.5×10^{-5} mol L⁻¹) was used and the production of $\bullet\text{O}_2^-$ was quantitatively determined by detecting the concentration of NBT with a UV-Vis spectrophotometer (UV-1650PC, Shimadzu, Japan).

5. Electrochemical measurements

To evaluate the flat-band potential (V_{FB}) of the BiOI and BiOI/MOF Mott–Schottky plots at a frequency of 1 kHz were measured using a standard potentiostat equipped with an impedance spectra analyzer. Electrochemical measurements were performed in a three-electrode system using a CHI 617B electrochemical workstation. The reference and counter electrodes were Ag/AgCl and platinum wire, respectively, and 0.5 M Na₂SO₄ aqueous solution served as the electrolyte. To prepare the working electrode, the as-synthesized 10 mg of BiOI and BiOI/MOF nanocomposites were first dispersed into ethanol (450 μL) and 50 μL Nafion mixtures using soft ultrasonic stirring

to obtain a uniform suspension. The solution containing the catalyst (30 μL) was dropped onto the pretreated indium–tin oxide (ITO) conductor glass substrate, which was then dried in an oven at 80 $^{\circ}\text{C}$ for 3 h. The measured potentials versus Ag/AgCl were converted to the normal hydrogen electrode (NHE) scale by $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197$.

References

[1] W. Cho, S. Park and M. Oh, *Chem. Commun.*, 2011, **47**, 4138–4140.

Supporting Figures

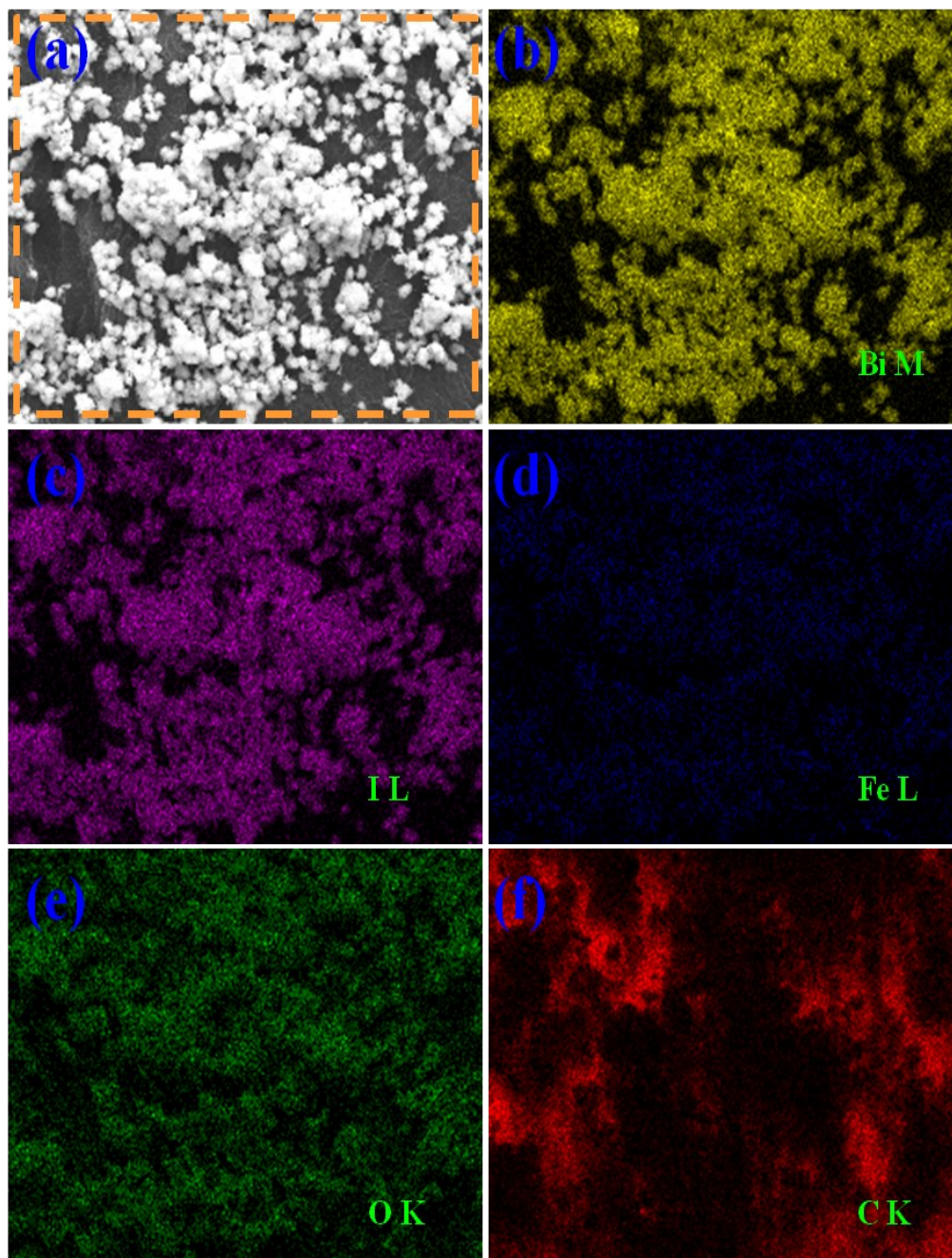


Fig. S1. EDS element mapping of BiOI/MOF nanocomposite showing the presence of (b) Bi, (c) I, (d) Fe, (e) O, and (f) C.

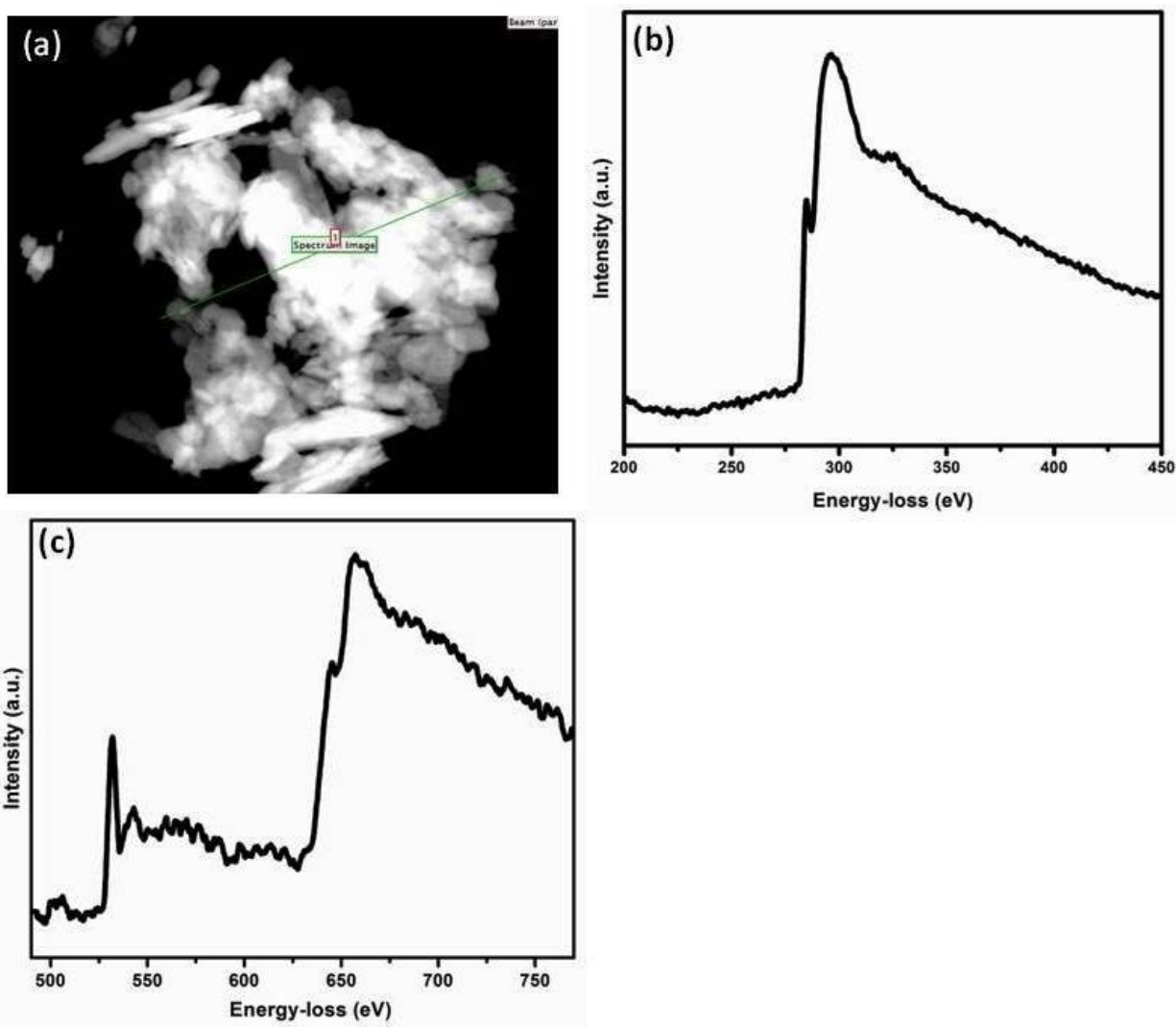


Fig. S2. (a) TEM and (b-c) EELS results of BiOI/MOF (2 wt.%) nanocomposites.

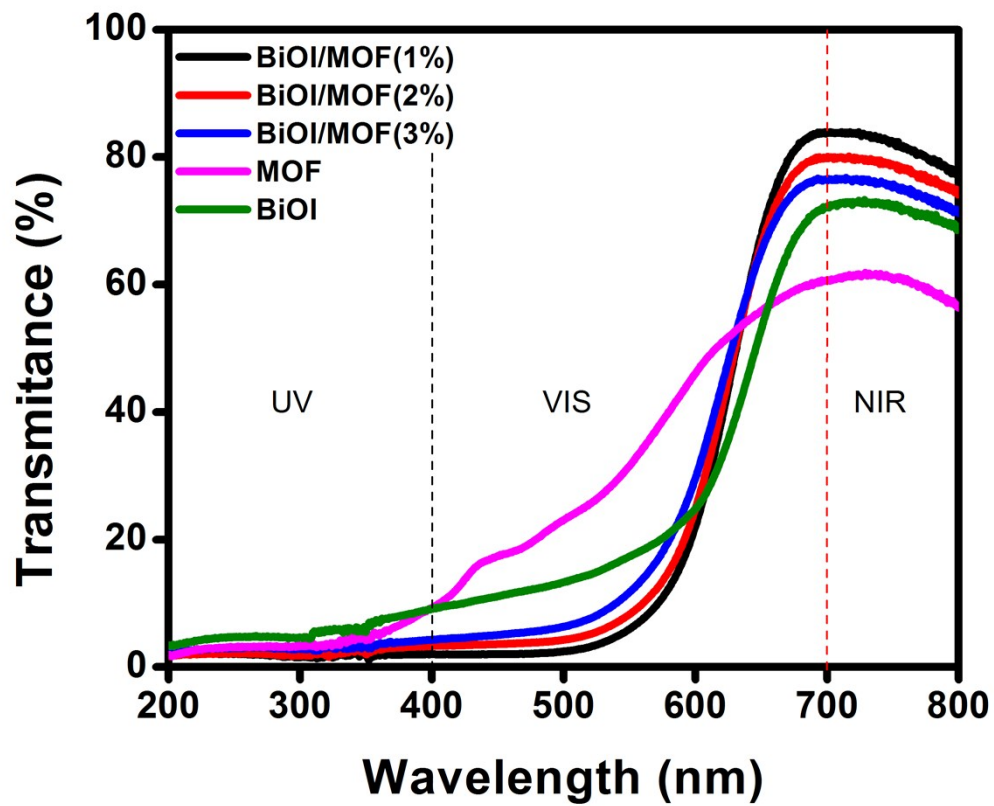


Fig. S3. UV-Vis diffuse reflectance spectra of BiOI, MOF, and BiOI/MOF photocatalyst composites.

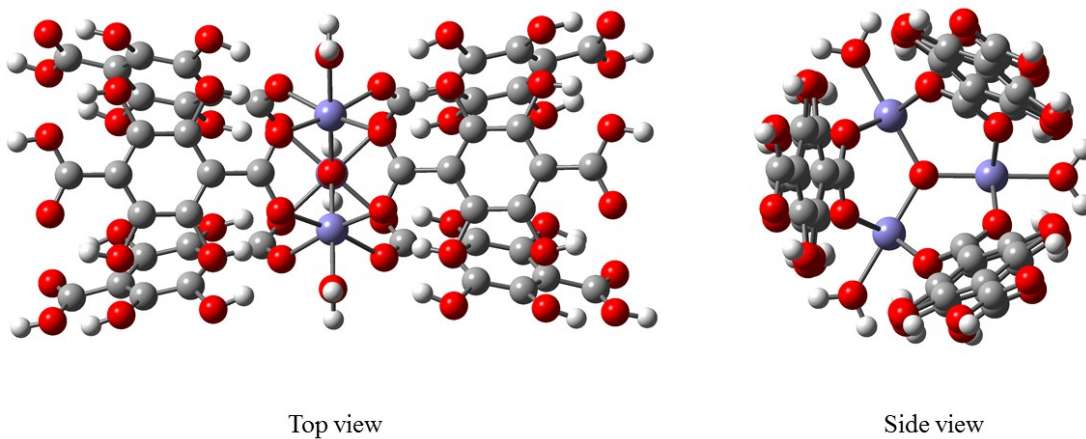


Fig. S4. Optimized cluster model of BiOI/MOF.

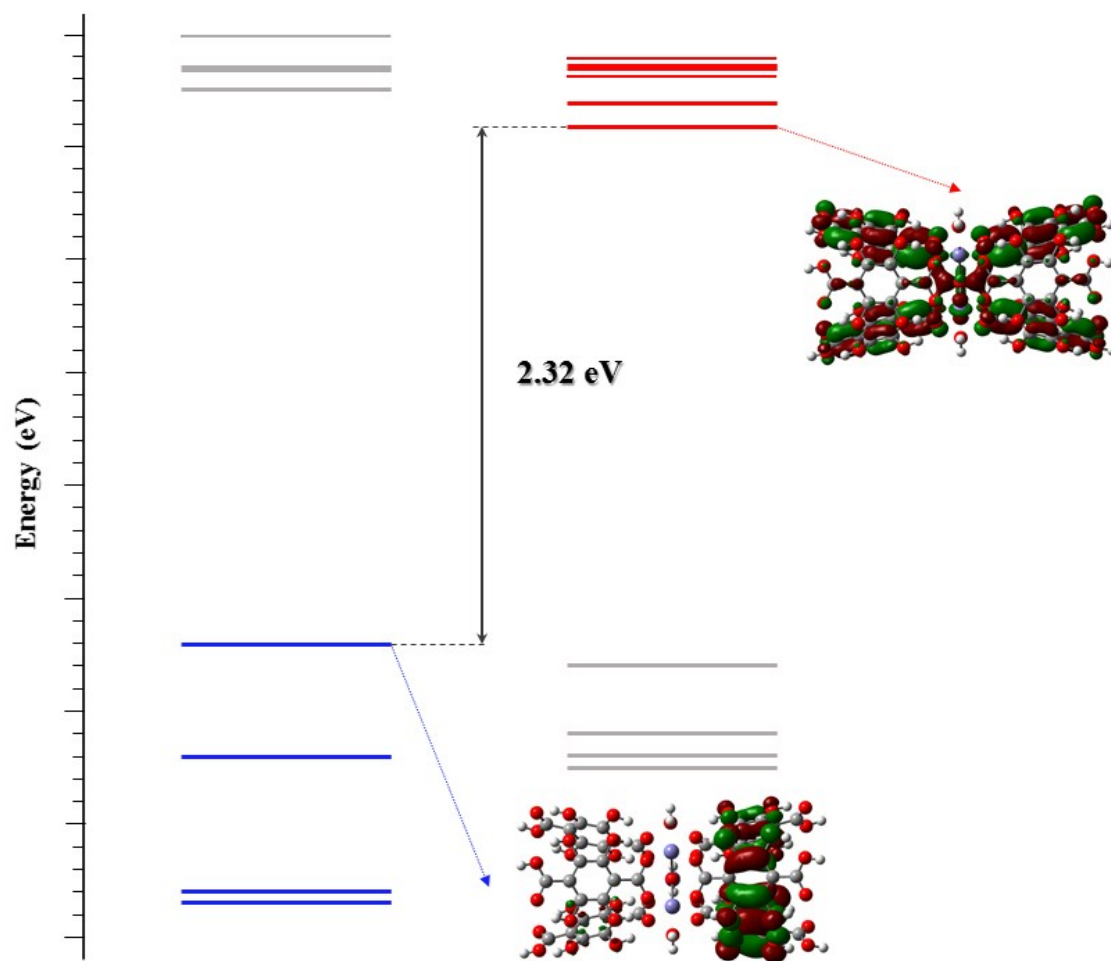


Fig. S5. Molecular orbital energy level diagram and frontier molecular orbitals of BiOI/MOF.

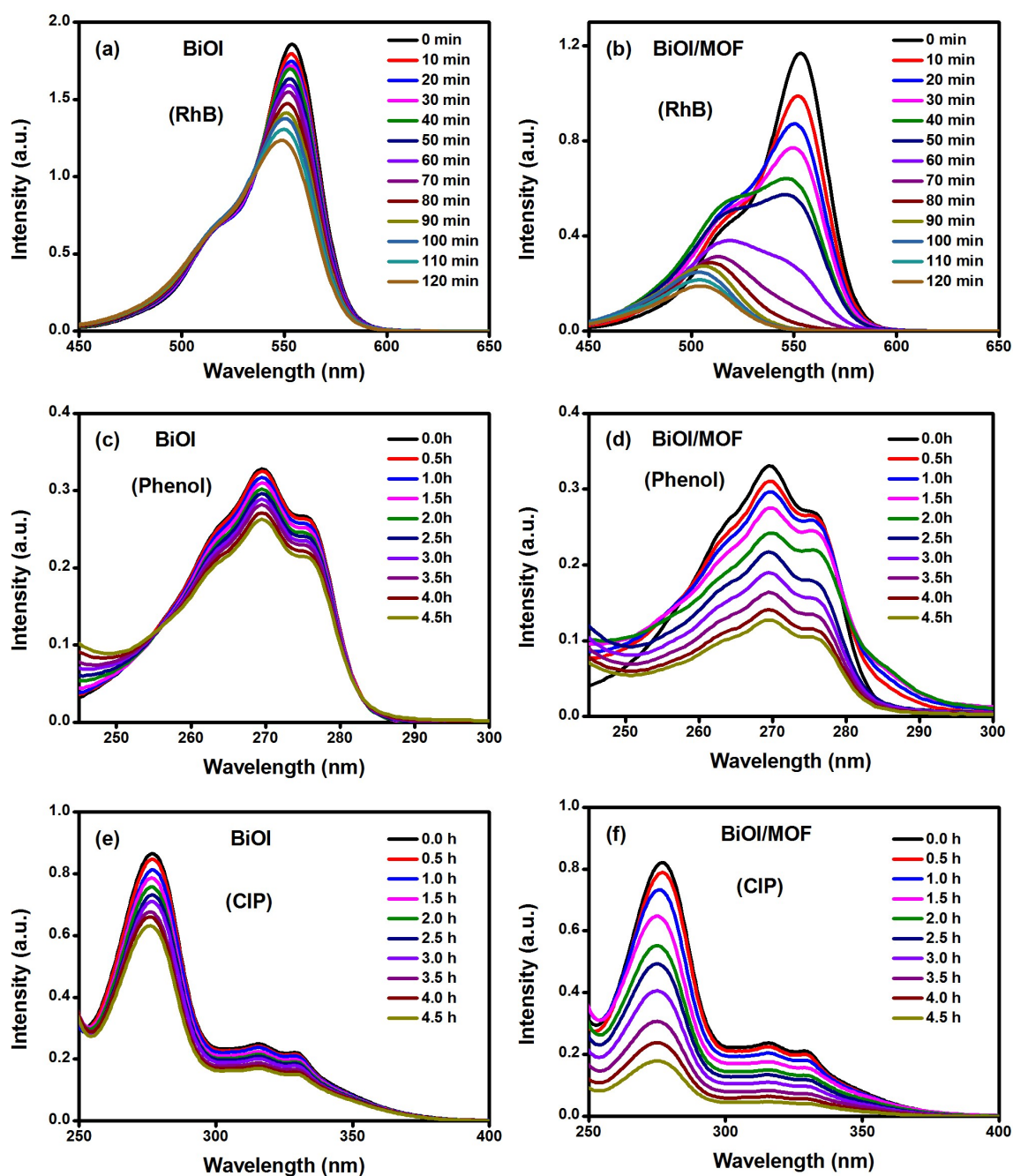


Fig. S6. Time-dependent absorption spectra of the RhB aqueous solution in the presence of (a) BiOI and (b) BiOI/MOF. Time-dependent absorption spectra the phenol aqueous solution in the presence of (c) BiOI and (d) BiOI/MOF. Time-dependent absorption spectra of the CIP aqueous solution in the presence of (e) BiOI and (f) BiOI/MOF.

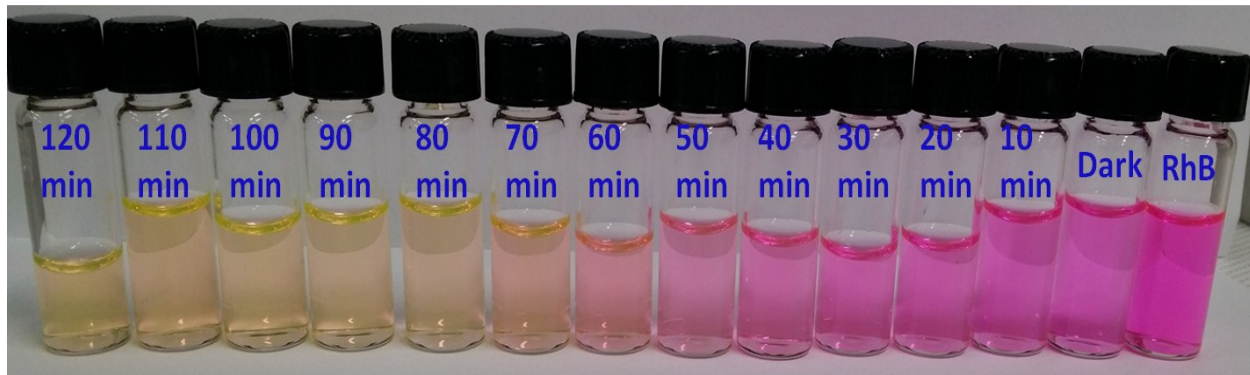


Fig. S7. The digital image of the aliquots indicating the color changes of the RhB solutions during the photocatalytic activity in the presence of BiOI/MOF nanocomposite.

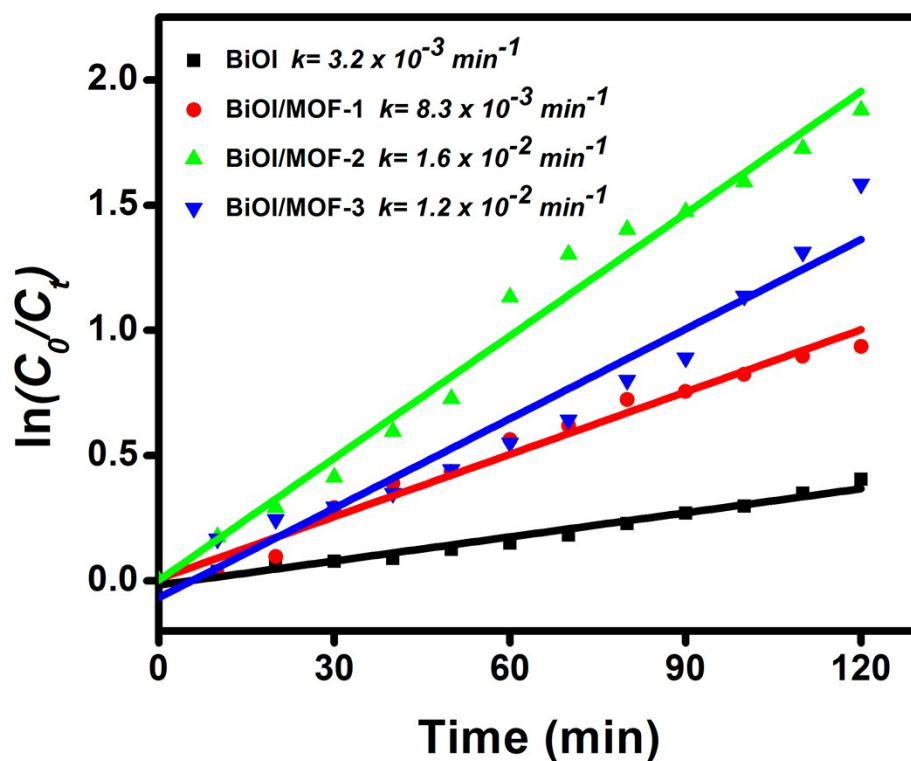


Fig. S8. The pseudo-first order photocatalytic degradation rate of RhB aqueous solution containing different photocatalysts (BiOI and BiOI/MOF (1, 2, and 3 wt.%) nanocomposites).

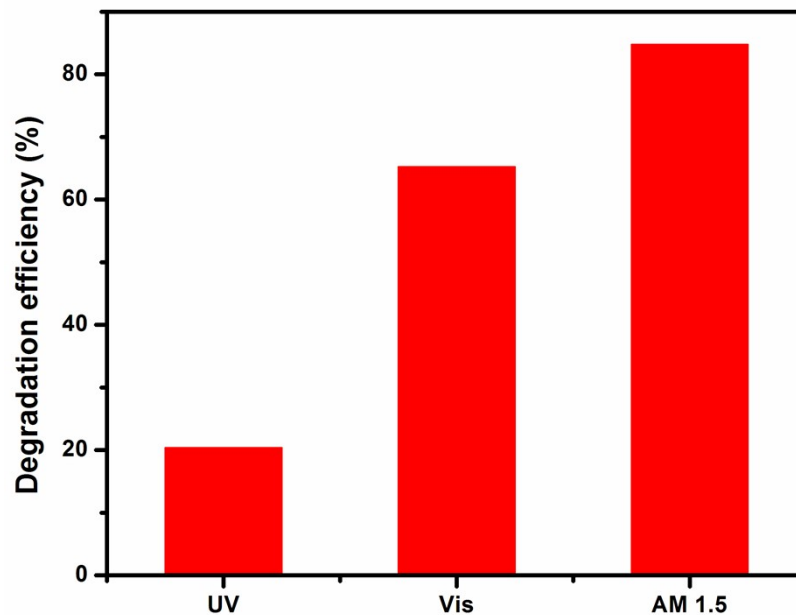


Fig. S9. Photocatalytic RhB degradation efficiency of BiOI/MOF (2 wt.%) nanocomposite under UV, Vis and simulated sun light (AM 1.5) irradiations.

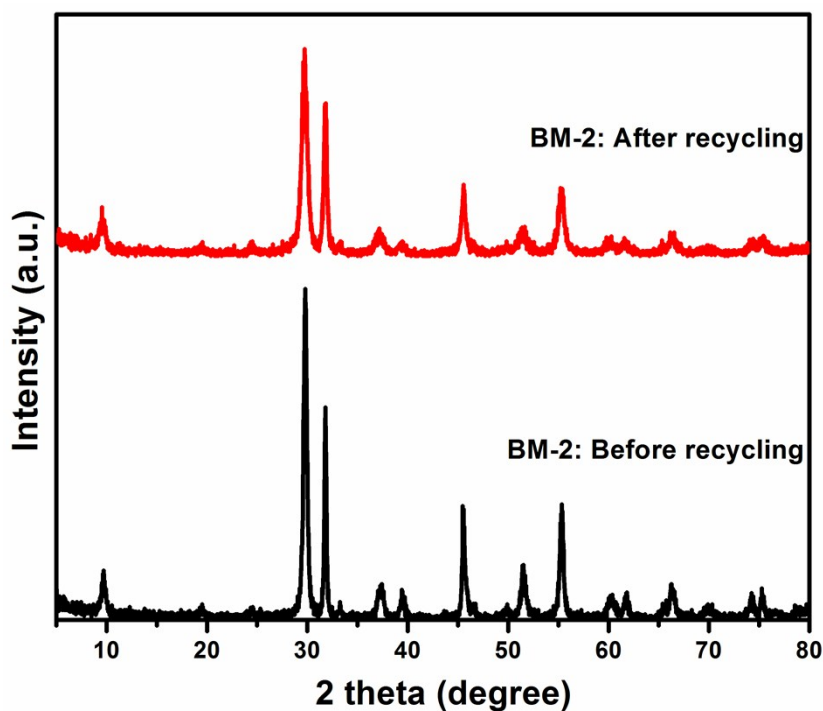


Fig. S10. The XRD patterns of BiOI/MOF (2 wt.%) (BM-2) nanocomposite before and after photocatalytic recycling measurement.

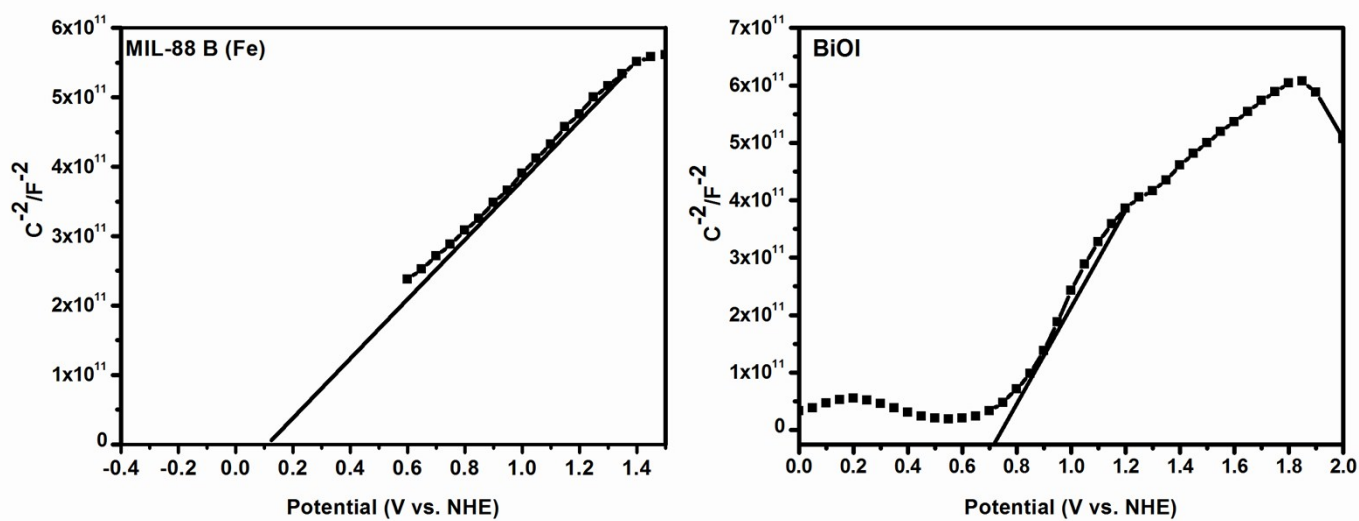


Fig. S11. Mott-Schottky plot of MOF and BiOI nanostructures.

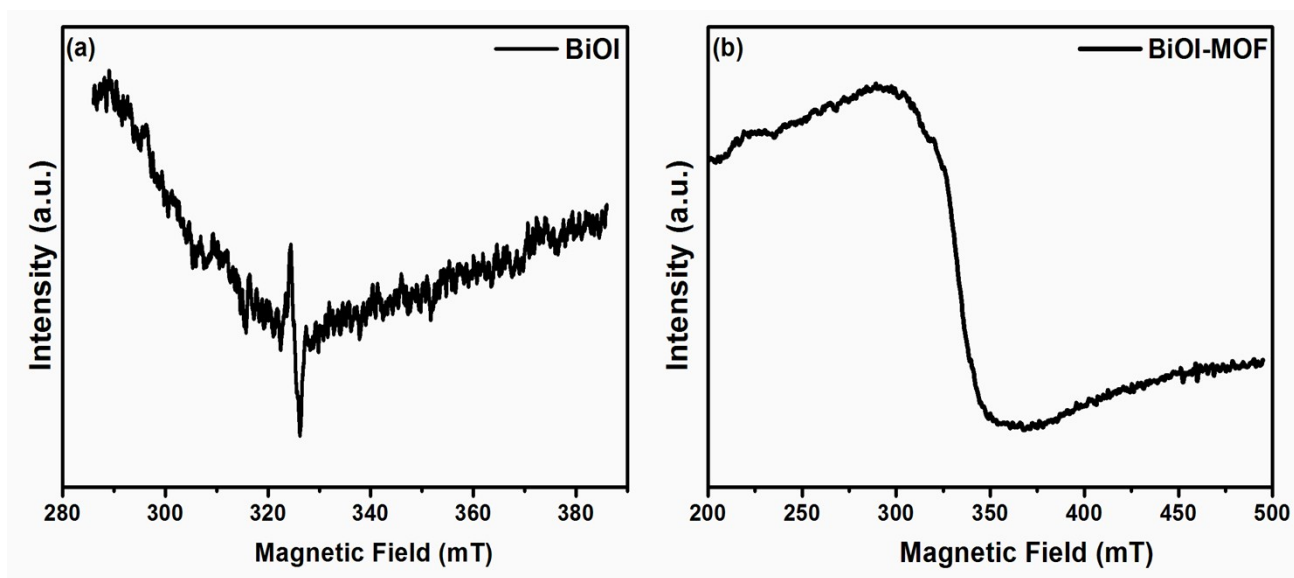


Fig. S12. EPR spectra of (a) BiOI and (b) BiOI-MOF nanocomposites.

Table S1. Elemental composition of as-synthesized nanostructures from EDS analysis.

Sample	Estimated composition in wt.%				
	Bi	O	I	Fe	C
BiOI	58.45	4.12	37.43	-	-
BiOI/MOF (1 wt. %)	56.79	3.86	37.24	0.69	1.42
BiOI/MOF (2 wt. %)	55.09	3.76	36.04	1.85	3.26
BiOI/MOF (3 wt. %)	54.49	3.65	35.12	2.56	4.18