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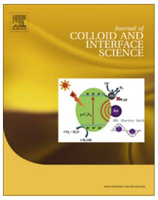


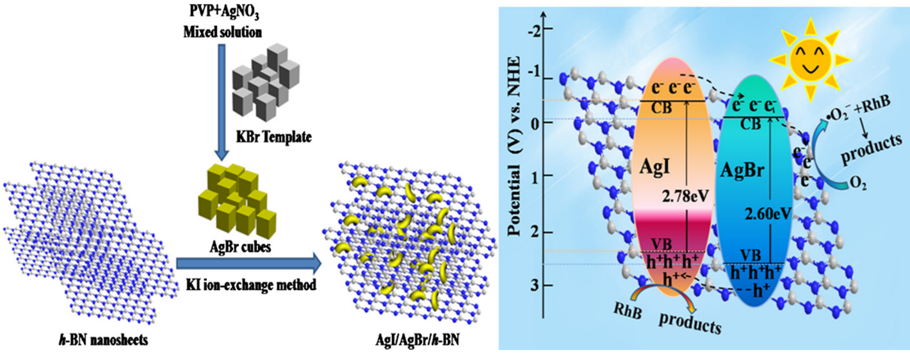
Regular Article

Integrating AgI/AgBr biphasic heterostructures encased by few layer *h*-BN with enhanced catalytic activity and stability

Wen Wu[a], Xiaomeng Lv[b,*], Jiaxi Wang[b], Jimin Xie[b]

[a] Department of Chemistry, Zhou Kou Normal University, Henan 466001, PR China
[b] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, PR China

GRAPHICAL ABSTRACT



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ABSTRACT

Using freshly prepared water-soluble KBr crystal as facile, low-cost sacrificial template, AgBr nanocubes were synthesized through one-pot precipitation method, then navy bean shaped AgI/AgBr biphasic heterostructures were synthesized through anion-exchange reaction and encased within few-layer *h*-BN to obtain final product. The obtained heterostructured AgI/AgBr/*h*-BN composite without plasmonic noble metal nanoparticles was used as stable and high active photocatalyst for dye degradation under visible light irradiation, comparing both with self-prepared normal AgBr, AgBr cubes, AgI/AgBr navy beans and other related catalysts reported in the literature. The significant boosting of activity was attributed to the formation of AgI/AgBr interface and the coupling of few-layer *h*-BN, the latter of which not only effectively suppresses the reduction of silver ions but greatly enhance the charge separation. Furthermore, it was suggested that the photogenerated holes and superoxide radical were the main active species according to photoelectron chemical measurements, electron spin resonance spin-trap analysis and radical trapping experiments. Finally, the possible mechanism of enhanced photocatalytic activity and stability was discussed and proposed. The work demonstrates that engineering Ag-based semiconductor coupling with *h*-BN would profit the design strategy for low-cost, solar-driven photocatalysts.

1. Introduction

With the development of modern industrialization and the increasing demand for energy, the semiconductor photocatalytic

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* Corresponding author.
E-mail address: laiyangmeng@163.com (X. Lv).

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technology has attracted wide attention to resolve the energy crisis and environment pollution [1–3]. The traditional photocatalyst TiO_2 was applied widely in the field of hydrogen generation, selective organic transformation and contaminant degradation for its environmentally benign, low-cost, availability and chemical stability [4–6]. Unfortunately, for its large band gap of c.a. 3.2 eV, TiO_2 can only be excited under UV light irradiation that only accounts for c.a. 5% of solar light. Meanwhile, the photogenerated electron-hole pairs can easily recombine and the photo-quantum yield can be decreased to some extent, which significantly restricts its practical applications in contaminant removal [7–9]. Therefore, developing highly efficient and stable visible-light-driven photocatalysts was still a significant challenge for renewable energy production and environment purification.

Recently, silver-based photocatalysts have attracted considerable attention for the photodegradation of organic pollutants or splitting water. However, it should be noted that there were some inherent limitations in the photocatalytic system. It was well known that the photosensitive semiconductor materials were unstable for the photocorrosion under light irradiation, which limited the recycle and could not suppress the recombination of photogenerated charge carries of the photocatalysts [10]. Fortunately, the well-controlled hierarchical, especially three-dimensional structures (e.g. cubes), were found not only provide high specific surface area and support a way to expand photoenergy conversion efficiency for the enhanced light harvesting, but shorten the diffusion paths of charge carriers, increase the active sites in porous micro/nanochannels and effectively improve the photocatalytic activity for the degradation of organic dyes [11–14]. Especially, silver halides/silver composite photocatalysts with the cube-like shapes have been synthesized by various methods and possess excellent photocatalytic activity. Wang et al. [15,16] have fabricated AgBr cubes by facile direct precipitation reaction or ion-exchange reaction. Bi et al. [17] and Yan et al. [18] have developed a facile and general route to synthesize Ag_3PO_4 microcubes. The Ag@AgBr and Ag@AgCl cubic cages have been synthesized using a water-soluble sacrificial salt-crystal-template [19–21], direct-precipitation process [22–24], a reverse micelle method [25], or one-step process of laser irradiation in liquids [26], etc. The above photocatalysts exhibited excellent photocatalytic performance towards decomposition of organic pollutants under visible light irradiation, however, several efforts have been devoted to further promote the separation of photogeneration electron-hole pairs that could dramatically enhance the photocatalytic activity and improve the stability of photocatalysts.

As a result, photocatalysts profit from plasmon-induced electron transfer processes have been developed, such as the ternary composite photocatalysts of Ag@AgBr/AgCl heterostructured nanocashews [27], Ag/AgCl/GO [28], and heterostructured Ag_3PO_4/AgBr/Ag [29], which were beneficial for the effective separation and prolong the lifetime of photoexcited carriers that could have remarkable photocatalytic performance and stability for the photodegradation of organic pollutants. Further exploration demonstrated that two dimensional (2D) graphene-like nanosheet materials, e.g., C_3N_4, MoS_2 and WS_2, possess special properties as photocatalysts and have been widely investigated [30–33]. However, another typical structural analogue of graphene, i.e., *h*-BN, though known as dielectric material with a band gap of 5–6 eV, still arouse wide interest. Theoretical calculations have demonstrated that *h*-B—N bond was partially ionic, and a slight buckling appeared on the curled surface [34–36], leading to the electronic properties of low-dimensional *h*-BN system differed considerably from those of bulk BN. Hence, the band gap of few-layered *h*-BN can be considerably reduced and engineered as support in photocatalytic application [37,38]. Consequently, several *h*-BN-based photocatalysts have been reported, such as BN/Ag_3PO_4 [39], BN/Ag_2CO_3 [40], BN/AgBr [41], BN/AgI [42], and BN/Ag_3VO_4 [43]. These Ag-based photocatalyst without plasmonic effect still exhibit high photocatalytic activity and stability.

Herein, navy bean shaped AgI/AgBr biphasic heterostructures loaded over few-layered *h*-BN nanosheets have been synthesized by a facile water-soluble KBr salt as sacrificial template, one-pot precipitation and anion-exchange reaction. The photocatalytic activity of the as-prepared AgI/AgBr/*h*-BN materials without plasmon noble metal showed distinctly enhanced photocatalytic performance and stability towards the degradation of rhodamine B (RhB) and methyl orange (MO) under visible light irradiation. Compared with the previously reported plasmonic photocatalyts or *h*-BN-based photocatalysts, our AgI/AgBr/*h*-BN hybrid nanostuctures are superior in three aspects: (1) The active component is a unique navy bean shaped AgI/AgBr biphasic heterostructures prepared by a facile, low-cost method. (2) Few-layered *h*-BN is three-dimensional nanostructured, which facilitate shorten diffusion paths to active sites. (3) Integration of unstable semiconductors and stable *h*-BN is effective in improving the photocatalytic performance, offering possible synthesis strategy of non plasmonic photocatalysts with heterostructures.

2. Experimental

2.1. Materials

Boric acid (H_3BO_3, AR), urea ($CO(NH_2)_2$, AR), silver nitrate ($AgNO_3$, AR), potassium bromide (KBr, AR), polyvinylpyrrolidone (PVP, AR), potassium iodide (KI, AR), absolute ethyl alcohol (EtOH, AR), 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and rhodamine B (RhB) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents in the experiments were used as received without further purification.

2.2. Preparation of the catalysts

The synthesis of the *h*-BN sample was once reported in our previous work [40]. In a typical procedure, boric acid and urea with a molar ratio of 1:24 were dissolved in 60 mL of deionized water and dried at 65 °C, until the evaporation of water was complete. The precursor was calcinated at 900 °C for 5 h in a N_2 atmosphere at tubular furnace and the white *h*-BN sample was obtained.

The AgBr nanocubes were prepared according to the reported method [19]. Typically, the $AgNO_3$/PVP ethanol solution was prepared in advance by dissolving $AgNO_3$ (0.15 g) and PVP (1.0 g) in 20 mL absolute ethanol under ultrasonication. Then, the as-prepared KBr saturated aqueous solution was injected into 100 mL absolute ethanol under intensive magnetic stirring at 0 °C, and a white suspension was formed immediately. Subsequently, the above $AgNO_3$/PVP ethanol solution was poured into the KBr ethanol suspension, and the mixture was stirred for 24 h. Finally, the as-prepared light yellow AgBr products were collected by centrifugation, washed several times with absolute ethanol, and dried at 60 °C overnight. The normal AgBr was synthesized by the precipitation method. Typically, $AgNO_3$ (0.27 g) was added into 20 mL of deionized water and stirred for 0.5 h. Then an aqueous solution of KBr (0.19 g, 20 mL deionized water) was dropped into the solution and stirred for 4 h in the dark. The yellow precipitate was collected, washed and dried under 60 °C overnight.

The AgI/AgBr/*h*-BN heterostructure nanocomposite was prepared by anion exchange method. In a typical procedure, BN (7 mg) and AgBr cubes (0.23 g) were dispersed in 20 mL of deionized water and sonicated for 0.5 h. Then, an aqueous solution of KI (0.044 g, 10 mL deionized water) was dropped into the above suspension and reacted under vigorous magnetic stirring for 5 h