



Oxygen vacancy enhanced photostability and activity of plasmon-Ag composites in the visible to near-infrared region for water purification



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ABSTRACT

Solid solution of BiOBr and BHO (BiO(OH)_{0.06}Br_{0.94}) with abundant oxygen vacancies was supported on Ag/AgBr using precipitation and deposition-precipitation methods. The photocatalyst showed high and stable photocatalytic activity for the degradation of chlorophenols and azodyes in water under visible to NIR light irradiation without any release of Ag⁺, which came from visible-excited AgBr and the SPR of Ag NPs in the visible and NIR region. The different interfacial charge-transfer processes were verified on the basis of cyclic voltammetry analyses and all experimental information. The conduction band (CB) electrons of photoexcited AgBr reacted with the adsorbed oxygen forming O₂^{•-}, while the valence band (VB) holes of AgBr were transported the VB of BiO(OH)_{0.06}Br_{0.94} to oxidize organic pollutants or H₂O to •OH. The plasmon-induced electrons from Ag NPs transferred to the CB of AgBr reacting with the adsorbed oxygen to O₂^{•-}, while the electrons trapped on the oxygen vacancies of BiO(OH)_{0.06}Br_{0.94} transferred to Ag NPs recombining with the plasmon-induced holes, inhibiting the release of Ag⁺, and the resulted VB holes of BiO(OH)_{0.06}Br_{0.94} oxidized organic compound. These interfacial charge transfers evidenced the high photoactivity and photostability of BiO(OH)_{0.06}Br_{0.94}/Ag/AgBr.

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1. Introduction

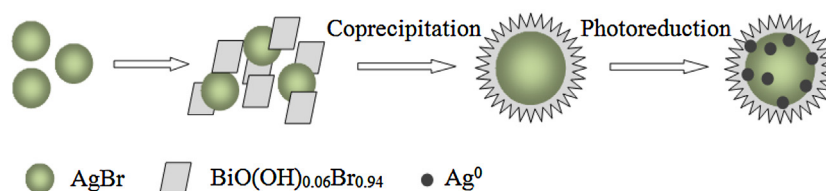
Photocatalytic solar-energy conversion has been identified as a robust new method for water purification and hydrogen generation at a lower cost and energy consumption [1]. To date, extensive development has been conducted on UV- and visible-light-active photocatalysts, such as UV-active TiO₂ and doped TiO₂ with anions and/or cations [2,3] in the visible range. However, in the entire solar spectrum reaching the earth, 3%, 44%, and 53% are in the UV, visible and near-infrared (NIR) light regions, respectively. Therefore, it is important to develop an efficient photocatalyst in the visible and NIR light regions from the viewpoint of usable solar energy. Unfortunately, only a small number of semiconductors have NIR absorption and activity [4]. A variety of efforts have been undertaken, including converting NIR light (approximately 980 nm) into visible and UV light through the use of up-conversion materials [5] and assembling quantum dot-metal hybrid nanostructures with a

designed band structure configuration for NIR-active photocatalysts [6].

An alternative strategy to improve performance is to use the surface-localized plasmon resonance (SPR) energy of irradiated noble metals (Au, Ag, Pt) deposited on semiconductors [7]. By manipulating the composition, shape, and size of plasmonic nanoparticles (NPs), it is possible to use the entire solar spectrum and to extend the absorption band of composite photocatalysts to regions that might be inaccessible to the semiconductors [8,9]. To date, a series of plasmonic photocatalysts [10–14] have been developed for water purification [15,16] and water splitting [17] using visible light. Despite these promising studies, one obstacle to its practical application is the stability of the photoinduced noble metal NPs during photocatalytic reaction. To the best of our knowledge, charge separation at a plasmon-excited metal nanoparticle without corrosion of the particle has never been reported. According to the reported works [7,18], SPR is responsible for the transfer of energetic electrons to adsorbates in the efficient conversion of solar to chemical energy. Moreover, it is worth noting that several findings suggested that energetic holes retained on plasmonic-metal nanoparticles have sufficient energy to drive the oxidation of water and organics on the surface of the metal [19,20]. However, it was observed that the resulting metallic ions were released into

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Scheme 1. Synthetic route to the plasmon-Ag composites.

water due to the limited trapping-hole rate from electron donors in solution [21–23]. Therefore, the corrosion and dissolution of the noble metal NPs are inevitable in the photocatalytic reaction, limiting the practical application of plasmonic photocatalysts [24,25].

Interfacial electron and hole transfers with comparable rates have been emphasized as being the most important for maintaining a high photocatalytic efficiency and stability of the noble metal NPs. Surface oxygen vacancies can act as photoinduced charge traps and adsorption sites, in which the charge can transfer to the adsorbed compounds, enhancing the separation of the photogenerated electron-hole pair [26]. Many investigations have indicated that oxygen vacancies play an important role in the process of photocatalysis [27,28]. Moreover, there is higher electron density on the oxygen vacancies, acting as electron donors [29]. It has been determined that adsorbed Au, Ag, and Pt ions on TiO₂ with oxygen vacancies were reduced to form metallic nanoparticles spontaneously [30,31]. Therefore, this reduction can act as an alternative method to control the surface oxygen vacancies for the photostability and activity of plasmon-Ag composites. Either multicomponent oxides with different ion radii and valences or solid solutions with different crystalline phases can be candidates for the surface formation of oxygen vacancies [32]. Bismuth oxyhalide compounds have a layered structure [33], and hydrated bismuth oxide (BHO) is a dihydrate, rather than a trihydrate, also with a layered structure according to previous works [34]. This property makes it feasible for both compounds to form a solid solution.

In the current study, a solid solution of BHO and BiOBr (BiO(OH)_{0.06}Br_{0.94}) was prepared by co-precipitation. Moreover, the solid solution-coated Ag/AgBr (BiO(OH)_{0.06}Br_{0.94}/Ag/AgBr) was obtained using precipitation and deposition-precipitation methods. For the first time, we demonstrated that BiO(OH)_{0.06}Br_{0.94}/Ag/AgBr possessed very high photocatalytic activity and stability in the visible to NIR light region for the degradation of phenolic and azodyes compounds, including 2-chlorophenol (2-CP), 2, 4-dichlorophenol (2, 4-DCP), trichlorophenol (TCP), acid red B (ARB), reactive red K-2BP (K-2BP), cationic red X-GRL (X-GRL), and methyl orange (MO), which are highly toxic and difficult to degrade biologically in aquatic systems. Surprisingly, the photocorrosion and dissolution of Ag NPs were only slightly observed throughout light irradiation

without the need of electron donors in solution. Photocatalytic and photostable mechanisms were proposed by surface charge transfer processes over the BiO(OH)_{0.06}Br_{0.94}/Ag/AgBr suspension with visible or NIR light irradiation.

2. Experimental

2.1. Chemicals and materials

The reagent 5-*tert*-butoxycarbonyl 5-methyl-1-pyrroline N-oxide (BMPO) used as the spin trapping agent in the electron spin resonance studies (ESR) was purchased from the Bioanalytical Lab (Sarasota, FL). 2-CP, 2,4-DCP, TCP, phenol, ARB, K-2BP, X-GRL, MO and all other chemicals were analytical grade purchased from the Beijing Chemical Company and used without further purification.

2.2. Preparation of catalysts

The catalysts were synthesized through a chemical precipitation method. In a typical process, 0.21 g of AgNO₃ in 2.3 mL of NH₄OH (25 wt% NH₃) was added to 200 mL of ultrapure water. Then, 8.66 mL of a 0.2 M KBr solution was added dropwise to the above solution, and subsequently, 0.24 g of Bi(NO₃)₃·5H₂O in 10 mL of a 60 vol% acetic solution was added dropwise to the suspension and stirred at room temperature for 12 h. The resulting precipitation was collected and washed several times with water and then photoreduced in 200 mL 10 vol% ethanol solution for 2 h under visible light ($\lambda > 420$ nm) irradiation. Next, the product was centrifuged and washed with water to neutral condition and was dried at 70 °C in air. The synthetic route was illustrated in Scheme 1. By the same procedure, at the given amount of AgNO₃ (0.21 g), four samples with different component were prepared when changed the amount of Bi(NO₃)₃·5H₂O and KBr (Table S1 in SI). It was found that these samples exhibited almost same photoactivity, however, the catalyst with 0.24 g of Bi(NO₃)₃·5H₂O dosage, had more higher activity (Fig. S1 in SI), which is used for all of the subsequent experiments.

As references, by the same method, Ag/AgBr was synthesized without Bi(NO₃)₃·5H₂O, another sample with 0.24 g of Bi(NO₃)₃·5H₂O was also prepared without AgNO₃, which was

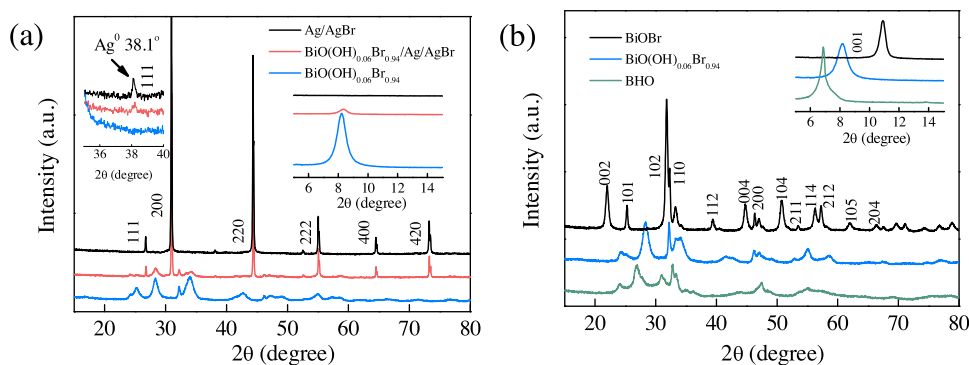


Fig. 1. XRD patterns of different samples (the insets show enlarged figure of 2θ from 36° to 40° of (a) and the low-angle peaks).

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