Supporting Information

Facial Synthesis of AgBr Nanoplates with Exposed {111} Facets and Enhanced Photocatalytic Properties

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EXPERIMENT

Preparation of AgBr nanoplates. The AgBr nanoplates were prepared using precipitation reaction with PVP as capping agent. Typically, 2.5 g of PVP (average MW 58000, K29-32, Acros) and 80 mg NaBr were added to 12 mL ethylene glycol (EG), and then the solution was kept at 60 °C for 30 min under intensive magnetic stirring. After both the PVP and NaBr were completely dissolved, 1 mL of EG solution of $AgNO_3$ (57 mg) was dropwise added to the above solution under intensive stirring, and the color of the solution turned yellow immediately with the $AgNO_3$ addition. After the solution was kept for another 30 min at 60 °C for a precipitation process, the temperature was elevated to 160 °C for 1 h to improve the crystalline quality of AgBr, and products were collected by centrifugation and washed with distilled water 3 times and absolute ethanol twice, and then dried overnight at 60 °C under vacuum condition. The irregular AgBr particles were prepared by a facile precipitation method with $AgNO_3$ and NaBr following the same process using EG without PVP as solvent. The large AgBr nanoplates were prepared by the process similar to that of the small nanoplates. Typically, 0.5 g of PVP and 80 mg NaBr were added to 12 mL ethylene glycol (EG), and the solution was kept at 160 °C for 5 min under intensive magnetic stirring, then 1 mL of EG solution of $AgNO_3$ (57 mg) was dropwise added to the above solution under intensive stirring, and the solution was kept for another 1 h at 160 °C. For comparison, Ag_3PO_4, as a new type of highly efficient photocatalysts, was prepared by a direct precipitation reaction. In a typical synthesis, 0.340 g of $AgNO_3$ was completely dissolved in distilled water in a flask at 60 °C under magnetic stirring. Then, 30 mL of Na_3PO_4 ($Na_3PO_4 \cdot 12H_2O$, 0.253 g) aqueous solution was dropwise added, and the color of the solution turned yellow immediately. After continuous stirring for 30 min, the products were collected by centrifugation and washed several times with distilled water, and then dried at 60 °C in vacuum overnight.

Characterization. The morphology of the samples was carried out on a FEI Quanta 400 scanning electron microscope (FEI Company, Oregun, USA). Transmission electron microscopy (TEM) investigations were carried out by a JEOL 3100 microscope with an weak beam current ~60 μA. The as-prepared sample was dispersed in ethanol and dropped onto a carbon film supported on a copper grid. The X-ray diffraction (XRD) spectra of the samples were recorded by a Rigaku Dmax 2200 X-ray diffractometer with Cu Kα radiation (λ=1.5416 Å). Diffuse reflectance absorption spectra of AgBr-based photocatalyst were recorded in the range from 300 to 800 nm using a Hitachi U-3010 spectroscopy with $BaSO_4$ as reference. Specific surface areas were measured at 77 K by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption (NOVA 2200e, Quanthachrome, USA). XPS spectra were measured on a Perkin-Elmer model PHI 5600 XPS system with a resolution of 0.3-0.5 eV from a monochromatic aluminum anode X-ray source.

Photocatalytic Experiment. Photocatalytic activities of the AgBr-based photocatalyst were evaluated by degradation of MO dyes under 300 W Xe lamp with UV cutoff filter (providing visible light with $\lambda \geq 400$ nm). MO solution (100 mL, 10^{-4} mol· L^{-1}) containing 0.1 g of the AgBr/Ag-based photocatalysts was placed in a 200 mL cylindrical quartz vessel. Before the light was turned on, the solution was stirred in the dark for 30 min to ensure an adsorption/desorption equilibrium between the catalysts and organic dyes.

Theoretical Calculations. Our electronic structure calculations were based on the density-functional theory (DFT) +*U* approach.[1] The exchange-correlation energy functional was represented by the local-density approximation (LDA).[2] Projector-augmented wave pseudopotentials were employed as implemented in the CASTEP code.[3] The valence configuration of the pseudo potentials are $4d^{10}5s^1$ for Ag, and $3d^{10}4s^24p^5$ for Br. The energy cutoff for a plane wave basis set is 400 eV, and a Monkhorst-Pack k-mesh of 4 × 4 × 4 is used. Since the computational band gap from LDA (0.705 eV) significantly underestimates the experimental value (2.6 eV),[4] $U_d = 7.2$ eV and $U_p = 7.0$ eV was adopted to obtain a band gap (2.666 eV). The obtained lattice constant from LDA+*U* was *a*=5.59 Å in comparison with an experimental value (5.774 Å).[4]

The relaxed unit cell was used to construct the surface models shown in Fig. 4. For each face, stoichiometric slab models (3 × 3) were used, consisting of 7 atomic layers and a total of 126 atoms for (100) and (110) surfaces and of 14 atomic layers and a total of 126 atoms for (111) surface. In the cases of slabs, the vacuum region has the same thickness as AgBr. These surface structures were fully relaxed to a force convergence of 0.05 eV Å^{-1}, where the second layer was fixed to represent a bulk region. Based on the geometry relaxations, the surface energy (γ) was computed using the formula:[5]

$$\gamma = \frac{E_{slab} - nE_{bulk}}{2A}$$

Where E_{slab} is the total energy of the slab, E_{bulk} is the total energy of the bulk per unit cell, n is the number of bulk unit cells contained in the slab, and A is the exposed area of one side of the slab.

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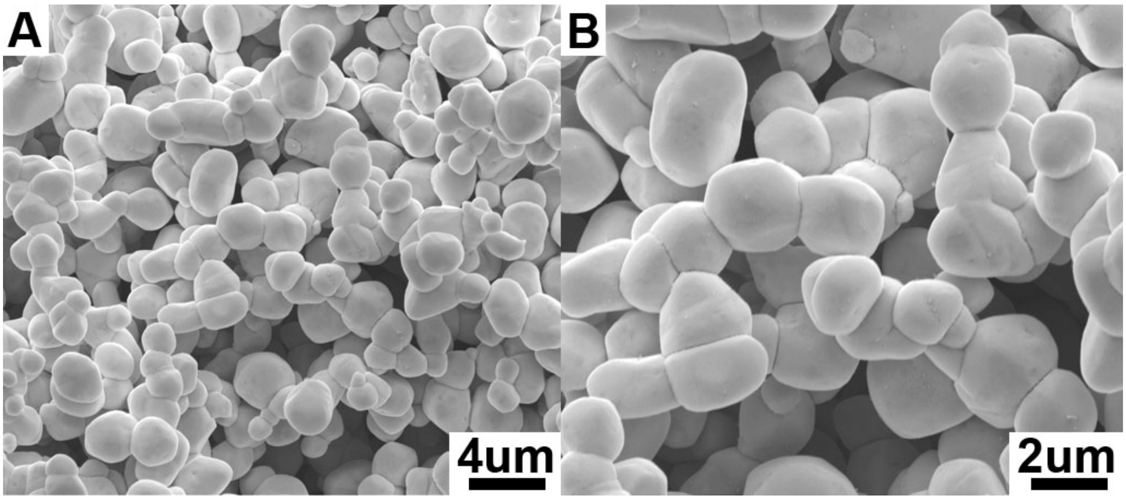

Fig. S1. SEM images of irregular particles prepared without PVP at low (A) and high magnifications (B).

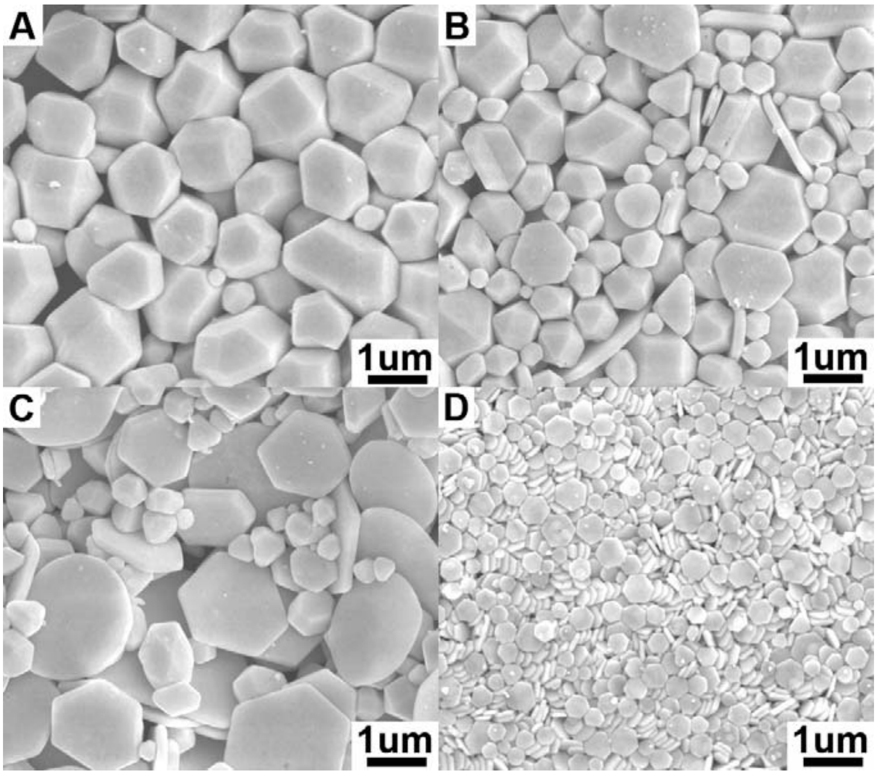

Fig. S2. SEM images of as-prepared AgBr nanoparticles produced with the different molar ratio of PVP to $AgNO_3$. (A) 6.7, (B) 13.4, (C) 40.2 and (D) 67.

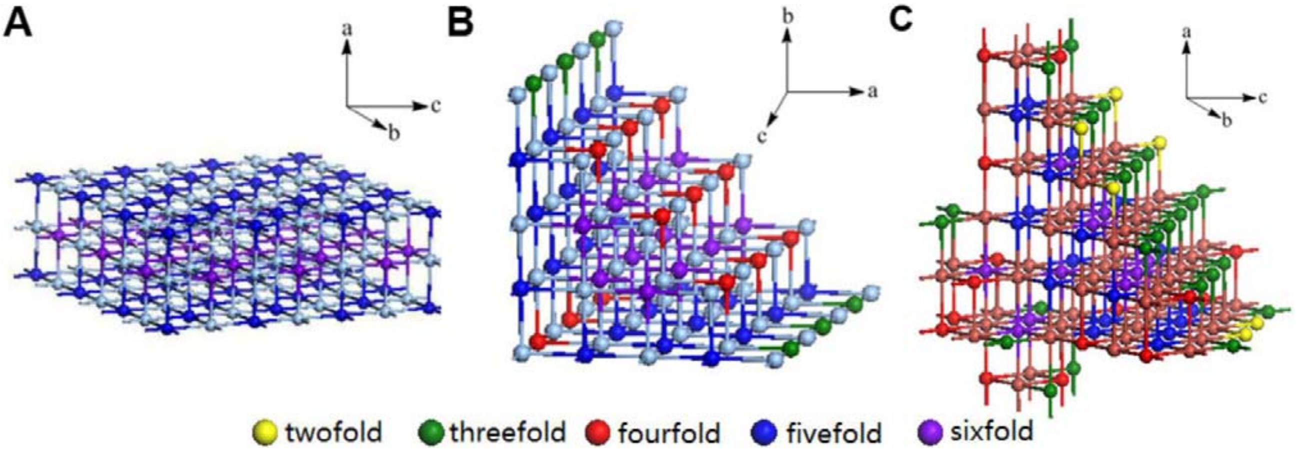

Fig. S3 The schematic models of AgBr (100) (A), (110) (B) and (111) (C) surfaces that contain several atom steps.

Fig. S3 shows the schematic models of AgBr (100), (110) and (111) surfaces that contain several atom steps. For face-centered cubic AgBr, Ag and Br atoms in the bulk are sixfold-coordinated by Br and Ag atoms, respectively. At the surface, the constituted atoms are usually coordinatively unsaturated. From

Fig. S3A, it can be seen that Ag and Br have identical atoms ratio on the (100) surface, and Ag is fivefold-coordinated with one dangling bonds. On the (110) surface, the atom ratio of Ag and Br is also identical, and Ag atoms contain threefold-coordinated with three dangling bonds and fourfold-coordinated with two dangling bonds. There are two possible structures of (111) surface of AgBr, and they are entirely constituted by Ag or Br atoms respectively, but the total-energy calculation shows that the surface entirely constituted by Ag atoms gives the best stability, which indicates that the {111} facets are most possibly enclosed by such structure, as shown in Fig. S3C, and it can be seen that all Ag atoms on this surface are coordinatively unsaturated, located in two-coordinated sites with four dangling bonds and three-coordinated sites with three dangling bonds, and thus are highly active for arresting negative charges.

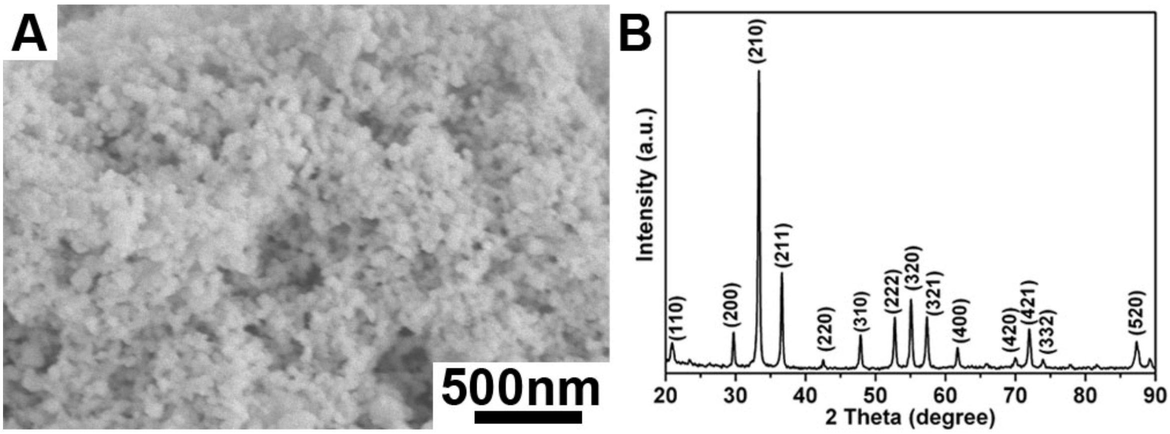

Fig. S4. SEM image and XRD pattern of as-prepared Ag_3PO_4 particles.

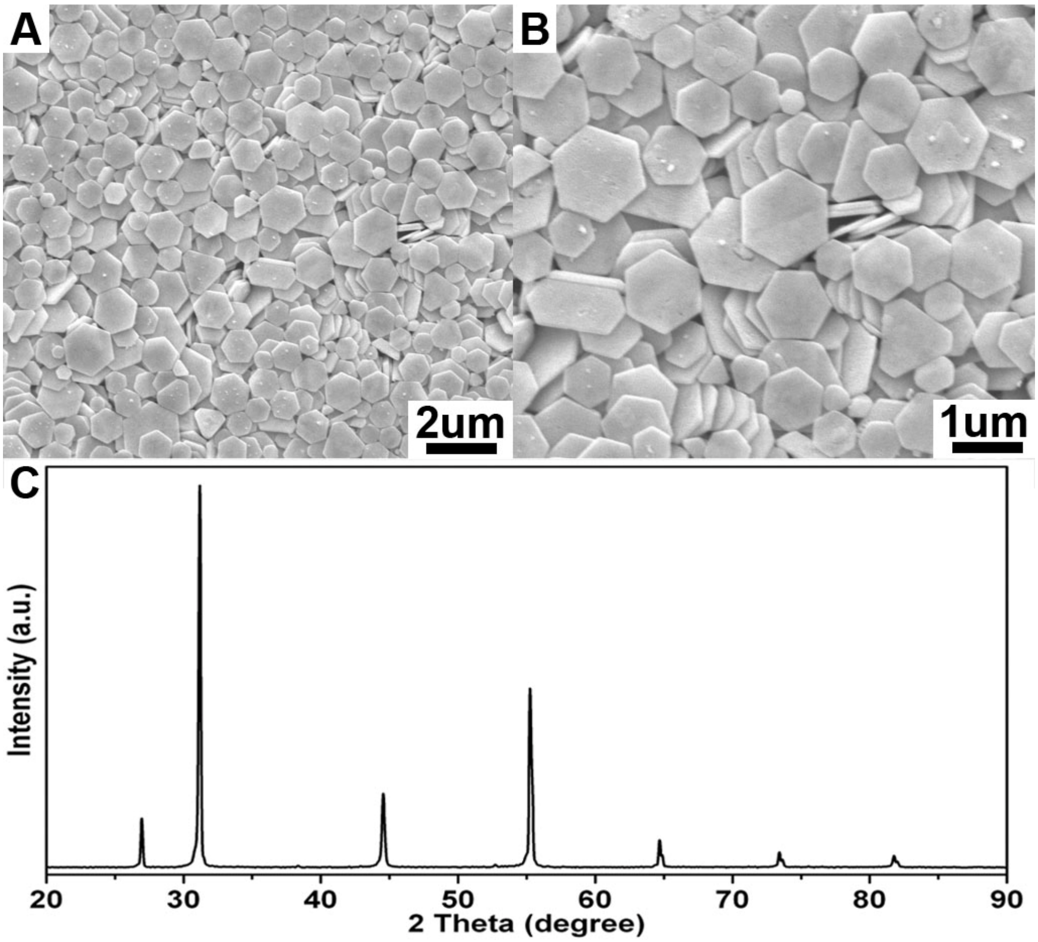

Fig. S5. SEM images at low (A) and high magnifications(B), as well as XRD pattern of the large AgBr nanoplates.