



Ag/TiO₂/freeze-dried graphene nanocomposite as a high performance photocatalyst under visible light irradiation

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ABSTRACT

Ag/TiO₂/freeze-dried graphene nanocomposites have been prepared via a facile one-step solvothermal method for the photocatalytic degradation of RhB under visible light irradiation. During the solvothermal process, reduction of graphene oxide and loading of Ag/TiO₂ nanoparticles on graphene sheets were achieved. Investigation of chemical state of products showed that covering of Ag/TiO₂ surface with higher weight ratio of graphene resulting in that Ag metals in Ag/TiO₂ were oxidized to Ag₂O in nanocomposite structure after solvothermal process. Degree of photocatalytic activity enhancement strongly depends on the coverage of Ag/TiO₂ surface by porous graphene. The sample of 1 wt% porous graphene hybridized Ag/TiO₂ showed the highest photocatalytic activity, which is related to high migration efficiency of photo-induced of electrons and reduction of electron–hole recombination rate due to high electrical conductivity of graphene. Expanding of absorption to visible light region was ascribed to surface plasmon resonance effect of Ag metals and presence of graphene. Investigation of photocatalytic performance of formic acid as a dye-less organic pollutant showed that dye sensitization effect of RhB molecules during evaluation of photocatalytic performance was negligible.

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1. Introduction

Dye wastewater is mainly from textile, leather, paper, rubber, plastic, cosmetics, pharmaceutical, and food industries. Because of the high toxicity of most synthetic dyes, if they are not treated properly before discharging into the natural water they can cause severe environmental pollution and human health hazards. Current treatment methods for dye wastewater include physically adsorption on various sorbents, chemical decomposition by oxidants, microbiological decoloration, and so on [1,2,29]. Recently, the photocatalytic degradation of organic pollutants has attracted increasing attention during the past decades. Because of its non-toxicity, photo and chemical corrosion resistance, availability, high chemical stability, and low production cost, TiO₂ semiconductor is the most attractive photocatalyst in the field of organic pollutant photodegradation [3]. However, TiO₂ has relatively high band-gap energy (3.2 eV for anatase and 3 eV for the rutile structure), and

therefore absorbs radiation only in UV region (~5% of solar light) [4]. Therefore, reducing the band-gap energy of TiO₂ for visible light absorption (~43% of solar light) can significantly increase the photocatalytic activity of TiO₂ [5]. Moreover, separation of the photo-induced electron–hole pairs and their transferring to the surface active sites also play an important role in photocatalytic activity [6]. Thus inhibition of the fast electron–hole recombination and expansion of the TiO₂ light absorption to the visible region are the key factors for improving the photocatalytic efficiency of TiO₂ [7]. To enhance the visible light absorption and reducing the fast electron–hole recombination of semiconductor photocatalysts, there are some approaches including using of semiconductors with suitable energy band-gap instead of TiO₂ such as WO₃ [8], doping base semiconductor with metallic particles or nonmetallic elements [9–11], and developing composite materials.

Owning to their individual benefits including excellent optical, catalytic and antibacterial properties, incorporating of the noble metals in TiO₂ has attracted tremendous research interests [12–14]. It has been shown that incorporating of Ag in TiO₂ structure improves the photocatalytic efficiency of TiO₂ based photocatalyst due to the surface plasmon resonance (SPR) effects

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of the Ag nanoparticles that can red shift the light absorption in to the visible light region [15]. Moreover, because of their high electric conductance, the Ag nanoparticles can also reduce the recombination of photo-generated electron hole pairs by transferring of the electrons to the surface of Ag loaded TiO₂ [16,19–21]. It should be noted that in high loading contents of Ag, the Ag itself can act as a recombination center and thereby enhance the recombination rate of photo-generated electron hole pairs [50].

Graphene is a new class of carbon materials with single atom thickness which has received much attention because of its high values in surface area (theoretical value 2600 m²/g), electron mobility (~15,000 m²/(V·S) at room temperature), thermal conductivity (~5000 W/(m·K)), and mechanical strength [18]. This unique properties of graphene are excellent to form hybrid structures with materials such as semiconductors, metals, and polymers for obtaining improved performance in many application such as energy, water treatment, catalysis, and electronic fields [17].

Due to its high electron mobility and extended π -electron conjugation, graphene can reduce the recombination of electron-hole pairs [22]. Graphene in Graphene-based photocatalysts can also inhibit from the aggregation of nanoparticles which anchored on graphene sheets, and therefore can enhance the surface area and reactive sites in the photocatalytic degradation process [23]. In summary, the photocatalytic properties of graphene-based photocatalysts are influenced by several factors, such as the electrical properties of graphene sheets, the interfacial contact and charge transfer between graphene and nanoparticles [24,25].

The porous structure of carbon materials enlarges the surface area, and thereby enhancing the capacity of the materials. For instance, porous graphene exhibits properties distinct from those of graphene [26]. In this work, the effect of synergetic addition of Ag nanoparticle and porous graphene in TiO₂ structure has been investigated. Ag nanoparticles were loaded on the surface of TiO₂ (P25) nanoparticles by using formic acid as a sacrificial component for photocatalytic reduction of Ag⁺ ions under UV irradiation light. Then, Ag/TiO₂/freeze-dried graphene nanocomposites were prepared via solvothermal method using of porous graphene oxide and Ag/TiO₂ as precursors. The high effective surface area of the porous graphene in the nanocomposite structure reduces the photo-induced electron-hole pair recombination rates and increases the photocatalytic activity.

2. Experimental

2.1. Materials

Titanium dioxide nanoparticles with 70% anatase and 30% rutile structure (P25) was purchased and used as received from Degussa, Germany. Graphite powder, KMnO₄, K₂S₂O₈, P₂O₅, formic acid and silver nitrate were purchased from Merck.

2.2. Synthesis of Ag/TiO₂

Ag/TiO₂ (AT) was prepared using TiO₂ nanoparticles (P25), AgNO₃ (source of silver ions), and formic acid (as a sacrificial component) as precursors by photocatalytic reduction process in acidic media. For preparing AT nanoparticles with 1 wt% silver content, we mixed silver-formic acid complex solution and TiO₂ suspension; silver-formic acid complex solution was prepared in such a way that 0.02 g of AgNO₃ was dissolved in 25 mL deionized water and then desired amount of 1 M formic acid solution was added to reach a molar ratio of 10:1 formic acid to silver nitrate. For preparing TiO₂ suspension, 1 g of TiO₂ nanoparticles was dispersed in 200 mL deionized water and pH was adjusted at 2 using 1 M nitric acid. After mixing of the as-prepared silver-formic acid complex

solution and TiO₂ suspension under dark condition and magnetically stirring for 2 h (to adsorption of the silver-formic acid complex on the TiO₂ surface), the mixture was subjected to UV light irradiation for reducing Ag⁺ to Ag nanoparticles. In this process, formic acid acts as a reducing agent for reduction of silver cations.

2.3. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized from natural graphite powder by modified Hummers method in two steps including pre-oxidizing and oxidizing process. Graphite powder (2 g) was put into a mixture of 12 mL of concentrated H₂SO₄, 2.5 g of K₂S₂O₈, and 2.5 g of P₂O₅. The solution was heated to 80 °C in an oil-bath and kept stirring for 24 h. Then, the above mixture which was diluted with 500 mL of deionized (DI) water, was filtered, and washed until the pH of rinse water became natural. The collected precipitates were dried under ambient condition overnight. This pre-oxidized graphite was then subjected to oxidation process described as follows. In a typical procedure, pre-oxidized graphite powder was added to a mixture of 120 mL of concentrated H₂SO₄ and 30 mL HNO₃ under vigorous stirring in an ice water bath. Then, 15 g of KMnO₄ was added while keeping the temperature below 20 °C. The mixture was stirred at room temperature for 96 h, and then diluted with 1 L of DI water. Then 20 mL of 30% H₂O₂ was added to end the reaction with turning the color of the mixture to a brilliant yellow. Subsequently, the mixture was filtered and washed with 1:10 HCl aqueous solution and DI water. The filter cake was dispersed in water and centrifuged with 1000 rpm for 2 min. The supernatant then underwent two more high-speed centrifugation steps at 8000 rpm for 15 min to remove small GO pieces and water-soluble byproducts. The final sediments were dried in two different ways including drying in oven at 60 °C and under freeze-drying condition. The porous GO was obtained by freeze-drying of the exfoliated GO (~5 mg/mL) in deionized water in three step manner. In first step, the materials were placed in a freeze-drying flask which rotated and cooled by dry ice. In second step (the primary drying process), which was conducted at a temperature of between –80 °C and –50 °C at pressure of 10^{–3} torr for 24 h, about 95% of the water in the material sublimated. In third step (the secondary drying process) the temperature was raised to 0 °C to break any physicochemical interactions that were formed between the water molecules and the frozen materials in this step the unfrozen water molecules were removed. The obtained products were denoted as freeze-dried GO (FD-GO) [27].

2.4. Synthesis of Ag/TiO₂/ graphene nanocomposites

Ag/TiO₂/freeze-dried graphene (AT-FDG) nanocomposites were synthesized using as-prepared AT and FD-GO powders by solvothermal method. At first, for preparing AT-FDG nanocomposites with 0.5, 1, 2, 3, 4, and 5 wt% graphene contents, desired amount of FD-GO was added into 60 mL deionized water and 30 mL anhydrous ethanol and ultrasonically dispersed for 30 min. Then, to this suspension, 0.5 g AT was added and magnetically stirred for 2 h to obtain homogeneous suspension. After this step, the mixture was transferred into a 100 mL Teflon-lined tightly sealed stainless steel autoclave. The autoclave was then heated to 120 °C and kept there for 24 h. After the complete solvothermal treatment, the resulted product was centrifuged, washed and finally dried in air at 60 °C.

2.5. Catalyst characterization

XRD experiment was carried out by a STOE Stadi P X-ray diffractometer using Cu K α irradiation ($\lambda = 1.54018 \text{ \AA}$). Diffuse reflectance UV–vis spectra were recorded in the reflectance mode

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