



New insight of Ag quantum dots with the improved molecular oxygen activation ability for photocatalytic applications



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ABSTRACT

Ag quantum dots (Ag QDs) modified BiOBr ultrathin nanosheets have been prepared via the reactable ionic liquid assisted solvothermal method. The Ag QDs were evenly dispersed on the surface of BiOBr nanosheets with the diameter less than 5 nm. The obtained Ag QDs/BiOBr materials displayed greatly enhanced photocatalytic activity for the degradation of antibiotic agent ciprofloxacin (CIP) and tetracycline hydrochloride (TC) under visible light irradiation. Through the various characterizations, the relationship between structure and activity was studied in details and some new insights of the key role of Ag QDs for the enhanced photocatalytic activity was presented. Different from the roles previously reported such as electron injection, plasmon resonance energy transfer and Schottky junction, the modified Ag QDs could activate the molecular oxygen via the hot electron reduction under the visible light irradiation in this system. And the Ag QDs worked as adsorption centers, charge separation centers and photocatalytic reaction centers, contributed to the increased photocatalytic activity. This study provided an approach to improve the molecular oxygen activation for pollutant removal, selective organic synthesis or donating abundant hot electrons for CO₂ photoreduction.

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1. Introduction

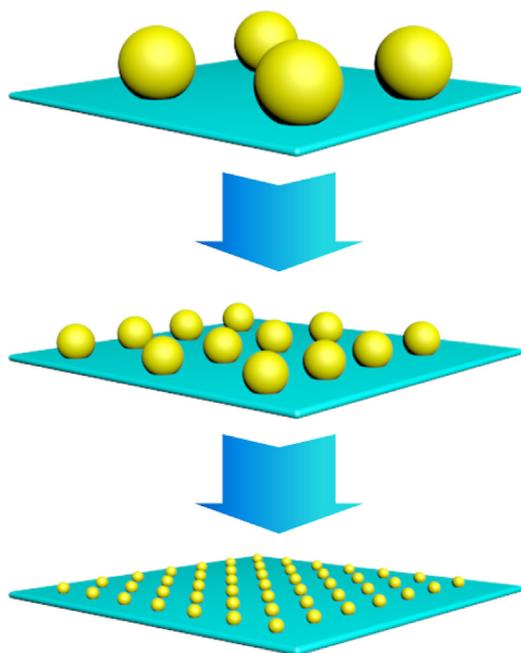
Semiconductor photocatalysis has emerged as a green, sustainable technology to addressing the increasingly energy shortage and environmental pollution issues [1,2]. Numerous attempts have been carried out to achieve excellent photocatalysts for water purification, water splitting, nitrogen fixation, CO₂ reduction for solar fuels production and so on [3–8].

Metal nanoparticles (such as Pt, Pd, Au, Cu, Bi, Ag) modified semiconductor photocatalysts has been widely studied for maximizing the performance of photocatalytic reactions due to the metal nanoparticles can work as capture center for photogenerated charge carriers, facilitating effective separation of electron-hole pairs [9]. In recent years, plasmonic photocatalysts have become the focus in photocatalysis field since the Awazu et al. found the surface plasmon resonance (SPR) effect of Ag nanoparticles could improve the photocatalytic activity for pollutant degradation [10]. Different from the function of capture center, the SPR of metal

nanoparticles such as Ag, Au, Bi was believed to be responsible for the increased photocatalytic activity [11,12]. The SPR was produced by the plasmonic metal NPs created a coherent oscillation of the free electrons in resonance with the electrical field of the incoming electromagnetic irradiation. Take Ag NPs for instance since it always exhibited the better SPR effects than other noble metals. Following the light absorption and SPR excitation in metal nanoparticles, the plasmon decay could take place through three mechanisms [13], (1) elastic radiative reemission of photons, (2) nonradiative Landau damping, where the photon energy was converted to single e⁻/h⁺ pair excitations; the excited primary electrons interact with other electrons through Coulombic inelastic scattering to produce many electrons, and (3) the interaction of excited surface plasmons with adsorbates, inducing a direct electron injection into the adsorbates. Up to now, several systems such as Ag/TiO₂ [14], Ag/AgCl [15], Ag/Cu₂O [16], Ag/BiOX (X = Cl, Br, I) [9,17,18], Ag/g-C₃N₄ [19], Ag/Bi₂WO₆ [20], and Ag/AgX/BiOX (X = Cl, Br) [21,22] have been reported. The results suggested that the Ag modification could improve the photocatalytic activity of the body photocatalyst. However, the mechanism of activity improvement in different systems above mentioned was conflict. For example, Zhu's group considered that the Ag nanoparticles mainly acted as the reservoir

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Scheme 1. Design plans of Ag QDs modified BiOBr ultrathin nanosheets.

of photoelectrons generated from C_3N_4 to increase the separation efficiency of electron-hole pairs [19]. Jiang's group regard as the Ag nanoparticles would produce the near-field electromagnetic radiative energy to boost the generation of charge carriers within TiO_2 nanotube and thus result in excellent photocatalytic performance [14]. Zhang's group demonstrated the Ag nanoparticles would produce SPR-excited electrons under visible light irradiation and then efficiently inject to the conduction band of $BiOCl$ to improve the photocatalytic activity [17]. Therefore, the substance of metal NPs for the enhanced photocatalytic activity should be further explored in details.

Recently, $BiOX$ ($X=Cl, Br, I$) have been widely studied due to its high-efficiency photocatalytic activity under visible or UV light irradiation [23–29]. The unique layered structure of $BiOX$ by interleaved $[Bi_2O_2]$ slabs with double slabs of halogen atoms could result in the inherent internal static electric fields [30]. It could lead to the effective separation of electron-hole pairs and the electrons would migrate to and accumulate in the (001) facet along with the holes migrate to (110) facet [18]. Among these $BiOX$ materials, $BiOBr$ was of great research interest since its suitable energy band structure and high-efficiency visible-light response photocatalytic activity [31–33]. Up to now, several strategies have been employed to construct the $BiOBr$ -based materials for optimizing the photocatalytic performance, such as tailored crystal facets [34,35], element doping or defect controlling [36], dehalogenation [37,38], and heterologous hybridization [39–46]. However, it was still far from enough for potential applications and need to further increased the photocatalytic activity. Considering the materials with ultrathin structure could enable more exposed surfaces so as endowing more surface active sites, the $BiOBr$ with ultrathin thickness may be the desired architecture. At the same time, compared to the bulk materials, the $BiOBr$ with ultrathin structure could enable the strikingly fast carrier transport from the inside to the surface, thus the higher separation efficiency of charge carriers can be achieved and advanced photocatalytic activity can be obtained [47]. What's more, consider the advantages of Ag NPs, it motive us to construct the Ag NPs modified $BiOBr$ ultrathin nanosheets to obtain the superior photocatalytic performance. Due to the large size Ag NPs could not display sufficient and favorable interface contactation with $BiOBr$ (Scheme 1),

we try to reduce the size of Ag NPs to less than 5 nm (Ag quantum dots (Ag QDs)), which could lead to the highly dispersion of Ag NPs. Since the small size of Ag QDs, the interface mismatch between the $BiOBr$ ultrathin nanosheets and Ag QDs can be minimized, and the nanoscale heterojunctions with intimate interface contacts can be constructed.

In this study, Ag QDs modified $BiOBr$ ultrathin nanosheets have been prepared through a facile ionic liquid assisted solvothermal method. The structures, morphologies, optical and electronic properties of the obtained materials was investigated. The photocatalytic performance was evaluated by the degradation of antibiotic agent ciprofloxacin (CIP), tetracycline hydrochloride (TC) and rhodamine B (RhB) under visible light irradiation. The structure-activity relationships and photocatalytic mechanism were discussed in details along with some new insight regarding the mode of action of Ag QDs for the improved photocatalytic activity was provided.

2. Experimental

2.1. Material and sample preparation

Phenol rhodamine B (RhB), antibacterial agent ciprofloxacin (CIP) and tetracycline hydrochloride (TC) were purchased from Sinopharm and used without further treatment. The ionic liquid 1-hexadecyl-3-methylimidazolium bromide ($[C_{16}mim]Br$) (99%) was obtained from Shanghai Chengjie Chemical Co. Ltd.

Ag quantum dots (Ag QDs) was prepared according to the reported literature [48]. 0.38 g $AgNO_3$ was added into 20 mL of oleylamine (OAm) and 0.4 mL of oleic acid (OA), and the magnetically stirred mixture was heated to $120^\circ C$ for 18 h. After cooled down to room temperature, 30 mL acetone was added to precipitate the product. After washing with ethanol for several times, the obtained Ag QDs were redispersed in 20 mL hexane.

In a typical synthesis of Ag QDs/ $BiOBr$ -0.5 materials, 1 mmol $[C_{16}mim]Br$ and 0.5 mL of Ag QDs hexane solution were dispersed into 8 mL ethanol to obtain solution A. 1 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved into 8 mL ethylene glycol (EG) to obtain solution B. The solution A was added into solution B dropwise under stirring and further stirred for 30 min. Then suspension was sealed in a 25 mL teflon-lined stainless-steel autoclave and heated at $140^\circ C$ for 24 h. The product was collected after centrifugation, washed with deionized water and ethanol for several times, and dried at $50^\circ C$. Pure $BiOBr$ and Ag QDs/ $BiOBr$ samples with different content of Ag QDs were synthesized using a similar route by tuning the addition of Ag QDs (0, 0.3, 0.5 and 1 mL).

Ag particles were prepared via the EG assisted solvothermal process. 0.1 g $AgNO_3$ was added into 20 mL EG and solvothermal treatment at $140^\circ C$ for 24 h. And the 0.5 wt% Ag/ $BiOBr$ and 1 wt% Ag/ $BiOBr$ materials were prepared using the above mentioned method only by using Ag particles for replacing the Ag QDs.

2.2. Characterization

The powder X-ray diffraction (XRD) were recorded on a Shimadzu XRD-6000 X-ray diffractometer with monochromatized $Cu K\alpha$ radiation ($\lambda=0.15418$ nm). The XPS spectra were collected by an ESCALab MKII X-ray photo-electron spectrometer and all binding energies were calibrated by using the contaminant carbon ($C1s=284.6$ eV) as a reference. A micro Raman spectrometer (Renishaw Invia) was employed to collect the Raman spectra in a backscattering geometry with a 532 nm laser as an excitation source. The morphology of the prepared Ag QDs/ $BiOBr$ were analyzed through a scanning electron microscope (SEM) (JSM-7001F, JEOL) equipped with an energy-dispersive X-ray spec-

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