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Facile synthesis of AgBr nanocubes for highly efficient visible light photocatalysts†

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AgBr nanocubes, with an average edge length of 500 nm, were synthesized by a facile precipitation reaction. A plausible growth mechanism was proposed. The as-prepared AgBr nanocubes were used as photocatalysts for the first time, exhibiting excellent photocatalytic activity under visible light illumination.

Nano- or microstructures have been intensively pursued and well developed in the past decades for their size, shape, crystalline structure and facet-dependent properties, such as catalytic performance,[1] biological/chemical sensing properties,[2,3] energy conversion and storage,[4–7] *etc.* Being confronted with an energy crisis along with environmental problems, photocatalysis for water splitting and degradation of organic pollutants using solar energy has received much attention.[8–12] Besides conventional TiO_2 photocatalysts, growing interest has been aroused in some new and visible-light-responsive photocatalysts, such as $InMO_4$ (M = Ta, Nb),[13,14] $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$,[15] $BiVO_4$,[16] Ag_2CrO_4,[17] AgX (X = Cl, Br),[18–20] C_3N_4,[21] Ag_3PO_4,[22,23] and so on.

AgBr, as a conventional photographic material with excellent photocatalytic performance under visible light irradiation, has attracted wide attention recently.[24–26] However, the synthesis of regular AgBr nanostructures and the study of morphology-dependent properties have been rarely reported.[27] Ye *et al.* introduced a replacement reaction for the synthesis of AgBr nanowires from commercial silver foils, and these one-dimensional nanowires exhibited much higher photocatalytic activity than spherical AgBr nanoparticles.[28] Recently, we reported the successful synthesis of AgBr tetrakaidecahedron and nanoplates using simple wet chemical methods with polyvinyl pyrrolidone (PVP) as a capping agent, and investigated their morphology and facet-dependent photocatalytic properties.[29,30]

In this work, we successfully prepared AgBr nanocubes in high yield by a facile precipitation reaction, and their photocatalytic properties were investigated for the first time. The photocatalytic results have clearly revealed that the as-prepared AgBr nanocubes exhibit high photocatalytic activity toward the degradation of methyl orange (MO) dye.

The AgBr nanocubes were synthesized through a facile precipitation route directly from a reaction of $AgNO_3$ and NaBr in ethylene glycol (EG) solution with the aid of the organic solvent, pyridine. Fig. 1A and B are typical scanning electron microscopy (SEM) images of the as-prepared AgBr products. It can be seen that the products are composed of regular cube polyhedrons with an average edge length of 500 nm. Irregular AgBr particles were prepared by a direct precipitation reaction with $AgNO_3$ and NaBr at room temperature, and the corresponding SEM images are shown in Fig. S1 (ESI†). Transmission electron micrographs (TEM) were carried out with a weak beam current, which further revealed that the product consisted of well-defined cubic structures with a square outline, as shown in Fig. 1C. The corresponding selected area electron diffraction (SAED) pattern (Fig. 1D) was obtained by directing the incident electron beam perpendicular to one square facet of an individual nanocube, and the square spot array was indexed to [200] and [020] of the face-centered cubic AgBr, which demonstrated that the as-prepared AgBr nanocubes are each enclosed by six {100} facets.

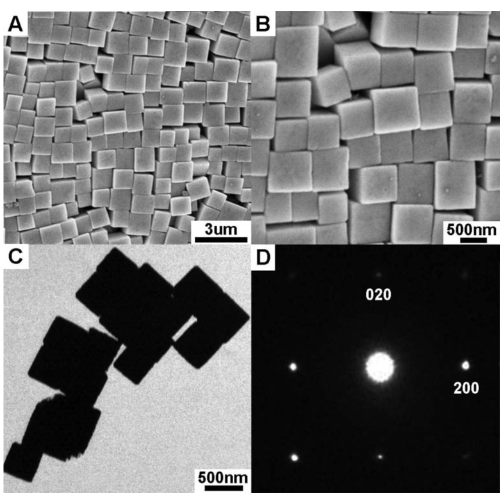

Fig. 1 SEM of as-prepared AgBr nanocubes. SEM images of as-prepared AgBr nanocubes at low (A) and high magnifications (B). TEM image (C) and the corresponding SAED pattern (D) of AgBr nanocubes.

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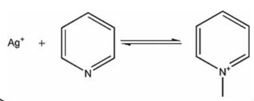
† Electronic Supplementary Information (ESI) available: Experiment details; SEM images of as-prepared irregular AgBr particles, AgBr nanoparticles produced with different amounts of PVP and pyridine, and different reaction times; XPS and FTIR spectra. See DOI: 10.1039/c2ce25750e

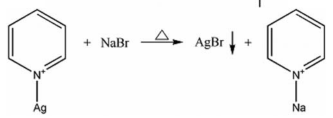
To investigate the possible growth mechanism of the AgBr nanocubes, some control experiments were carried out by simply adjusting the amount of pyridine, polyvinyl pyrrolidone (PVP) and the reaction time. Without PVP, a similar cube-like morphology is obtained, but the sample is not well grown with uniform sizes, suggesting that PVP does not play a dominant role in the formation of AgBr nanocubes. With increasing amounts of PVP added, it is shown that PVP can modify the cubes and lead to the well faceted structure and narrow size distribution, as shown in Fig. S2 (ESI†).

However, in the absence of pyridine, no AgBr nanocubes can be obtained, but instead, some AgBr truncated bipyramids are found, which could result from the adsorption effect of PVP as a surfactant (Fig. S3, ESI†). Similar morphologies have been synthesized in our previous reports.[23]

Whereas after adding pyridine, the AgBr nanocubes appear, and the sizes become small and uniform with increasing amounts of added pyridine. Therefore, pyridine is very essential to the formation of AgBr nanocubes in the present reaction system. Pyridine molecules can easily coordinate with silver ions to form pyridine salt, which can slow the reaction of the formation of AgBr following the below equations:[31]



(1)



(2)

Moreover, AgBr has a face-centered cubic structure, and the AgBr cubes are enclosed by {100} facets. From the atomic arrangement scheme (Fig. 2), it can be seen that Ag and Br have an identical atomic ratio on the (100) surface, and Ag is fivefold-coordinated with one dangling bond. Meanwhile, the nitrogen atom on pyridine features a basic lone pair of electrons, with a negative charge, and may prefer to interact with positively charged Ag to compensate for the local surface charge imbalance and thus stabilize the (100) crystal surfaces to form AgBr nanocubes.

However, with an excessive amount of pyridine added, the AgBr particles become small, and no precipitation will be obtained when it exceeds 6 mL, which should be due to the strong coordination ability of pyridine silver ions. In addition, the morphology evolution of AgBr products was also investigated with different reaction times. As shown in Fig. S4 (ESI†), it can be seen that it evolves from nanocubes to irregular and large particles with an increasing reaction time. As the pyridine is volatile, it will be gradually lost with an increasing reaction time, so the adsorption effect on the surface of AgBr nanocubes may be weakened, and therefore the irregular AgBr particles are eventually obtained.

XRD patterns of the AgBr nanocubes and irregular AgBr particles are shown in Fig. 3A, and they can both 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 AgBr nanocubes have a higher crystal quality than the irregular AgBr particles, which may be due to their higher preparation temperature and regular crystal structure. Moreover, the intensity ratios of various peaks of irregular AgBr particles are consistent with the standard values, while, those of AgBr

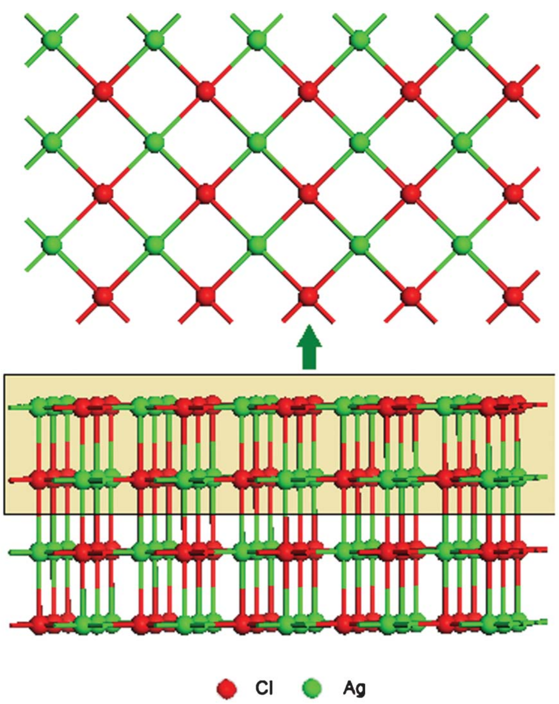


Fig. 2 Schematic model of the AgBr (100) surface that contains several atom steps.

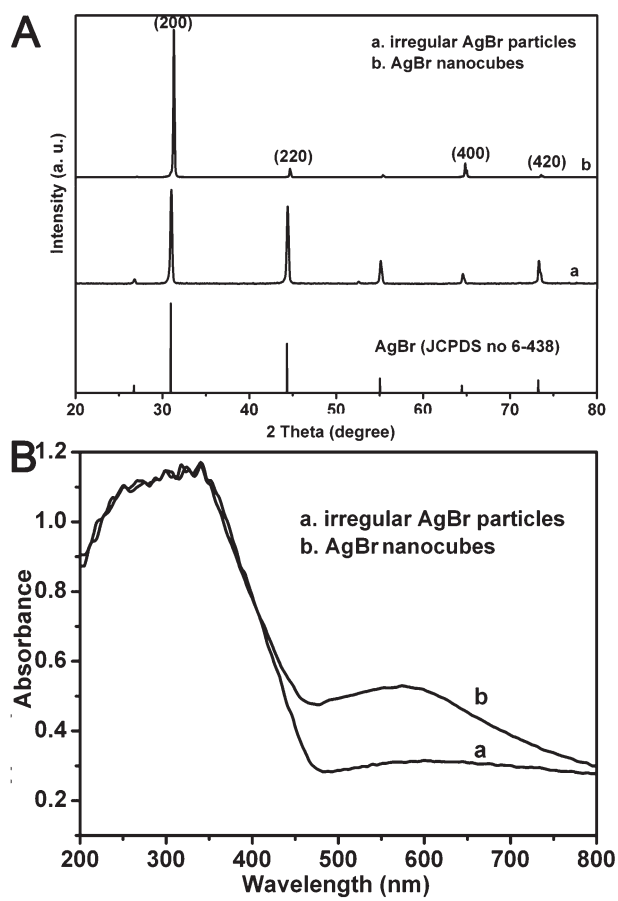


Fig. 3 XRD patterns (A) and diffuse reflectance absorption spectra (B) of irregular AgBr particles and nanocubes.

nanocubes are obviously different from that of normal cubic phase AgBr. The XRD pattern of AgBr nanocubes shows a strong and sharp diffraction peak at 2.89 Å, assigned to the (200) reflection, suggesting that the nanocubes are enclosed by six {100} facets with high crystal quality.

Fig. 3B displays the typical UV-Vis diffuse reflectance spectra (DRS) of the as-prepared samples, and it can be seen that the irregular AgBr particles can absorb visible light with a wavelength shorter than 500 nm. Compared with irregular AgBr particles, the DRS of AgBr nanocubes shows it has an obvious absorption of light with wavelengths higher than 500 nm, which manifests the existence of a trace amount of Ag resulting from the reduction of AgBr by heated EG, and that is not deleterious to their photocatalytic activities. The corresponding XPS spectra providing further structural information for AgBr nanocube photocatalysts are shown in Fig. S5 (ESI†). It can be seen that the XPS spectrum has peaks at 367.4 and 373.4 eV, which can be assigned to Ag(I) $3d_{5/2}$ and $3d_{3/2}$, while the weak XPS peaks at 367.7 and 373.7 eV are assigned to Ag(0) $3d_{5/2}$ and $3d_{3/2}$, suggesting the existence of a trace amount of Ag, which is consistent with the results of DRS.[32,33]

The photocatalytic activity of the as-prepared AgBr nanocubes was evaluated by photodegradation of MO dye under visible-light irradiation. For comparison, Ag_3PO_4, a new type of highly efficient photocatalyst, was prepared by a direct precipitation reaction with $AgNO_3$ and Na_3PO_4 at 60 °C and its photocatalytic performance was investigated. As shown in Fig. 4, both of the AgBr-based photocatalysts show better photocatalytic performance than Ag_3PO_4. Meanwhile, it can be clearly seen that the AgBr nanocubes show greatly enhanced photocatalytic activities, and the photodegradation rate of MO dyes over them is about twice as fast as that of irregular AgBr particles. The specific surface area of AgBr nanocubes is 2.61 $m^2\ g^{-1}$, which is higher than 1.59 $m^2\ g^{-1}$ of irregular particles, but our previous result showed that the small difference between the surface area of the AgBr photocatalysts were not the decisive factor in photocatalytic properties.[29,30] Moreover, the photocatalytic activities of as-prepared AgBr nanocubes are comparable to that of tetrakaidecahedrons and nanoplates, which may be primarily ascribed to their novel cubic structure and exposed {100} facets with special atomic configurations, suggesting that the photocatalytic properties of AgBr can be significantly improved by tailoring its shape and surface structure.

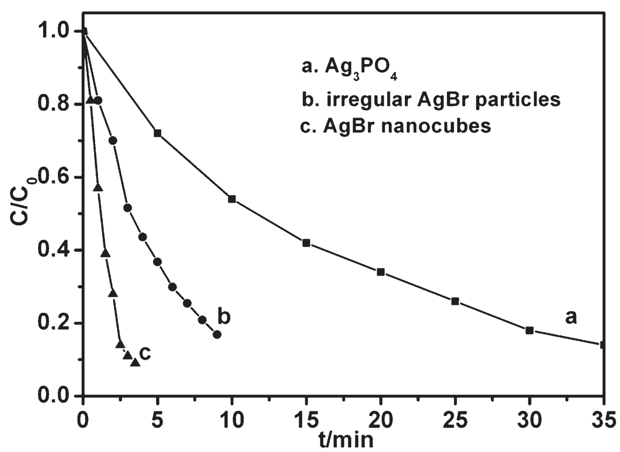


Fig. 4 Photodegradation of MO dye over as-prepared samples. Ag_3PO_4 (a), irregular AgBr particles (b) and AgBr nanocubes (c).

In summary, we have proposed a facile route for the synthesis of AgBr nanocubes with an average edge length of 500 nm *via* a facile precipitation reaction with the aid of pyridine. Pyridine not only plays the role of coordination agent for silver ions in the reaction system, but may also selectively adsorb on the AgBr (100) surface. The as-prepared AgBr nanocubes were used as a photocatalyst for the first time, which exhibited excellent photocatalytic activities under visible light illumination.

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