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Highly efficient and stable Ag–AgBr/TiO_2 composites for destruction of *Escherichia coli* under visible light irradiation

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ABSTRACT

A series of Ag–AgBr/TiO_2 composites were prepared by a sol–gel method followed by photoreduction. Effect of Ag–AgBr content on the physicochemical properties and antibacterial activities of the Ag–AgBr/TiO_2 composites was investigated. These composites showed intrinsic antibacterial activities against *Escherichia coli* (*E. coli*) in the dark attributed to the Ag nanoparticles dispersed in the composites. Under visible light irradiation, inactivation of *E. coli* over these Ag–AgBr/TiO_2 composites was attributed to both their photocatalytic disinfection activities and intrinsic antibacterial properties. The Ag–AgBr/TiO_2 with an optimum Ti/Ag atomic ratio of 10 exhibited superior visible-light photocatalytic activities for ibuprofen degradation and mineralization as compared to the other Ag–AgBr/TiO_2 composites and also Ag–AgBr/P25, Ag/TiO_2 and TiO_2. It is probably because of the coexistence of two visible-light active components (AgBr and Ag nanoparticles) and the most effective separation of photogenerated electrons and holes in this photocatalyst. Correspondingly, the photocatalyst achieved a much higher efficiency of *E. coli* destruction than Ag–AgBr/P25 and TiO_2. *E. coli* was almost completely inactivated (7-log reduction) within 60 min by the photocatalyst with a rather low dosage of 0.05 g L^{-1} under white LED irradiation. Furthermore, the Ag–AgBr/TiO_2 showed high stability for photocatalytic destruction of *E. coli* and the dark repair and photoreactivation did not occur after the photocatalytic process. Finally, the action spectrum of this photocatalyst for *E. coli* inactivation and the influence of several inorganic ions present in surface water were also investigated.

1. Introduction

Microbiological safety of drinking water continues to be a growing concern as much of the world's population still suffers from the hazardous condition of public water supplies. Although conventional drinking water disinfection processes such as chlorination, ozonization and advanced filtration process are effective for eliminating most of pathogenic microorganisms, these processes still have several drawbacks such as formation of potentially mutagenic and carcinogenic disinfection by-products (DBPs), high costs or low efficiencies (Malato et al., 2009). Photocatalytic disinfection with UV-irradiated TiO_2 appears to be a cost-effective and environmentally-friendly alterative to inactivate various microorganisms (Chen and Mao, 2007).

Deposition of noble metal nanoparticles such as Ag (Xiong et al., 2011), Au (Primo et al., 2011) and Pt (Kowalska et al., 2008) on TiO_2 has been found to be an effective approach to

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improve the photocatalytic activity of TiO_2. The Schottky barrier formed at the metal-TiO_2 interface could act as an efficient electron trap to suppress the recombination of photogenerated electron–hole pairs (Linsebigler et al., 1995). On the other hand, the metal nanoparticles (Ag and Au) exhibit strong visible light absorption because of their surface plasmon resonance (SPR) property (Rycenga et al., 2011). In particular, it is known that the metallic Ag nanoparticles showed good antibacterial properties against bacteria (Rai et al., 2009). Composite materials containing Ag nanoparticles such as Ag–TiO_2, Ag–SiO_2, Ag–Al_2O_3, etc., have been developed and tested for antibacterial purposes (Zhang and Chen, 2009). Xiong et al. reported that the combined effect of the antibacterial property of Ag nanoparticles itself and the photocatalytic activity led to significant improvement of antibacterial activity of Ag–TiO_2 composite under UV irradiation (Xiong et al., 2011). Most studies of Ag–TiO_2 have focused on enhancing their photocatalytic activity under UV irradiation. To our knowledge, there have been very limited reports on Ag–TiO_2 photocatalysis under visible light. It is possibly due to the fact that the Ag–TiO_2 showed relatively low visible-light photocatalytic performance. Moreover the oxidation of Ag nanoparticles under visible light irradiation could lead to release of Ag^+ (Yu et al., 2009).

Silver halides (AgX) as photosensitive materials have been widely employed as light sensitive ingredient in photographic film and paper. When AgX crystal absorbs a photon of light, an electron is liberated and subsequently combined with an interstitial Ag^+ ion to yield metallic Ag. This phenomenon reflects that AgX is unstable under light irradiation. In most cases of photocatalysis with AgX, it actually exists in the form of Ag-AgX with the formation of Ag nanoparticles on its surface. Interestingly, it has been reported that the Ag-AgX system showed high photocatalytic activity and stability under visible light (An et al., 2010; Kuai et al., 2010). Nevertheless, these Ag-AgX composites often have large particle sizes of about several micrometers, which could lead to the low surface areas and the high recombination rate of the photogenerated charge carriers before they could relax to the surface. Thus the visible-light photocatalytic activity of this Ag-AgX system is somewhat restricted. Recently, Ag-AgX-based structures with Ag-AgX dispersed on a support have attracted a considerate attention. The Ag-AgX/support could increase the surface areas and facilitate interfacial charge transfer in the three-component systems, leading to remarkably enhanced photocatalytic activities as compared to that of Ag-AgX (Hou et al., 2011; Zhang et al., 2011).

Ag-AgX-based composites applied for photocatalytic destruction of *Escherichia coli* under visible light irradiation have been reported (Elahifard et al., 2007; Lan et al., 2007; Zhang et al., 2010). Hu's group prepared Ag/AgBr/TiO_2 by the deposition-precipitation method using P25 as support. The Ag/AgBr/TiO_2(P25) showed high bactericidal activity and stability for destruction of *E. coli* under visible light irradiation (Lan et al., 2007). However, such deposition method is difficult to achieve an effective interaction between the Ag-AgX and TiO_2 (P25) components which play a critical role in charge transfer within the composites. This deficiency inhibited its photocatalytic performance to some extent.

In this study, various Ag–AgBr/TiO_2 composites were synthesized by a facile one-pot method. Ag nanoparticles and AgBr coexisted in the derived composites and evenly dispersed in the matrix of TiO_2 particles. The effect of Ag–AgBr content on the Ag–AgBr/TiO_2 composites was investigated. Antibacterial activities against *E. coli* of the obtained photocatalysts in the dark and under visible light irradiation were systematically studied. The visible light-emitting diode (Vis-LED) was employed as the excitation light source. The Vis-LEDs have been widely used in outdoors and indoors lightings. They could be the good artificial light source for the photoreactors in the absence of solar light, because of their long lifetime, high energy efficiency, high spectral purity and flexible configuration (Wang and Lim, 2010). Ag^+ released from the prepared photocatalysts in the dark and under visible light irradiation was monitored and the stability of the Ag–AgBr/TiO_2-*x* composites was investigated. Moreover, the bacterial regrowth test in the dark was conducted. To study the action spectrum of the photocatalyst for *E. coli* inactivation, different LEDs that emit white, blue, green and yellow lights were used. To evaluate the durability of the Ag–AgBr/TiO_2 composite when used to treat surface water, the effects of various main inorganic ions present in the surface waters on the *E. coli* inactivation under visible light irradiation were also investigated.

2. Experimental

2.1. Material preparation and characterization

The Ag–AgBr/TiO_2 composites were synthesized by a sol–gel method followed by photoreduction. Firstly, 0.16 g of $AgNO_3$ (≥98%, Merck) and 2 mL of ammonia (25 wt %, Merck) were dissolved in ethanol (45 mL) to obtain solution A. The ethanol solution B (45 mL) containing 0.91 g of cetyltrimethylammonium bromide (CTAB, ≥98%, Merck) and certain amount of titanium isopropoxide (TTIP, ≥98%, Merck) with the atomic ratio of Ti/Ag = 5, 10, 15 was also prepared. The mixture of these two solutions was stirred continuously for 3 h at room temperature. The resulting gel was then dried at 70 °C overnight and calcined at 450 °C for 2 h. Subsequently, the obtained yellow powder of AgBr/TiO_2 was dispersed into deionized (DI) water under vigorous stirring and white LED irradiation for 2 h. Finally, the product was centrifuged and thoroughly rinsed with DI water, and then dried at 70 °C. The as-prepared photocatalysts were denoted as Ag–AgBr/TiO_2-*x* ($x = 5, 10, 15$), where *x* refers to the stoichiometric atomic ratio of Ti/Ag. As reference, Ag/TiO_2-10 was synthesized following this procedure without introducing CTAB. Pure TiO_2 was also synthesized via the similar sol–gel route. Ag–AgBr/P25-10 was prepared by the deposition-precipitation method. 1 g of P25 was added to 80 mL of ethanol. After the suspension was sonicated for 30 min, 1.2 g of CTAB was added. The mixture was then stirred for 30 min until CTAB was completely dissolved. Solution of $AgNO_3$ (0.21 g) and ammonia (25 wt %, 2 mL) in ethanol was subsequently added into the mixture and stirred for 3 h. The subsequent procedure was similar to preparation of above-mentioned Ag–AgBr/TiO_2-x.

X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) in a 2θ range of 5–80°. Field emission scanning electronic microscope (FESEM, JEOL JSM-6340F) and transmission electron microscope (TEM, JEOL JEM-2010) operated at