# ELECTRONIC SUPPLEMENTARY INFORMATION

Oxygen-vacancy rich 3D novel hierarchical MoS<sub>2</sub>/BiOI/AgI ternary nanocomposite: Toward enhanced photocatalytic activity by photogenerated electron shuttling in Z-scheme manner

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#### **1. Experimental Section**

All the chemicals and reagents such as bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O, potassium iodide (KI), silver nitrate (AgNO<sub>3</sub>), sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>), 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 MoS<sub>2</sub> nanostructures

MoS<sub>2</sub> nanosheets were prepared slightly modifying to the earlier method.<sup>1</sup> In briefly, 0.3g of sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>) was dissolved in deionized water under magnetic stirring condition and 0.6g of thioacetamide (C<sub>2</sub>H<sub>5</sub>NS) was added and stirred for 10 min. Then the above transparent solution was transferred into 100 ml Teflon-lined autoclave and heated at 200 °C for 24 hours. After cooling down the autoclave at room temperature, black precipitates were washed with deionized water several times by centrifugation and then dried at 80 °C for 8 hours. Finally, MoS<sub>2</sub> nanosheets were collected for further use.

#### 1.2 Preparation of BiOI, BiOI/AgI and MoS<sub>2</sub>/ BiOI/AgI photocatalyst

In a typical synthesis, different amounts of the as-prepared  $MoS_2$  was ultrasonically dispersed into 20 mL ethylene glycol (EG) and 1 mmol of Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O dissolved in it. Afterwards, 1 mmol of KI was dissolved in 20 mL deionized water and then added dropwise into the above  $MoS_2$  and Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O suspension under strong magnetic stirring condition. Then, the suspension was stirred for 1 h at room temperature. Finally, 0.5 mmol

of Ag(NO<sub>3</sub>) was dissolved in 20 mL deionized (DI) water and added in the above suspension drop wise under magnetic stirring and subsequently the solution was stirred for 2 hours at room temperature. The precipitate MoS<sub>2</sub>/BiOI/AgI then separated, washed with deionized water several times and then dried at 80 °C for 8 hours. Similarly, BiOI/AgI photocatalysts were synthesis using different molar ratio of Ag(NO<sub>3</sub>) where as pure AgI was synthesize with 1:1 molar ratio of KI and AgNO<sub>3</sub>, without dispersing MoS<sub>2</sub> and Pure BiOI was synthesized under the same conditions except adding MoS<sub>2</sub> and AgNO<sub>3</sub>.

### 2. Characterization of 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 Ka 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 $\alpha$  X-ray source (hv = 1486.6 eV) at an energy of 15 kV/150 W. The electron spin resonance (ESR) was performed using a JES-FA100 (JEOL) spectrometer at 173 K. The UV-visible diffuse-reflectance spectrum was recorded using a UV-3600 UV-VIS-NIR spectrophotometer (UV-1650PC, Shimadzu, Japan). For steady-state and time-resolved photoluminescence study, BiOI, BiOI/AgI, and MoS<sub>2</sub>/ BiOI/AgI photocatalyst were excited by the second harmonic (355 nm) of a cavity-dumped oscillator (Mira/PulseSwitch, Coherent, 1 MHz, 710 nm, 150 fs). Emission was collected using the lens, spectrally resolved using a monochromator, detected using a photomultiplier, and recorded using a time-correlated single photon counter (PicoHarp, PicoQuant). The instrumental response of the entire system was 0.05 ns.

#### **3.** Photocatalytic Experiments

Photocatalytic activities of different photocatalysts such as BiOI, BiOI/AgI, and MoS<sub>2</sub>/BiOI/AgI nanocomposite were explored by the degradation of RhB (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). 100 mg of photocatalyst was dispersed in 100 mL RhB dye solution in a 150 mL Pyrex conical flask. Before irradiation, the photocatalyst suspension was magnetically stirred at room temperature in the dark up to 60 min to attain adsorption-desorption equilibrium. (To confirm adsorption-desorption equilibrium time, 100 mg of MoS<sub>2</sub>/BiOI/AgI nanocomposite was dispersed in 100 mL RhB (10 mg/L) aqueous solution, which was magnetically stirred in the dark up to 150 min at room temperature. Every specific time interval, 2.0 mL of suspension was taken out, centrifuged and measured the concentration of RhB in the supernatant liquid at 553.8 nm (maximum wavelength) using a UV-Vis spectrophotometer (UV-1650PC, Shimadzu, Japan). 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 dye concentration was analyzed at 553.8 nm of characteristic maximum absorption wavelength of RhB with a UV-Vis spectrophotometer (UV-1650PC, Shimadzu, Japan) at room temperature. A colorless phenol was also chosen as a model substrate to further ensure the visible light photocatalytic activity. To measure the photocatalytic degradation of phenol, similar to the dye degradation experiment, 100 mg of photocatalyst was dispersed in 100 mL aqueous solution of phenol (Daejung Chemicals, South Korea) (10 mg/L) in a 150 mL conical flask, then magnetically stirred at room temperature in the dark to reach adsorption-desorption equilibrium. After that during irradiation time, 2.0 mL suspension was withdrawn at regular 10 min time intervals and centrifuged to remove the photocatalyst and then the phenol concentration was analyzed at its maximum absorption wavelength of 269.9 nm with a UV-Vis spectrophotometer (UV-1650PC, Shimadzu, Japan) at room temperature. The visible light photocatalytic activity of the MoS<sub>2</sub>/BiOI/AgI nanostructures was tested through the degradation of phenol. For the recycling experiment, previously used MoS<sub>2</sub>/BiOI/AgI photocatalyst was centrifuged out from the solution, dried for 8 h at 80 °C and then reused the same concentration RhB dye degradation.

#### 4. Active Species and •OH Radical Experiments

To examine the effect of reactive species including hole,  $\cdot$ O<sub>2</sub>-, and  $\cdot$ OH, ethylenediaminetetraacetic acid (EDTA), benzoquinone (BQ), and t-butyl alcohol (TBA) were added during the photocatalytic process. To measure the amount of  $\cdot$ OH producing from BiOI, BiOI/AgI and MoS<sub>2</sub>/BiOI/AgI photocatalyst, terephthalic acid (TA) (5x10<sup>-4</sup> M in a 2x10<sup>-3</sup> M NaOH solution) was used as a probe molecule. TA could react with  $\cdot$ OH radicals to produce high fluorescent 2-hydroxy terepththalic acid (TAOH) photoluminescence signal at around 425 nm and measured by a Hitachi F-7000 fluorescence spectrometer.

#### 5. Photoelectrochemecal Measurements Experiments

Photo-electrochemical measurements were performed in a three-electrode system using a CHI 617B electrochemical workstation. A solar simulator equipped with an AM 1.5G filter and 150 W

Xe lamp (Abet Technologies) was used as the irradiation source. The reference and counter electrodes were Ag/AgCl and platinum wire, respectively, and 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution served as the electrolyte. To prepare the working electrode, the as-synthesized 10 mg of BiOI, BiOI/Agi and MoS<sub>2</sub>/BiOI/AgI nanocomposites were first dispersed into ethanol (450  $\mu$ l) and 50  $\mu$ l Nafion mixtures using soft ultrasonic stirring to obtain a uniform suspension. The solution containing the catalyst (30  $\mu$ l) was dropped onto the pretreated indium–tin oxide (ITO) conductor glass substrate, which was then dried in an oven at 100 °C for 3 h. Photo-responses were measured at 0.0 V during on-off cycling of the solar simulator. Electrochemical impedance spectroscopy (EIS) was carried out at open circuit potential over the frequency range of 10<sup>5</sup> and 10<sup>-1</sup> Hz with an AC voltage magnitude of 5 mV.

## References

[1] Y. Chen, J. Lu, S. Wen, L. Lu and J. Xue, J. Mater. Chem. A, 2014, 2, 17857–17866.

# Figures



**Figure S1** EDS element mapping (a) MoS<sub>2</sub>/BiOI/AgI; (b) Bi; (c) O; (d) I; (e) Ag; (f) Mo; (g) S; and (h) EDS spectrum of MoS<sub>2</sub>/BiOI/AgI composite.



Figure S2 The XPS survey spectrum of pure BiOI and MoS<sub>2</sub>/BiOI/AgI composite.



**Figure S3** (a) Absorption spectra of the RhB aqueous solution in the presence of MoS<sub>2</sub>/BiOI/AgI adsorbent; (b) Effect of contact time on RhB adsorption by MoS<sub>2</sub>/BiOI/AgI; (c) The curve of adsorption-desorption equilibrium of MoS<sub>2</sub>/BiOI/AgI photocatalyst by RhB dye and (d) Adsorption efficiency of different nanocomposites in 60 min dark condition (Adsorbent dose 100 mg, RhB concentration 10 mg/L; 25° C room temperature, pH of aqueous RhB solution = 7).



**Figure S4** UV-Vis absorption spectra of RhB aqueous solution containing (a) pure BiOI, (b) BiOI/AgI (1:0.5), and (c) 2 wt. % MoS<sub>2</sub>/BiOI/AgI composite.



**Figure S5** UV-Vis absorption spectra of RhB aqueous solution containing different (a) 1:0.2 BiOI/AgI, (b) 1:0.4 BiOI/AgI, (c) 1:0.5 BiOI/AgI, and (d) 1:0.7 BiOI/AgI molar ratio of BiOI/AgI composites.



**Figure S6** UV-Vis absorption spectra of RhB aqueous solution containing different a) 1 wt.%, (b) 2 wt.%, (c) 3 wt.%, and (d) 6 wt.% MoS<sub>2</sub>/BiOI/AgI composites.



**Figure S7** (a) Absorption spectra of aqueous phenol solution with pure BiOI photocatalyst, (b) 2 wt. % MoS<sub>2</sub>/BiOI/AgI photocatalyst, and (c) Comparative photocatalytic activities of pure BiOI and 2 wt. % MoS<sub>2</sub>/BiOI/AgI photocatalysts for the phenol degradation



Figure S8 XRD patterns of the 2 wt. % MoS2/BiOI/AgI nanocomposite after 5 recycles runs



**Figure S9** Figure S9: (a) XPS survey spectrum of pure AgI (after recycling), MoS<sub>2</sub>/BiOI/AgI composite (before and after recycling); Narrow scan of Ag 3d of MoS<sub>2</sub>/BiOI/AgI composite (b) before recycling (c) after recycling and (d) Narrow scan of Ag 3d of pure AgI after recycling.



Figure S10 The deconvoluted peaks of MoS2/BiOI/AgI nanocomposite



Figure S11. The PL spectra of BiOI, BiOI/AgI and MoS<sub>2</sub>/BiOI/AgI nanocomposite