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Ag–AgBr/TiO_2/RGO nanocomposite: Synthesis, characterization, photocatalytic activity and aggregation evaluation

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ABSTRACT

Ag–AgBr/TiO_2 supported on reduced graphene oxide (Ag–AgBr/TiO_2/RGO) with different mass ratios of grapheme oxide (GO) to TiO_2 were synthesized via a facile solvothermal-photo reduction method. Compared to the single-, two- and three-component nanocomposites, the four-component nanocomposite, Ag–AgBr/TiO_2/RGO-1 with mass ratio of GO to TiO_2 at 1%, exhibited a much higher photocatalytic activity for the degradation of penicillin G (PG) under white light-emitting diode (LED-W) irradiation. The PG degradation efficiency increased with the increase of mass ratio of GO to TiO_2 from 0.2% to 1%, then it decreased with the increase of mass ratio of GO to TiO_2 from 1% to 5%. The zeta potentials of RGO-nanocomposites became more negative with the presence of humic acid (HA) due to the negatively charged HA adsorption, resulting in the shift of points of zero charge to lower values of pH. The aggregations of nanocomposites were more significant due to the bridging effect of HA. Furthermore, the aggregated particle sizes were larger for RGO-nanocomposites compared to other nanoparticles, due to the bindings of the carboxylic and phenolic functional groups in HA with the oxygen-containing functional groups in the RGO-nanocomposites. The microfiltration (MF) membrane was effective for the nanocomposites separation. In the continuous flow through submerged membrane photoreactor (sMPR) system, backwashing operation could efficiently reduce membrane fouling and recover TiO_2, and thus indirectly facilitate the PG removal.

Introduction

TiO_2 has been introduced as one of the most promising and suitable photocatalysts for degradation of organic pollutants. TiO_2-assisted heterogeneous photocatalysis has become a potentially cost-effective and environmentally-sustainable water and wastewater treatment alternative (Fox and Dulay, 1993; Klavarioti et al., 2009). However, the rapid recombination rate of photo-generated electron-hole pairs has greatly hampered the practical application of TiO_2. Recently, TiO_2-graphene and/or TiO_2-reduced graphene oxide (RGO) composites have received increasing attention (Bai and Shen, 2012; Machado and Serp, 2012). Since graphene, a single layer of sp^2-bonded carbon atoms compacted into a two dimensional (2D) planar honeycomb lattice, has many exceptional properties (*i.e.* high theoretical specific surface area, superior mechanical and chemical stabilities, high thermal and electronic conductivities, *etc.*), (Geim, 2009), it is expected that TiO_2-graphene or TiO_2-RGO composites

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could exhibit high charge separation efficiency, leading to high photocatalytic activity. It is accepted that the robust bonding between TiO_2 and the graphene sheet is essential for the effective charge transfer and separation during photocatalysis. Zhang et al. (2009) and Fan et al. (2011) prepared composites with P25 nanoparticles supported on graphene or RGO via hydrothermal, UV-assisted photocatalytic reduction, and hydrazine reduction method. However, it is found that P25 nanoparticles were difficult to be anchored onto the graphene sheets evenly due to their aggregation property. Thereafter, the in-situ growth of TiO_2 on graphene sheets is an important approach to obtain the robust bonding between TiO_2 and the graphene sheet.

It has been reported that plasmonic Ag–AgBr composites could exhibit high visible-light photocatalytic activity (Kuai et al., 2010; Wang et al., 2010). However, their visible-light photocatalytic activities could be restricted to some extent due to their micrometer-large particle sizes, which could induce the low surface areas and the high recombination rate of the photo-generated charge carriers. In order to efficiently harness solar energy for photocatalysis, Ag–AgBr/TiO_2 composites have attracted great attention in recent years (Hou et al., 2012; Hu et al., 2006; Tian et al., 2012; Wang et al., 2012). The nanojunctions between Ag–AgBr and TiO_2 could efficiently promote the separation of photoexcited electron-hole pairs. However, it is difficult to achieve the effectively hetero structured multi-semiconductor system due to the serious aggregation associated with the Ag–AgBr deposition onto P254 (Hu et al., 2006). To overcome this problem, Ag–AgBr could be controlled to deposit onto thorny anatase TiO_2 tubes (Tian et al., 2012). Nevertheless, it is generally complex and time-consuming. In addition, Ag/TiO_2 has also attracted increasing attention in the field of visible-light photocatalysis due to the surface plasm on resonance (SPR) effect of Ag nanoparticles, during which visible light incident upon the surface of Ag nanoparticles can induce collective oscillations of the conduction electrons with a resonant frequency (Moskovits, 2011; Rycenga et al., 2011; Vasilaki et al., 2015; Zhang et al., 2014a, 2015).

Great attention has been paid to the investigation of the nanoparticles aggregation (Godinez and Darnault, 2011). It is critical to predict their transport and mobility in the aqueous environment, and thus their extent of threat to the environment and public health. In this context, one of the key challenges for applying the TiO_2 suspension system is that the TiO_2 particles have to be separated from the product water. In recent years, hybrid membrane photoreactor (MPR) systems coupling photocatalysis and membrane process have attracted attentions for the TiO_2 particles separation (Lim et al., 2011; Molinari et al., 2010; Mozia, 2010) Compared to nanofiltration (NF), microfiltration (MF) and ultrafiltration (UF) are low pressure membrane processes widely used for colloid removal during water treatment, with the former being more cost-effective due to its higher membrane permeability and lower energy consumption. The application of visible-light source has the potential to alleviate the inherent problem associated with polymeric membrane deterioration when exposure to UV (Chin et al., 2006; Molinari et al., 2002) in the combined MPR system with the membrane module incorporated into the photoreactor. TiO_2 deposition on the membrane surface and/or inside its pores (Choo et al., 2008; Doll and Frimmel, 2005) would induce membrane fouling along with the loss of TiO_2 particles from the photoreactor for photoactivation, and thus lower the photocatalytic degradation efficiency of pollutants. Therefore, efforts should be made to prevent TiO_2 deposition, such as backwashing, air bubbling, membrane module vibration, and/or intermittent membrane cleaning, *etc.*

The main objective of this study was to synthesize a series of photocatalytic nanocomposites, Ag–AgBr/TiO_2 supported on reduced graphene oxide (Ag–AgBr/TiO_2/RGO) with different mass ratios of GO to TiO_2. They were characterized using X-ray diffraction (XRD), N_2 adsorption–desorption isotherm, Raman, thermo gravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), diffuse reflectance spectra (DRS) and photoluminescence (PL). Their photocatalytic activities were evaluated for the degradation of penicillin G (PG) under white light-emitting diode (LED-W) irradiations. The nanocomposite aggregations as a function of pH were investigated with and without the presence of humic acid (HA). A novel submerged membrane photoreactor (sMPR) system comprising a Vis-LED photoreactor and a submerged hollow fiber MF membrane module was developed. The performances of the sMPR system operated in the continuous flow-through mode with and without backwashing were investigated with regard to the PG degradation, TiO_2 separation and TMP change.

1. Experimental

1.1. Chemicals and materials

Millipore Co. MilliQ (MQ) water with resistivity of 18.2 MΩ cm was used throughout the study unless otherwise stated. All chemicals were used as received without further purification. Natural graphite (SP1) was purchased from Bay Carbon Company (USA). Sodium nitrate ($NaNO_3$, 99%), potassium permanganate ($KMnO_4$, 99%), sulfuric acid (H_2SO_4, 98%), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl, 37%), barium chloride ($BaCl_2$, 99%), potassium dihydrogen phosphate (KH_2PO_4, 98%), titanium butoxide ($Ti(OC_4H_9)_4$, 97%) and HA were procured from Aldrich. Absolute ethanol (99.9%), cetyltrimethyl ammonium bromide (CTAB, ≥98%), silver nitrate ($AgNO_3$, ≥98%), ammonia (25 wt.%), methanol (high performance liquid chromatography, HPLC grade), and penicillin G (PG) were procured from Merck.

1.2. Synthesis of nanocomposites

Detailed experimental procedure for synthesis of GO, and characteristics of the as-synthesized GO are shown in Electronic Supplementary Information. Ag–AgBr/TiO_2/RGOnanocomposites weresynthesizedusingafacilesolvothermal-photoreduction method (Wang et al., 2013b). Typically, an appropriate amount of GO was dissolved in 45 mL of absolute ethanol followed by ultra sonication for 2 hr. Then, 0.91 g of CTAB and 3.4 mL of titanium butoxide were added to obtain solution A. 0.16 g of $AgNO_3$ and 2.0 mL of ammonia were added to another 45 mL

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