Supporting Information for

Direct Conversion of Bi Nanospheres into 3D Flower-like BiOBr Nanoarchitectures with Enhanced Photocatalytic Properties

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Experimental Section

1. Materials
Sodium bismuthate dehydrate (NaBiO$_3$·2H$_2$O), ethylene glycol (EG), Iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O), sodium bromide (NaBr), bismuth powder were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Polyvinylpyrrolidone (PVP) (Mw≈1300000) and Rhodamine B (RhB) were purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). All the reagents were analytical grade and used directly without further purification.

2. Synthesis of Bi nanospheres
In a typical synthesis, 0.15g of NaBiO$_3$·2H$_2$O was added into 35 mL of EG, and then 0.62 g of PVP (Mw≈1300000) was added into this solution with vigorous stirring. Then the mixture was transferred into a stainless steel autoclave with Teflon liner. The autoclave was sealed and maintained at 180 °C for 24 h. The obtained products were centrifuged and washed with absolute ethanol and were finally dried at 60 ºC.

3. Synthesis of flower-like BiOBr hierarchical nanostructures
In a typical flowerlike BiOBr hierarchical nanostructures synthesis, the as-synthesized bismuth nanospheres (0.2 g) dispersed in 50 mL H$_2$O, and a proper amount of Fe(NO$_3$)$_3$·9H$_2$O was dissolved in this bismuth nanospheres solution, then 10 mL of NaBr (0.1M) was added to the mixture and was stirred at room temperature for 30min. The obtained samples were washed with de-ionized water and absolute ethanol to remove the possible impurity by centrifugation, and then dried at 60 ºC.

4. Photocatalytic activity test
Photocatalytic activity of the as-synthesized BiOBr was evaluated by the degradation of Rodamine B (RhB) under visible light irradiation of a 300 W Xe lamp with a 420 nm cut off filter. In the experiment, 0.02 g BiOBr was added into 100 mL RhB solution (1×10$^{-5}$ mol L$^{-1}$) at room temperature. Prior to irradiation, the suspension was stirred in the dark to ensure the establishment of an adsorption-desorption equilibrium between the photocatalyst and RhB. Then the solution was exposed to visible light irradiation under magnetic stirring. At each irradiation time interval, 4 mL of the suspension was collected and then centrifuged to remove the BiOBr powder. The concentration of RhB was analyzed by a Shimadzu UV-2550 spectrophotometer, and the characteristic absorption of RhB at 554 nm was used to monitor the photocatalytic degradation. All of the measurements were carried out at room temperature.

5. Characterizations
The X-ray diffraction spectra (XRD) measurements were performed on a Philips X’pert MPD instrument using Cu Ka radiation (50 kv). The XRD patterns were recorded from 10° to 80°with a scanning rate of 0.067°/s. SEM images were taken using a field-emission scanning electron microscope (JSM-6701F, JEOL) operated at an accelerating voltage of 5 kV. TEM images were recorded on a FEI TF20 field-emission transmission electron microscope, using an accelerating voltage of 200 kV. UV/vis absorption spectra were taken at room temperature on a UV-2550 (Shimadzu) spectrometer. X-ray photoelectron spectroscopy (XPS) was performed by an ESCALAB250xi photoelectron spectrometer with X-Ray Monochromatisation as the excitation source to analyze samples’ elemental composition. The Brunauer-Emmett-Teller (BET) specific surface area of the powders was analyzed by nitrogen adsorption in a
Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). All the as-prepared samples were degassed at 150 °C for 4 h prior to nitrogen adsorption measurements.
Additional Figures

Fig. S1 (A) XRD pattern and (B, C and D) SEM images of the as-prepared Bi nanospheres
Furthermore, the X-ray photoelectron spectroscopy (XPS) measurement has also been performed to investigate the surface compositions and chemical states of the as-prepared BiOBr sample, and the results are shown in Fig.S2. The XPS survey spectrum in Fig.S2A shows that except for C, Bi, O and Br, no peaks of other elements are observed in the spectrum, indicating the high purity of the product. The peak values at 284.5 eV can be readily assigned to the binding energies of C1s. Fig. S2B-D show the magnification XPS spectra of Bi4f, Br3d and O1s, respectively. The two strong peaks at the Bi region (Fig. S2B) of 159.1 and 164.4 eV are respectively assigned to Bi4f 7/2 and Bi4f 5/2, which corresponded to Bi$^{3+}$ in BiOBr according to the previous results. (Chemical Engineering Journal 222 (2013) 120-127) The three peaks at 68.3, 69.0 and 529.7 eV correspond to Br3d 5/2, Br3d 3/2 and O1s, respectively, which are indexed as Br$^{-}$ and O$^{2-}$ in a bismuth-oxygen bond in BiOBr. Hence, the XPS results further confirm that Bi nanoparticles are fully converted to BiOBr, and the as-synthesized product could be determined as pure BiOBr based on the results of XRD and XPS measurements.

**Fig. S2** XPS spectra of the BiOBr product: (A) survey XPS spectrum, (B) Bi 4f, (C) Br 3d, and (D) O 1s.
**Fig. S3** EDS pattern of as-synthesized BiOBr hierarchical nanostructures.
**Fig. S4** SEM images of commercial Bi powder