

# **Fabrication of $\text{BiOCl}_x\text{Br}_{1-x}$ /alumina composite films with highly exposed {001} facets and their superior photocatalytic activities**

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## **Electronic Supplementary Information (ESI)**

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## Experimental Section

**Synthesis of Aluminium oxyhydroxide (boehmite) sol.** Boehmite ( $\text{AlOOH}$ ) sol was first prepared by hot hydrolysis ( $>80\text{ }^{\circ}\text{C}$ ) of Aluminium tri-sec-butoxide  $\text{Al}[\text{OCH}(\text{CH}_3)\text{C}_2\text{H}_5]_3$  (ASB), and subsequent peptization of boehmite precipitates using  $\text{HCl}$ .<sup>[22]</sup> The molar ratios of water/ASB and  $\text{HCl}$ /ASB were 100 and 0.10, respectively. After peptization, the sol was stirred vigorously under reflux for 5 h and then kept another 48 h under the same conditions. The sol was then concentrated to about 8 equivalent wt%  $\text{AlO}_{1.5}$  content by distilling off the secondary butanol and a part of the water. A stoichiometric amount of methanol was then added to the sol to maintain the  $\text{AlO}_{1.5}$  content at 4 wt %.

**Synthesis of  $\text{BiOCl}_x\text{Br}_{1-x}$ .** Bismuth nitrate (9.2 g) was dissolved in deionized water (40 ml) and glacial acetic acid (40 ml) into a 250 mL beaker and stirred at room temperature for 15 min until a clear, transparent solution is formed. Then CTAB (1.379 g dissolved in 25 ml of ethanol and 10 mL of water) and CTAC (19.379 g of 25 wt % aqueous solution) were added to the above solution in one batch, and the mixture was stirred for an additional 60 min at room temperature. The precipitate thus formed was filtered and washed five times with ethanol (50 mL) and five times with water (200 mL) to remove the nonreactive organic species. The white solid was then dried (in air) and became ready for use.

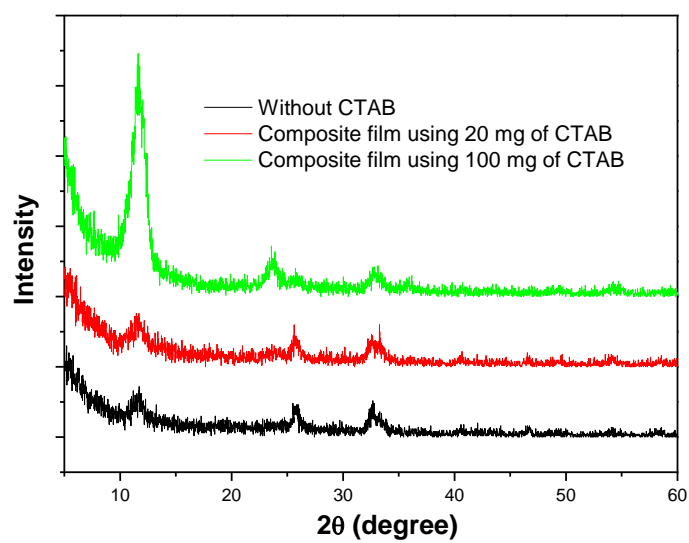
**Synthesis of  $\text{BiOCl}_x\text{Br}_{1-x}$  loaded alumina film.**  $\text{BiOCl}_x\text{Br}_{1-x}$  (480 mg) were dispersed in 1-propanol in presence of CTAB (20-100 mg) via ultrasonic treatment (5 min) followed by the addition of 4 g of boehmite sol maintaining 75 wt % of

$\text{BiOCl}_x\text{Br}_{1-x}$  in the final film. The resulting mixture was then re-sonicated for 5 min. The composite sol becomes highly viscous and was used for coating of glass beakers and glass slides by simple smearing technique. 2 g of this composite sol was used to coat a beaker. Lastly, the films were heat-treated at 350 °C with lifting speed 1°C/min and kept for 10 h.

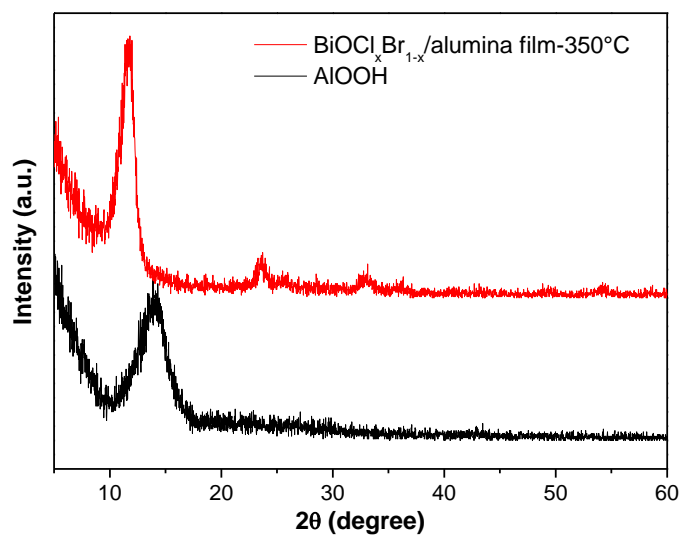
**Characterizations.** Sample structure and morphologies were observed by Extra High Resolution Scanning Electron Microscopy (Magellan<sup>TM</sup> 400L) and High Resolution Transmission Electron Microscope (Tecnai F20 G2). X-ray diffraction patterns were collected by using Bruker AXS D8 Advance. UV-visible absorption spectra were monitored by Carry 100 Bio and Diffuse Reflectance analysis was carried out by Integrating Sphere (JASCO V-650 Series ISV-722). FTIR spectra were collected by Bruker (Alpha-T). Surface area was determined by the  $\text{N}_2$  sorption analysis (Brunauer–Emmett–Teller (BET) method) using NOVA-1200e instrument. For  $\text{N}_2$  sorption, samples were prepared by scratching off the powders from the coated substrate with a blade.

**Photocatalytic Measurements.** The photocatalytic activity experiments of the products for the degradation of Rhodamine B (RhB) were performed at ambient temperature using a 300W Xe lamp source. Incident light intensity was fixed at 48 mW/cm<sup>2</sup>, and the reactor was placed 10 cm away from the light source.

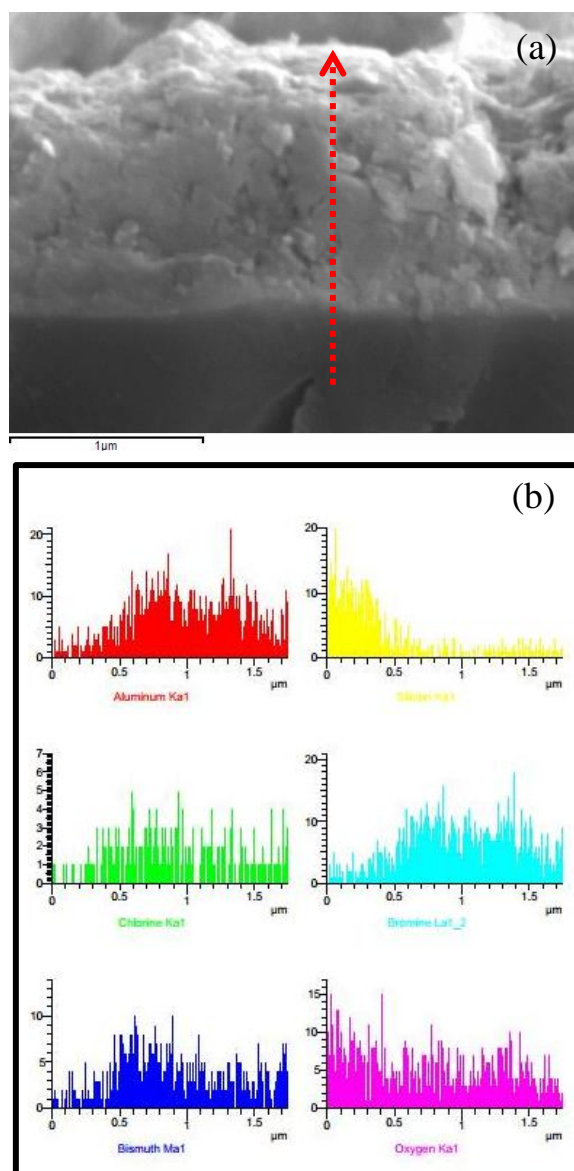
Typically, 200 mL of 5ppm RhB aqueous solution was placed in a 250 ml coated beaker. Prior to irradiation, the system was kept in the dark for 1 h to ensure the adsorption/desorption equilibrium. During the degradation, the concentration of RhB was monitored by colorimetry with a UV–Vis spectrometer.



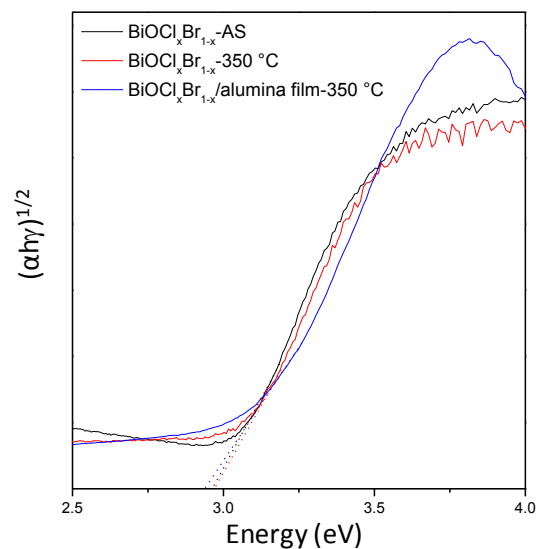
**Fig. S1.** GIXRD patterns of  $\text{BiOCl}_x\text{Br}_{1-x}$ /alumina composite films (heat-treated at 350 °C) using different amounts of CTAB.



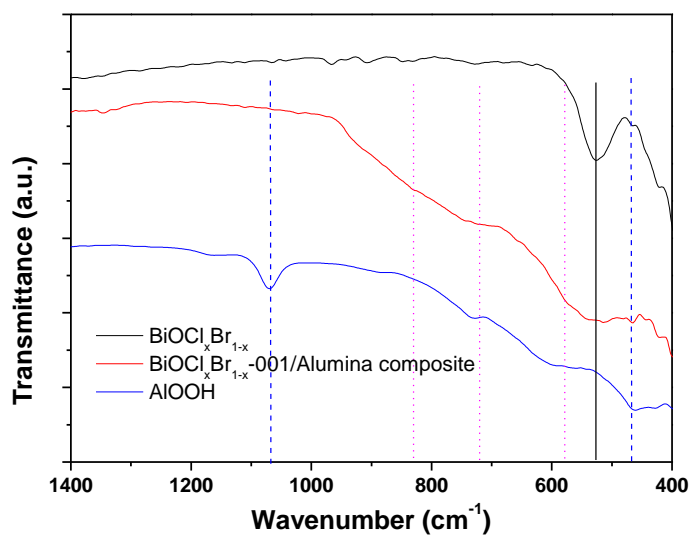
**Fig. S2.** XRD patterns for the AlOOH and  $\text{BiOCl}_x\text{Br}_{1-x}$ /alumina composites.



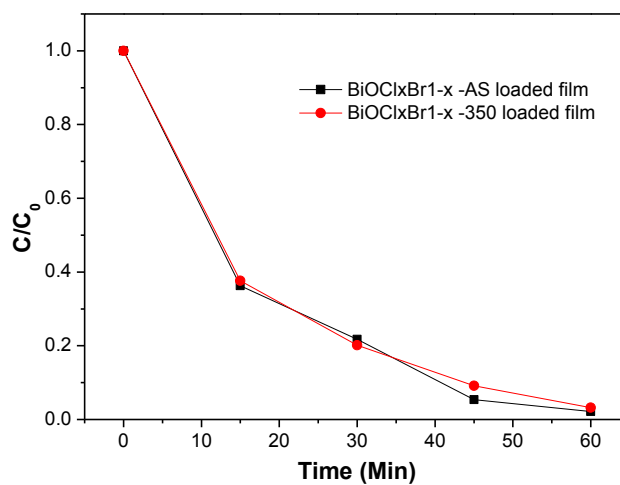
**Fig. S3.** SEM-EDX line scanning analysis along the thickness of the composite film: (a) cross-section image of the film; red line with arrow depicts the EDS scanning line; (b) intensity distributions of Al, Si, Cl, Br, Bi and O along the distance.



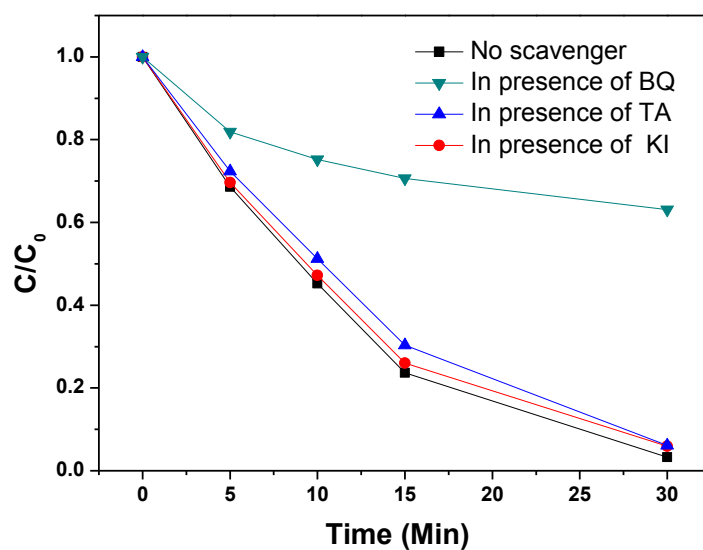
**Fig. S4.** Diffuse reflectance spectra (DRS) of 75 wt%  $\text{BiOCl}_x\text{Br}_{1-x}$  loaded  $\text{Al}_2\text{O}_3$  films obtained after calcinations at  $\sim 350^\circ\text{C}$ . DRS of  $\text{BiOCl}_x\text{Br}_{1-x}$ -AS and  $\text{BiOCl}_x\text{Br}_{1-x}$ - $350^\circ\text{C}$  were also shown for comparison.



**Fig. S5.** FTIR spectra of pure  $\text{BiOCl}_x\text{Br}_{1-x}$ ,  $\text{AlOOH}$  and composite films. Peaks for  $\text{BiOCl}_x\text{Br}_{1-x}$  (black solid line),  $\text{AlOOH}$  (blue dash line) and  $\text{Al}_2\text{O}_3$  (pink dotted line) were given in the figure.



**Fig. S6.** Photocatalytic activities of the ~75 wt% BiOCl<sub>0.8</sub>Br<sub>0.2</sub>-AS and BiOCl<sub>0.8</sub>Br<sub>0.2</sub>-350°C loaded coatings towards RhB decomposition. 100 mg of P123 was used instead to CTAB to create mesoporosity without any change in crystallinity of the BiOCl<sub>0.8</sub>Br<sub>0.2</sub>.



**Fig. S7.** Photocatalytic activities of the BiOCl<sub>0.8</sub>Br<sub>0.2</sub>/alumina films in presence of different scavengers to trap the active species.