

## *Supporting Information for*

# **Hollow Ag@AgBr Heterostructures with Highly Efficient Visible-Light Photocatalytic Properties**

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## **Experimental Section**

### **1. Materials**

All the chemicals were analytical grade and used as received without any further purification, unless otherwise stated. Silver nitrate (AgNO<sub>3</sub>), potassium bichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), sodium bromide (NaBr), and polyvinylpyrrolidone (PVP) (MW = 40000) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Deionized water with a resistivity of 18.25 MΩ·cm was used in all reactions.

### **2. Synthesis of Ag<sub>2</sub>CrO<sub>4</sub> nanorods**

The Ag<sub>2</sub>CrO<sub>4</sub> nanorods were prepared by using silver-ammino complex as the silver ion source. In a typical synthesis, AgNO<sub>3</sub> (0.168 g) was solved in 30 mL of deionized aqueous solution, ammonia aqueous solution (0.1 M) was added with drop by drop to the above solution to form a transparent solution. Then, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> aqueous solution (15 mg·mL<sup>-1</sup>, 10 mL) was added, and dark-purple Ag<sub>2</sub>CrO<sub>4</sub> crystals with rod-like structure have been synthesized.

### **3. Synthesis of hollow AgBr nanorods**

The as-synthesized Ag<sub>2</sub>CrO<sub>4</sub> nanorods (0.331 g) and PVP (0.04 g) were placed in 50 mL of deionized water in a 100 mL beaker under a magnetic stirring rate of 350 rpm. After PVP were completely dissolved, 11 mL aqueous solution of NaBr (20 mg·mL<sup>-1</sup>) was injected dropwise with a syringe. The reaction was continued for 20 min and a light yellow dispersion containing AgBr hollow nanorods was obtained. Then the product was collected by natural sedimentation and rinsed with distilled water several times.

### **4. Preparation of hollow Ag@AgBr nanorods**

The obtained hollow AgBr nanorods is dispersed into deionized water and irradiated under sunlight for about 1 h. When the color of the mixture gradually changed from light yellow to gray, it indicates the formation of some Ag nanograins on the surfaces of the AgBr nanorods, and the Ag@AgBr photocatalyst is prepared, after which the photocatalyst is collected and dried at 60 °C for 12 h.

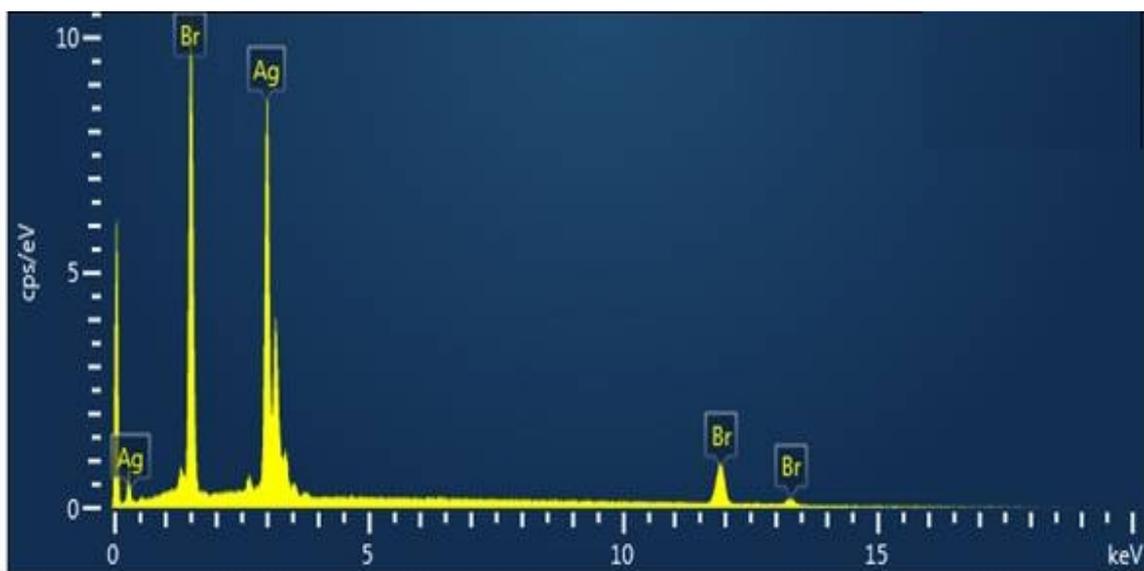
### **5. Photocatalytic Reactions**

In this catalytic activity of experiment, the samples (0.2 g) were put into a solution of RhB dye (100 mL, 10 mg·L<sup>-1</sup>), which was then irradiated with a 300W Xe arc lamp equipped with an ultraviolet cutoff filter to provide visible light with  $\lambda \geq 420$  nm. The degradation of RhB dye was monitored by UV/Vis spectroscopy (UV-2550, Shimadzu). Before the spectroscopy measurement, these photocatalysts were removed from the photocatalytic reaction systems by a dialyzer.

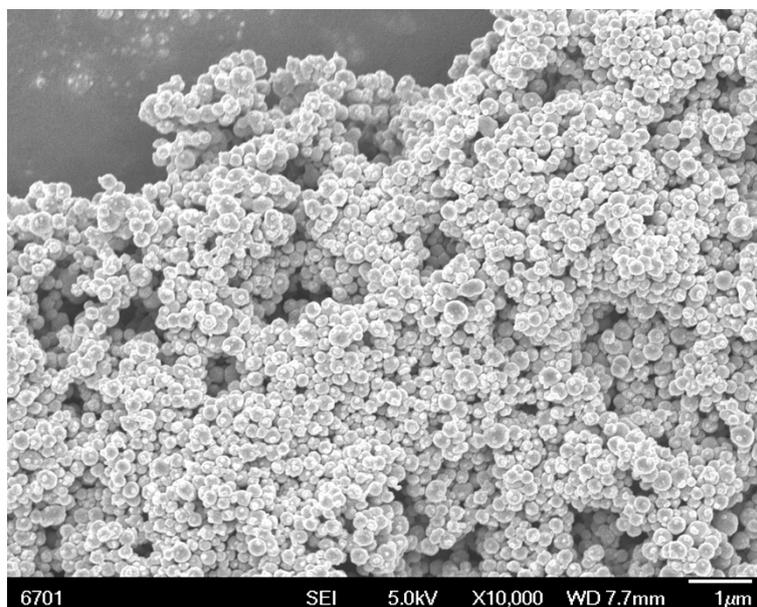
## **6. Characterization**

The morphology and size of the as-prepared products were characterized by using a field-emission scanning electron microscope (JSM-6701F, JEOL), and the SEM-EDS line analysis was performed with a field-emission scanning electron microscope operated at an accelerating voltage of 5 kV (Quanta 450, FEI). The XRD measurements were performed on a PANalytical X'Pert PRO instrument with CuK $\alpha$  radiation (40 kV). The XRD patterns were recorded from 20 to 80° with a scan rate of 0.0678 s<sup>-1</sup>. UV/Vis diffuse-reflectance spectra were recorded on a UV-2550 (Shimadzu) spectrometer by using BaSO<sub>4</sub> as reference. The elemental composition was determined by XPS (Kratos Axis Ultra DLD). HRTEM imaging was carried out by using an FEI Tecnai TF20 microscope operated at 200 kV.

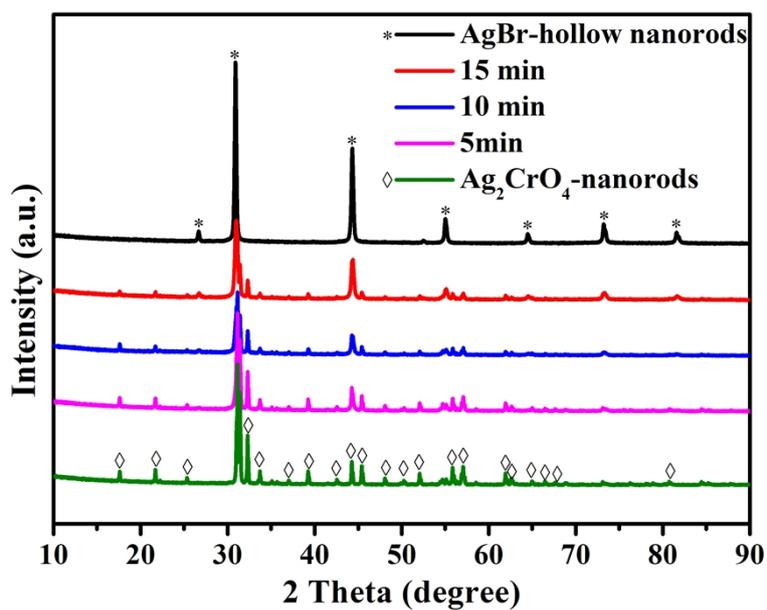
**Additional Figures:**



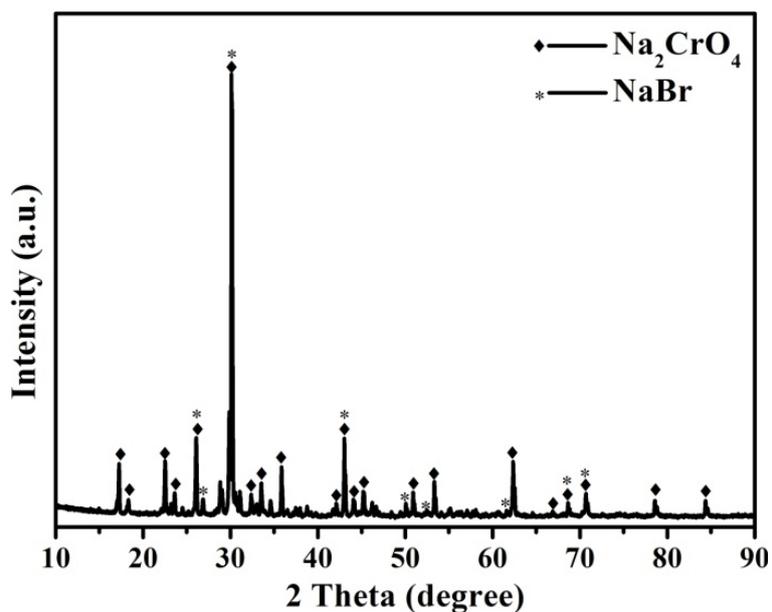
**Figure S1.** EDS spectra of the as-synthesized Ag@AgBr hollow nanoframes.



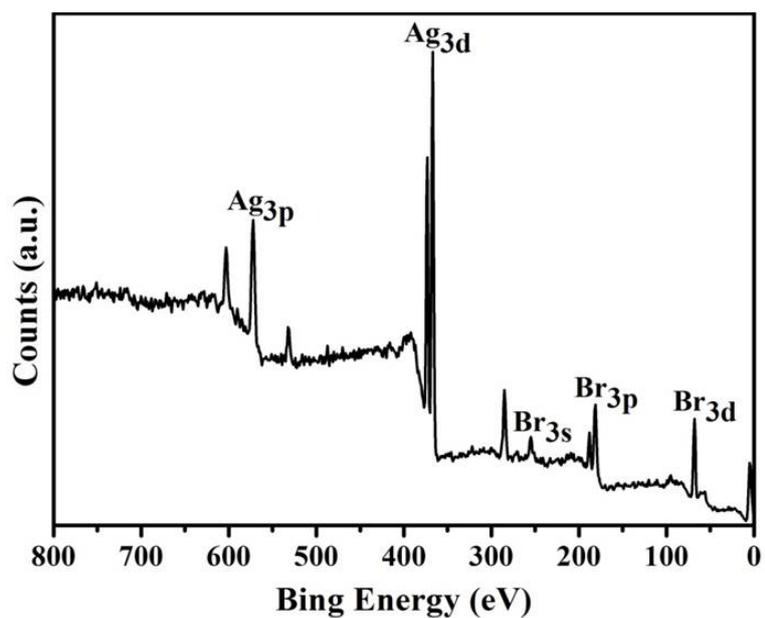
**Figure S2.** SEM image of the product formed through fast anion-exchange reaction of  $\text{Ag}_2\text{CrO}_4$  nanorods with  $\text{Br}^-$  ions.



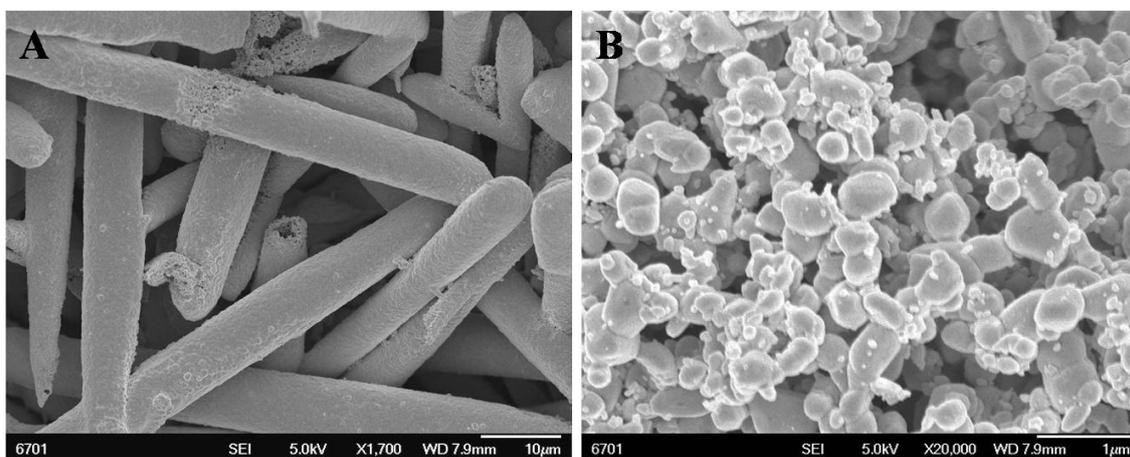
**Figure S3.** XRD patterns of the hollow AgBr nanorods formed at different times: 0 min ( $\text{Ag}_2\text{CrO}_4$ ), 5 min, 10 min, 15 min, and AgBr hollow nanorods (20 min), which include those shown in Figure 3A–3E.



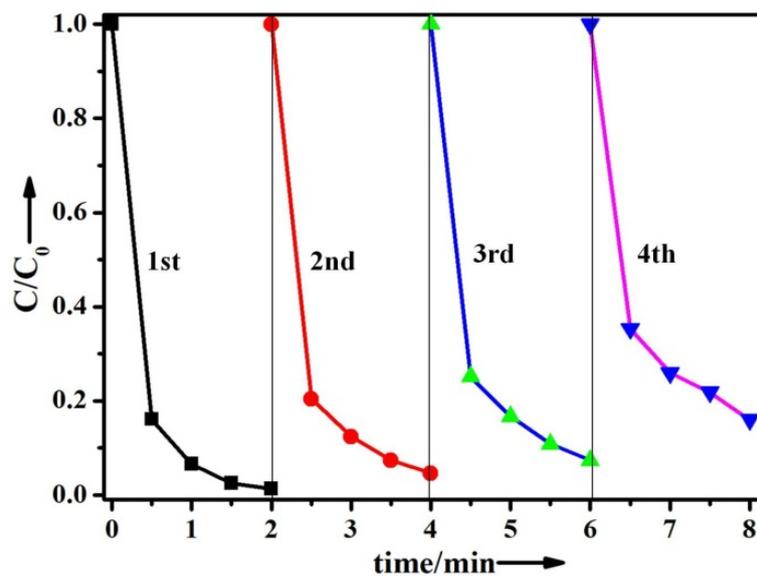
**Figure S4.** XRD pattern of the product obtained from the reaction of supernatant fluid.



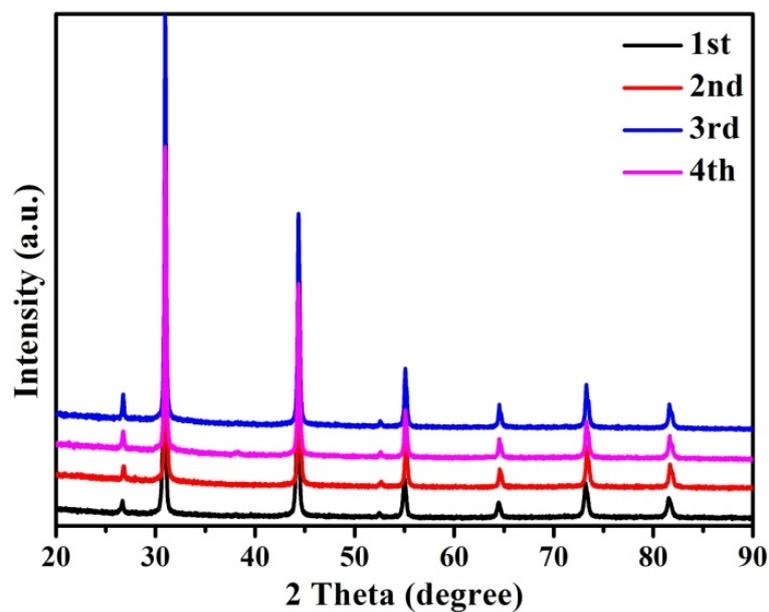
**Figure S5.** XPS spectra of the as-synthesized Ag@AgBr hollow nanoframes as shown in Figure 1C



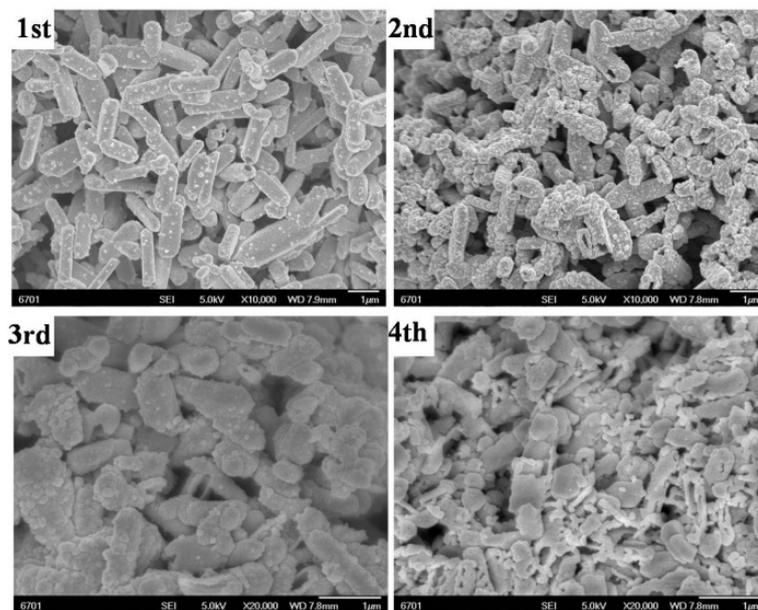
**Figure S6.** SEM images of A) hollow Ag@AgBr microrods and B) Ag@AgBr nanoparticles



**Figure S7.** Recycling experiments of the hollow Ag@AgBr nanorods in the photodegradation of RhB



**Figure S8.** XRD patterns of the hollow Ag@AgBr nanorods after they are used for photocatalytic reaction



**Figure S9.** SEM images of the hollow Ag@AgBr nanorods after they are used for photocatalytic reaction