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Preparation, characterization and photocatalytic application of TiO_2–graphene photocatalyst under visible light irradiation

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Abstract

A series of TiO_2–graphene photocatalysts (TGPPC) were prepared from titanium dioxide and graphene oxide (GO) by a simple hydrothermal method. The structure, surface morphology and chemical composition were characterized by Fourier-transform infrared spectroscopy (FT-IR), ultraviolet–visible absorption spectra spectrum (UV–vis), UV–vis diffuse reflectance spectroscopy (DRS), X-ray diffractometer (XRD), Raman, scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDS), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and X-ray photoelectron spectroscopy (XPS). XPS results confirm the interaction of TiO_2 with graphene. The TGPPC was applied to the degradation of methylene blue (MB) under visible light irradiation; and the results indicate that TGPPC exhibits excellent photocatalytic activities for MB. The degradation efficiency of MB could be obtained 98.8% at a GO content of 20% and a time of 100 min. Photocatalytic degradation behavior of MB was investigated by the pseudo-first-order kinetics; and the photocatalytic degradation mechanism was proposed. The obtained results indicate that the prepared TGPPC has a potential application for the industrial effluents treatment containing MB.

Keywords: Graphene; Photocatalytic degradation; Methylene blue; Visible light irradiation

1. Introduction

Recently years, synthetic organic dyes are mostly used in the textile, plastics, paper, leather and cosmetic industry, and most of them are non-biodegradable and toxic [1]. During the processing operation or manufacturing, large amount of dyes are lost into the effluents and hence causes serious threat to the environment [2]. In addition, if these dyes are released into lakes or rivers without prior treatment, the colored wastewater containing dyes and resistance to conventional physical, chemical and biological wastewater treatment processes, can block the sunlight and oxygen penetration, which is harmful to the surrounding ecosystem, especially the aquatic creatures and human life. Moreover, the wastewater generated from the textile industry is generally high in both biochemical oxygen demand (BOD) and chemical oxygen demand (COD) because it comprises spent textile dyes, suspended solids, mineral oils, electrolytes, surfactants, etc. [3,4]. Hence, their removal from industrial wastewater is highly desirable below environmentally accepted levels before safe disposal to public health.

Conventional techniques of removing dyestuffs from wastewater such as coagulating sedimentation, filtration and adsorption, have the advantage of transferring the dyes from one medium to another, but the disadvantage of not degrading or mineralizing them [2]. Therefore, some approaches namely, biodegradation and photocatalytic degradation, etc., have been proposed and applied for dyes treatment. Among degradation techniques, photocatalytic degradation of organic pollutants has received much attention for pollutants removal and environmental purification [5]. Photocatalytic degradation is an economical and advanced method which can completely degrade and convert organic dyes to harmless chemicals [6].

During the past few decades, the use of metal oxide semiconductor materials, such as TiO_2 and ZnO, as photocatalysts has been extensively explored to degrade recalcitrant

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organic substances [6,7]. Although TiO_2 is a popular and universally recognized catalyst and the most frequently employed photocatalysts, many researchers were motivated to explore the properties of modified TiO_2 in photocatalytic reactions. However, due to the large band gap such as band gap of TiO_2 (anatase: 3.2 eV; rutile: 3.0 eV), many semiconductors commonly used can generate electron–hole pairs only when illuminated by ultraviolet light, which is a limit to the photo-electronic transition efficiency of solar photocatalysis because the portion of UV-light in the solar spectrum is only about 3–5% of total sunlight [8,9]. Therefore, the development of visible-light-driven photocatalysts is necessary to make adequate use of solar energy in decontaminating water.

Graphene, a sp^2-bonded carbon sheet with a thickness of single atom, has recently received tremendous attention as TiO_2 in the area of photocatalysts for its high electrical conductivity [10]. In TiO_2–graphene hybrids, graphene can slow the electron–hole pairs, increasing charge transfer rate of electrons and surface-adsorbed amount of chemical molecules through π–π interactions [11,12]. Moreover, the formation of Ti–O–C bonds can expand the light absorption to longer wavelengths [13]. Thus the integration of nanosized anatase TiO_2 with two-dimensional graphene nanosheets offers a great opportunity to design and synthesize TiO_2–graphene hybrid materials with improved visible-light photocatalytic activity.

In this work, we report the preparation of TiO_2–graphene by hydrothermal method, which is used as an effective photocatalyst for photocatalytic degradation of methylene blue (MB) under visible light irradiation. A fast decomposition of the MB dye was observed with a degradation efficiency of 98.8% within 100 min.

2. Experimental

2.1. Materials

Graphite powder (99 wt%), potassium permanganate ($KMnO_4$, 98 wt%), sulfuric acid (H_2SO_4, 98 wt%), hydrogen peroxide (H_2O_2, 30 wt%), sodium nitrate ($NaNO_3$, 99 wt%), methylene blue (MB) and titanium dioxide (TiO_2, 98 wt%) were purchased from Shanghai Chemical Reagent Co. Ltd, in Shanghai, China. All reagents used in this research were superior to chemically pure and used without further purification.

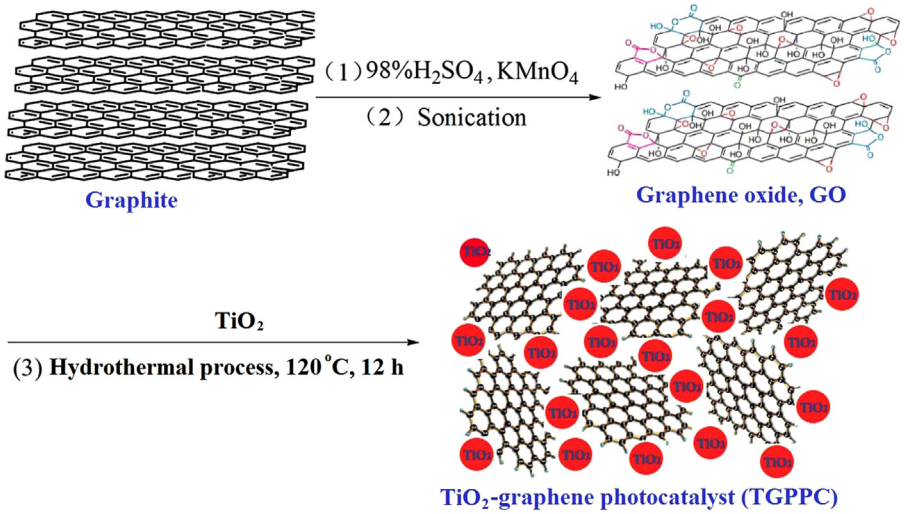
2.2. Preparation of graphene oxide (GO)

GO was prepared from natural graphite powder by a modified Hummers method. In a typical procedure, 23 mL of concentrated H_2SO_4 was added into the 250 mL flask which was cooled to 0 °C in an ice bath, and then 1 g of graphite and 1 g of $NaNO_3$ were added slowly into the flask respectively. Under vigorous stirring, 3 g of $KMnO_4$ was added into the reaction suspension and kept on an ice bath for 1 h. Later, the ice bath was removed and the reaction mixture was heated to 35 °C for 3 h for gas releasing under continuous stirring. Thereafter, 46 mL of deionized water was added slowly and the reaction temperature was raised to 98 °C for a certain time (1 h, 6 h and 12 h, respectively). Then, the resultant bright-yellow suspension was terminated by addition of 140 mL deionized water, followed by 10 mL of hydrogen peroxide solution (H_2O_2, 30 wt%). For purification, the solid product was separated by centrifugation and washed with 5% hydrogen chloride solution, and deionized water until pH = 7. Finally, the powder was vacuum-dried at 60 °C for 12 h.

In this work, the graphene oxide products with different oxidation time of 1 h, 6 h and 12 h [14] were expressed as GO-1, GO-6, and GO-12, respectively.

2.3. Preparation of TiO_2–graphene photocatalyst (TGPPC)

The TiO_2–graphene photocatalysts (TGPPC) with different mass ratios of GO were obtained via the hydrothermal method based on previous work with modifications [15]. First, 20 mg of GO-1 (or GO-6 or GO-12) was dispersed in a mixing solution of H_2O (80 mL) and ethanol (40 mL) by ultrasonic



Scheme 1. The synthetic route of TGPPC.