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Facile synthesis of AgBr nanoplates with exposed {111} facets and enhanced photocatalytic properties†

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AgBr nanoplates with exposed {111} facets have been synthesized in high yield by a facile precipitation reaction, and the as-prepared nanoplates exhibited greatly enhanced photocatalytic properties for the degradation of organic pollutants, which may be primarily ascribed to the relatively higher surface energy of {111} facets.

Design and synthesis of the morphology-controlled nano- or microstructures have been intensively pursued in the past decades for their size, shape and facet-dependent properties.¹ Nano- or microcrystals exposed with high-reactivity facets are of great importance to both fundamental studies and technological application owing to the high density of atomic steps, ledges, kinks and dangling bonds, and have attracted great research interest.^{2,3} Unfortunately, the synthesis of these types of nano- or microcrystals is challenging due to the rapid diminishing of highly reactive facets during the crystal growth process as a result of the minimization of surface energy. Though faced with the difficulty, researchers have synthesized many nanocrystals exposed with highly reactive facets by taking particular measures.⁴ Typically, the TiO₂ microcrystals exposed with a large percentage of highly reactive {001} facets have been successfully synthesized by Lu's group, which show enhanced photocatalytic activities.⁵ Ye and her collaborators have also demonstrated that the exposed facets have an important effect on the enhanced photocatalytic activities of BiVO₄ and Ag₃PO₄, recently.^{6,7}

AgBr, as a conventional photographic material, its excellent photocatalytic properties have attracted wide attention recently.^{8–10} However, the synthesis of regular AgBr nanostructures is rare, and the studies of morphology-dependent properties have been rarely reported.^{11,12} Furthermore, to the best of our

knowledge, the facet effect on the photocatalytic properties of AgBr has never been investigated.

Herein, we successfully prepared AgBr nanoplates in high yield by a facile precipitation reaction using polyvinylpyrrolidone (PVP) as a capping agent. Moreover, studies of their photocatalytic properties have clearly revealed that the as-prepared AgBr nanoplates exhibit greatly enhanced activity toward the degradation of organic pollutants. Density functional theory (DFT) calculations suggest that AgBr {111} facets possess a relatively higher surface energy than ordinary {100} and {110} facets, which may contribute significantly to the enhanced photocatalytic activity.

Fig. 1A and B are typical scanning electron microscopy (SEM) images of the as-prepared AgBr products, and it can be seen that the products are composed of plate-like hexagons, which are 150–300 nm in width and 30–50 nm in thickness. Transmission electron microscopy (TEM) was carried out with a weak beam current, which further revealed that the product consisted of well-defined plate-shaped structures with a hexagonal outline, as shown in Fig. 1C. The correspondingly selected area electron diffraction (SAED) pattern (Fig. 1D) was obtained by

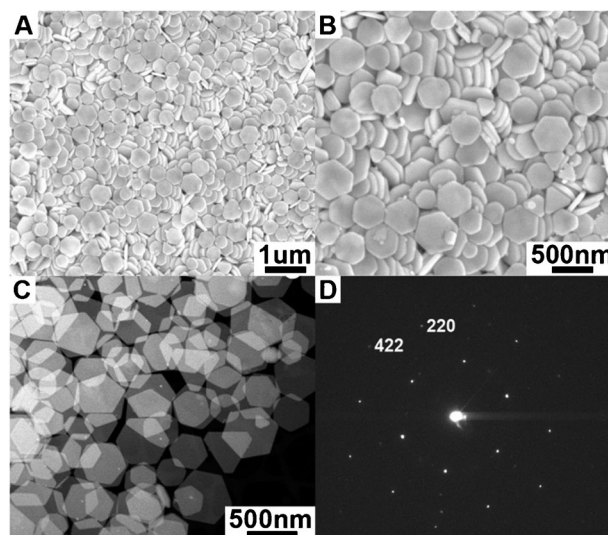


Fig. 1 SEM images of as-prepared AgBr nanoplates at low (A) and high magnifications (B). TEM image (C) and the corresponding SAED pattern (D) of AgBr nanoplates.

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† Electronic supplementary information (ESI) available: Experiment details: AgBr particles prepared without PVP and with different molar ratio of PVP to AgNO₃. Schematic models of AgBr surfaces. SEM images and XRD pattern of as-prepared Ag₃PO₄ particles, large AgBr nanoplates. See DOI: 10.1039/c1cc16423f

directing the incident electron beam perpendicular to one hexagonal facet of an individual nanoplate, and one set of diffraction spots could be indexed as the 220 and 422 reflections, respectively, which demonstrated that the two hexagonal facets were bounded by the {111} facets. To investigate the possible growth mechanism of the AgBr nanoplates, the morphology evolution of AgBr products was investigated by simply adjusting the amount of PVP. In the absence of PVP, irregular AgBr microspheres were obtained (Fig. S1, ESI[†]). When the molar ratio of PVP to AgNO₃ increased to 6.6, the as-prepared product was mainly composed of tetrakaidecabedrons, as shown in Fig. S2A (ESI[†]), and with the molar ratio further increased, the products experienced a shape evolution from tetrakaidecabedrons to a mixture of tetrakaidecabedrons and nanoplates and finally to uniform nanoplates. Thus, the suitable amount of added PVP plays a key role in the formation of AgBr nanoplates, which may selectively stabilize the AgBr {111} facets. To further understand the proposed mechanism, the structural features and the crystal growth habit of the face-centered cubic AgBr were taken into account. From the atomic arrangement scheme (Fig. S3, ESI[†]), it can be seen that the AgBr {111} facets are entirely constituted by Ag atoms, and all Ag atoms 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. Meanwhile, PVP, as a non-ionic surfactant, has an easily polarized functional group '-C=O' in its repeated unit. 'O', with a negative charge, prefers to interact with positively charged 'Ag' to compensate the local surface charge imbalance and thus stabilize the crystal surfaces. Therefore, AgBr nanoplates exposed with {111} facets were finally achieved by preferential adsorption of PVP during the crystal growth process.

XRD patterns of the AgBr nanoplates and irregular AgBr particles are shown in Fig. 2A, and both patterns can be indexed to the face-centered cubic structure of AgBr (JCPDS no. 6-438), and no impurity phase is found. By further observation, it can be seen that the intensity ratios of various peaks of irregular AgBr are consistent with the standard value, however, which of AgBr nanoplates are obviously different from that of normal cubic phase AgBr. The intensity ratio of (222) to (200) peaks and (222) to (220) peaks for AgBr nanoplates are 0.78 and 4.30, respectively, which are obviously higher than the standard ratios, 0.28 and 0.36, suggesting that the nanoplates are dominated by {111} facets and the facades of the nanoplates should be enclosed by {111} facets. Fig. 2B displays the typical UV-Vis diffuse reflectance spectra (DRS) of the as-prepared samples, and it can be seen that the absorption edge of AgBr nanoplates shows a little red shift compared with irregular AgBr particles, and the corresponding bandgap narrows down. Such red shift should be primarily attributed to the particular atomic configurations on {111} facets, and be favorable to improve the photocatalytic activities. Similar results have been demonstrated previously in TiO₂ and Ag₃PO₄ based photocatalysts.^{7,13}

The photocatalytic activity of the as-prepared AgBr nanoplates was evaluated by photodegradation of the MO dye under visible-light irradiation. For comparison, Ag₃PO₄, a new type of highly efficient photocatalyst, was prepared by a direct precipitation reaction with AgNO₃ and Na₃PO₄ at 60 °C

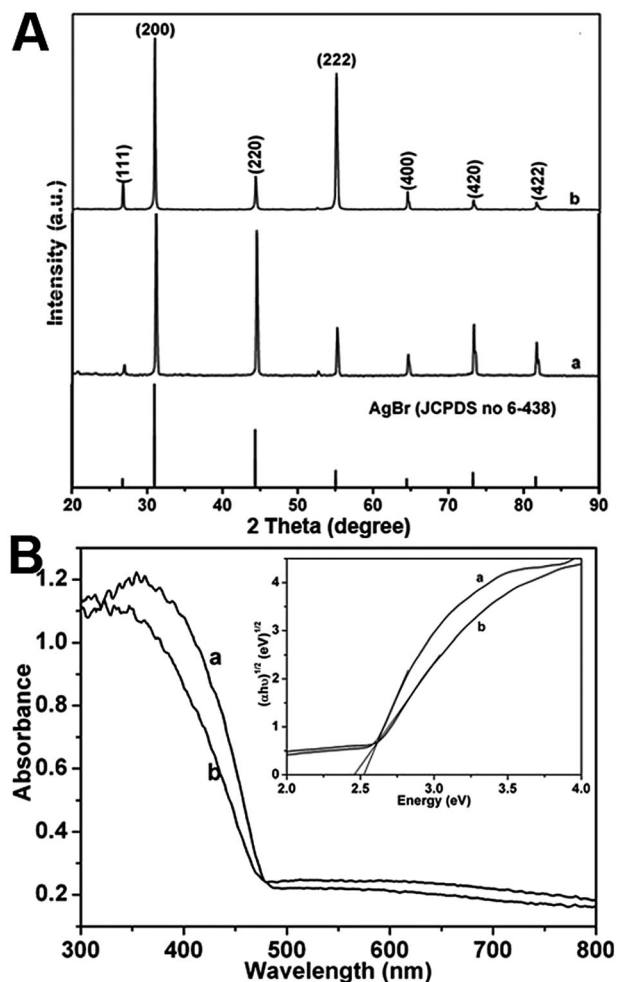


Fig. 2 XRD pattern (A) and diffuse reflectance absorption spectra (B) of as-prepared AgBr nanoplates (a) and irregular particles (b). The inset in B shows the corresponding plots of $(\alpha h\nu)^{1/2}$ versus photon energy.

and its photocatalytic performance was investigated (the SEM image and XRD pattern of as-prepared Ag₃PO₄ are shown in Fig. S4 (ESI[†])). As shown in Fig. 3, both of the AgBr-based photocatalysts have better photocatalytic performance than Ag₃PO₄. Meanwhile, it can be clearly seen that the AgBr

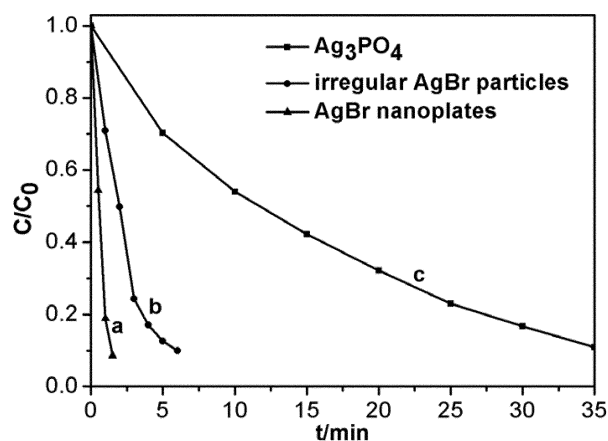


Fig. 3 Photodegradation of MO dyes over the AgBr nanoplates (a), irregular AgBr particles (b), Ag₃PO₄ (c).

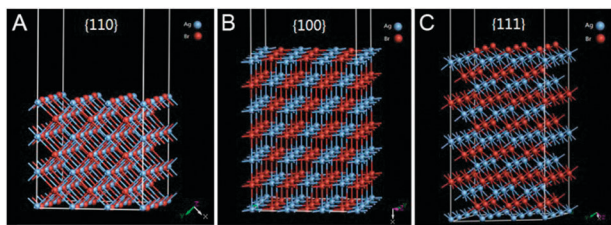


Fig. 4 Relaxed geometries for the (A) {110}, (B) {100} and (C) {111} surfaces of AgBr based on a 126-atom slab model. The vacuum region was set to the same thickness as AgBr.

nanoplates show a super highly photocatalytic activity, and the photodegradation rate of MO dyes over them is about 4 times faster than irregular AgBr particles. The Brunauer–Emmett–Teller (BET) nitrogen adsorption analysis showed that the specific surface areas of the AgBr nanoplates and irregular particles were 2.64 and 1.22 m² g⁻¹ (the specific surface area of Ag₃PO₄ was 10.45 m² g⁻¹), respectively, so the increased specific surface areas should be one factor for the enhanced photocatalytic activities of AgBr nanoplates. To further elucidate the reasons for the enhanced photocatalytic activities, AgBr nanoplates with a large size were synthesized by another method (Fig. S5, ESI†), and their photocatalytic properties were investigated. Though their specific surface areas decreased to 1.77 m² g⁻¹, they presented comparable photocatalytic activities to small AgBr nanoplates, which indicates that the increased specific surface areas of the as-prepared small AgBr nanoplates have a weak contribution to their enhanced photocatalytic activities, and thus it can be speculated that the exposed facets of AgBr nanoplates affect the photocatalytic activities primarily.

To further investigate the facet effect on the photocatalytic properties of AgBr nanoplates photocatalyst, DFT calculations were employed to study the surface energy of AgBr {001}, {110} and {111} facets. Actually, there are two possible structures of the (111) surface of AgBr, which are entirely constituted by Ag or Br atoms, respectively, and the total-energy calculation shows that the surface entirely constituted by Ag atoms gives the best stability, suggesting that the {111} facets are most possibly enclosed by such structure. The relaxed unit cells used to construct the surface models are 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 the (111) surface. The exact calculation results show that the surface energy of the AgBr (111) surface is estimated to be 1.253 J m⁻², which is higher than that of AgBr (100) (ca. 0.495 J m⁻²) and (110) (ca. 0.561 J m⁻²), indicating that the {111} facets of AgBr are more reactive than {110} and {100}, and thus it should facilitate the dye adsorption and provide more catalytically active sites.

In summary, AgBr nanoplates with exposed {111} facets were prepared by a facile modified precipitation method with PVP as a capping agent. Studies of their photocatalytic performance indicate that these nanocrystals have super highly photocatalytic activities, which are about 4 times quicker than

irregular AgBr microspheres. DFT calculation results suggest that the AgBr (111) surface is mainly constituted by Ag atoms and has a relatively higher surface energy than {100} and {110} facets, the main exposed facets of usual AgBr/Ag, and thus are very favorable for enhancing the photocatalytic activities of AgBr/Ag nanoplates. Our work here not only provides a super highly reactive photocatalyst, but also demonstrates that the morphology and exposed facets have an important influence on the photocatalytic activities of AgBr photocatalysts.

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