Research Paper

Facile *in-situ* design strategy to disperse TiO$_2$ nanoparticles on graphene for the enhanced photocatalytic degradation of rhodamine 6G

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A B S T R A C T

Photogenerated electron/hole recombination greatly limits the catalytic efficiency of TiO$_2$, and recently modification with graphene substance has been regarded as an effective way to enhance the photocatalytic performance of TiO$_2$. When referring to the fabrication of graphene based materials, the reduction process of graphene oxide has been demonstrated to be a key step. Therefore, it is highly required to develop an efficient and simple route for the GO reduction and the formation of TiO$_2$@rGO composites. In this study, we have demonstrated a facile and environmentally friendly strategy for *in-situ* preparation of the TiO$_2$@rGO "dyade" hybrid and systematically investigated the photodegradation efficiency of the resultant composite by utilizing rhodamine 6G as the model pollutant. The obtained TiO$_2$@rGO has a significant enhancement in photo energy adsorption leading to the effective photocatalytic degradation reactions. The results indicated that the best performance was conducted by the TiO$_2$@rGO (10 wt%, 120 min's irradiation), which exhibited more than triple the higher photodegradation rate than commercial TiO$_2$ (P25) nanoparticles mainly due to two aspects, the rapid separation of h^+/e^- and to improve adsorption. This work provides new insight into the synthesis of TiO$_2$@rGO composites as a high performance photocatalyst for the degradation of organic contaminant.

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1. Introduction

Recently, the photocatalytic process for dye containing wastewater degradation has attracted considerable attention. Among a great number of semiconductors, TiO$_2$ has been identified as one of the most promising photocatalysts which expects to play an important role in environmental remediation [1,2], solar energy [3] and other fields [4,5], due to its nontoxicity, low cost, abundant resources and high catalytic efficiency [6]. However, fast h^+/e^- recombination greatly limits the practical application of TiO$_2$ [7], and various attempts have been applied to improve the catalytic

efficiency of TiO$_2$ in recent decades. For example, Zhang et al. [8] reported that boron-doped TiO$_2$ with a tunable anatase/rutile ratio, obtained through a simple one-step calcination method using titanium and boron mixture as the precursor, showed more than 4 times higher reaction rate in atrazine degradation than the bare TiO$_2$ nanoparticles. Wang et al. [9] demonstrated that the degradation rate of rhodamine B could be improved to 7.2 times by combining with the g-C$_3$N$_4$ via a facile calcination method using tetrabutyl titanate and melamine as the feedstocks. Recently, modifying TiO$_2$ with carbonaceous substances, such as carbon nanotubes (CNTs) and graphene which have large specific surface area and high carrier mobility, is regarded as an effective strategy to further enhance the photocatalytic performance of TiO$_2$ [10–12].

Among various carbonaceous materials, graphene, which was discovered as a one-atom-thick sheet composed of sp^2-hybridized carbon atoms in a hexagonal lattice, is rapidly gaining interest from a wide spectrum of research fields. This is mainly due to its extraordinary physicochemical properties [13,14], such as remarkable

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mechanical strength, high thermal conductivity ($5000\,Wm^{-1}\,K^{-1}$), outstanding electron mobility ($250,000\,cm^2\,V^{-1}\,s^{-1}$) and specific surface area ($2630\,m^2\,g^{-1}$).

To combine the advantages of both TiO_2 and graphene, the resultant composites could not only hinder the recombination of h^+/e^- by transferring the photoexcited electron to graphene surface, but also further enhance the surface area of TiO_2 for better adsorptive properties [15]. Therefore, numerous efforts have been paid to integrate TiO_2 with graphene for the photodegradation efficiency improvement. Recently, various methods [16–18], such as physical mixing, hydrothermal, electrochemical deposition, sol-gel and self-assemble approaches, have been applied to form TiO_2/graphene nanocomposites. For example, Zhang et al. [19] reported that a physical mixing of P25 and graphene composite was obtained through a hydrothermal method, which shows enhanced adsorption and photocatalytic degradation of methylene blue imitated wastewater. Liang et al. [20] demonstrated that TiO_2/graphene composites produced by hydrolysis and hydrothermal treatments showed 110% improved photodegradation efficiency over pure TiO_2. However, these traditional strategies have their inevitable shortcomings, such as involvement of toxic reductive agents (eg. N_2H_4, $NaBH_4$), requirement of high pressure/temperature (>500 °C), additives of acid/alkali, time- and energy-consuming. Therefore, their practical applications have been limited.

In 2008, Kamat et al. [21] demonstrated a facile and chemical free strategy to effectively reduce graphene oxide (GO) sheets through an on-demand UV-assisted methodology. Furthermore, during the reduction process, the photoactive TiO_2/graphene composites could be simultaneously synthesized either. However, the practical application of the as-prepared TiO_2@rGO composites has not been systematically studied and the preparation conditions need further optimization to enhance its catalytic performance.

In this paper, TiO_2@rGO composites have been successfully synthesized through a facile in-situ UV-assisted photoreduction method. Then, by regulating the GO dosage and irradiation duration, the relationship between the reduction degree of GO and the photocatalytic efficiency of the reluctant complex has been investigated using rhodamine 6G (Rh 6G) as the target contaminant. Furthermore, for practical application, the performance of the resultant composites in simulated dye wastewaters with different pH value have been investigated. The results illustrate that the obtained TiO_2@rGO composite is able to absorb a high amount of photo energy and drive effectively photodegradation reactions. This work may provide a facile, promising, and environmentally friendly strategy for the large-scale preparation of graphene-based composite materials.

2. Experimental

2.1. Materials

Sulfuric acid (H_2SO_4, 98 wt%), ammonium hydroxide ($NH_3 \cdot H_2O$), potassium hypermanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30 wt%), hydrochloric acid (HCl, 37 wt%), absolute ethanol (C_2H_6O) were all of analytical grade. All of the chemicals above were obtained from Chengdu Kelong Chemical Reagent Company (Sichuan, China) and used as received without further purification. Graphite powder (purity > 99.95%) was purchased from Aladdin Industrial Corporation (Shanghai, China). TiO_2 (P25) nanoparticles powder was supplied by Degussa Company (Germany). Rhodamine 6G was obtained from Sigma-Aldrich. Deionized (DI) water used for all experiments was generated from Milli-Q water purification system (Ulupure Corporation).

2.2. Synthesis of graphene oxide

The graphene oxide was synthesized from natural graphite powder (99.95%) by the modified Hummers method [22]. In a typical synthesis, the producing procedure was as followed: (1) the graphite powder (2.0 g) and sodium nitrate (1.2 g) were put into a round-bottom flask. Then, 60 mL concentrated H_2SO_4 was added dropwise. The resultant dark blue mixture was further treated with ultrasonic, and then was placed into an ice bath apparatus and allowed for intensive mixing using magnetic stirrer. (2) Subsequently, potassium hypermanganate (8.8 g) was slowly added and the mixture was stirred for 12 h. During the processing, an ice bath should be utilized to avoid the temperature exceeding 20 °C. (3) Then, 72 mL distilled water was carefully added, and the temperature should be maintained under 20 °C until the instillment was terminated. The mixture was continuously stirred at 50 °C for another 12 h. (4) After that, the reaction temperature was regulated to 35 °C and stirred for another 12 h untill the color of the mixture was changed from yellowish-brown colour to bright yellow colour. Then, 22 mL H_2O_2 was slowly added and the resultant mixture was stirred for 3 h, resulting in plenty of bubble formation. (5) Finally, the mixture was washed by 5% HCl solution and ethanol by turns until the pH value of supernate became neutral, and the initial product was dispersed in absolute alcohol by sonication.

2.3. Synthesis of TiO_2@rGO composite

The synthesis of TiO_2@rGO nanocomposite was conducted simultaneously with the photoreduction of GO nanosheets in a simple GO/TiO_2 ethanol system. Commercial TiO_2 nanoparticles (P25), a well-known commercial photocatalyst with high catalytic activity and good dispersion, was pretreated in furnace at 500 °C for 2 h to remove the adsorbed substances and keep a clean surface.

In a typical synthesis, the producing procedure was as followed: (1) firstly, the prepared GO solution was diluted by absolute ethanol and the concentration would be regulated at 0.5 mg/ml. (2) Then, 0.7 g TiO_2 powder was added in 70 mL above GO/ethanol solution under continuous stirring at room temperature to obtain a milky suspension. (3) After stirring, the mixture was treated by ultrasound for 30 min to form a homogeneous flaxen suspension solution and to make GO sufficiently contact with TiO_2 nanoparticles. (4) Then, the resultant mixing solution was bubbled with nitrogen to remove the dissolved oxygen and further disperse the TiO_2 nanoparticles in solution. (5) After bubbling for 30 min, the suspension was irradiated under UV condition. With increasing irradiation time, the color of the suspension gradually changed from flaxen to black, suggesting the effective reduction of GO to rGO. (6) Finally, the obtained mixture was dried at 60 °C for 12 h to obtain the TiO_2@rGO nanocomposites.

The weight ratio of GO to TiO_2 would be regulated at 0, 0.5, 1, 2, 5, 10 wt%. The irradiation duration was controlled to 5, 15, 30, 60, 120 min, respectively. A 300W mercury lamp equipped with a cutoff filter (providing UV light with $\lambda \leq 400$ nm) was used as an excitation light source.

2.4. Characterizations

Transmission electron microscopy (TEM) observations were performed on a JEM-2100 TEM system (JEOL, Tokyo Japan) at an acceleration voltage of 200 kV. The composition and crystallinity of the samples were characterized by X-ray powder diffraction patterns (XRD) on a DX-2700 X-Ray diffractometer using Cu-Kα radiation ($\lambda = 1.540562$ Å, 40 kV, 30 mA) as the X-ray source at a scanning rate of 3°/min in the range of 3° to 80°. XPS measurements were performed using a K-Alpha Probe (Thermo Scientific, USA) with a monochromated Al-Kα radiation (300 W). Fourier Trans-