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## Enhanced adsorption and photodegradation of phenol in aqueous suspensions of titania/graphene oxide composite catalysts

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## ABSTRACT

This study uses a hydrothermal method to synthesize titania@graphene oxide (TGO) composite catalysts for the photodegradation of phenol under UV illumination in liquid phase. The graphene oxide (GO) sheets were derived from natural graphite powders using a modified Hummers' method. One efficient hydrothermal method reinforces the adhesion between GO sheets and titania nanoparticles (T), forming composite catalysts. The adsorption capacities of phenol on T, GO, and TGO composites were experimentally determined, and the order of adsorption efficiency was found to be TGO > GO > T. The photocatalytic performance on the composite catalysts was systematically evaluated by the pseudo first-order kinetic model. Experimental results reveal that the TGO composite exhibits the best photocatalytic activity, including apparent rate constant and equilibrium catalytic ability, among the tested samples. This enhanced performance may be attributed to the well-dispersed titania nanocatalysts that are attached to the GO sheets, which offer homogeneous active sites for phenol adsorption, followed by photodegradation. Accordingly, the robust design of TGO composite catalysts offers an effective route for the treatment of organic wastewater.

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### 1. Introduction

In recent years, due to massive industrial growth, a large quantity of non-biodegradable artificial organic compounds has been produced. The structure of these compounds is complicated and they not decomposed easily by microorganisms. Once released, they have a significant impact on the environment. Phenol and its derivatives are widely used in industry, often leading to the formation of stable chemical species. Over time, these stable pollutants are accumulated in the food chain and eventually enter the human body, risking public health by causing severe health issues, including cancer [1]. One effective way to convert these organic compounds into harmless species is heterogeneous photocatalysis at a low energy cost. In a typical photocatalytic reaction, photons that have a higher energy than the band gap energy of the catalyst

(such as TiO<sub>2</sub>, ZnO, CdS, and WO<sub>3</sub>) excite the valence electrons of the catalyst to produce electrons in the conduction band and holes in the valence band. The conduction electrons form superoxide anions ( $\bullet\text{O}_2^-$ ) when they come in contact with O<sub>2</sub>, and the holes produce OH $\bullet$  upon contact with moisture (H<sub>2</sub>O). Eventually, these strong radicals oxidize organic pollutants, turning them into CO<sub>2</sub> and H<sub>2</sub>O. The advantages of photocatalytic treatments are (i) no need of an additional oxidizing agent, leading to no secondary pollution as in the traditional methods; (ii) fast reaction time; and (iii) low operating costs [2–4].

Based on the relative position of the energy band gap and conduction band of the semiconductor, as well as the oxidation–reduction potential of water and hydrogen, semiconductor photocatalysts can be classified into four types: redox type, reduced type, oxidized type, and non-oxidized reducing type [5]. Redox photocatalysts, such as strontium titanate (SrTiO<sub>3</sub>), TiO<sub>2</sub>, and CdS, are commonly used because they possess strong oxidation and reduction capacities (enough to split water to produce hydrogen and oxygen). Among them, TiO<sub>2</sub> is the most widely studied semiconductor because of its low cost, excellent stability and high photocatalytic efficiency [6]. However, the photogenerated electrons and holes in TiO<sub>2</sub> have a tendency to recombine, limiting

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the photocatalytic efficiency [7]. One way to improve the catalyst efficiency is to prevent the recombination of electrons and holes by coupling TiO<sub>2</sub> to metal or other semiconductors, such as carbon nanomaterials [8]. Graphene, a two dimensional carbon material, has triggered great interest in the field of nanoscience due to its enormous surface area, electrical conductivity, flexibility and extraordinary mechanical strength [9–12]. Fundamentally, graphene sheets are single layers of carbon atoms in the sp<sup>2</sup> bonding configuration. This exceptional structure enables its application in a wide range of fields, such as nano-electronics, sensors, batteries, supercapacitors, hydrogen storage and nanocomposites [13–18]. These properties have prompted great interest in developing graphene-based TiO<sub>2</sub> photocatalysts that can be successfully applied in pollutant treatments, hydrogen production and other fields [19–23]. Accordingly, graphene–TiO<sub>2</sub> composites have lower band gap energy than plain TiO<sub>2</sub>, enabling the formation of electrons and holes with only visible light [22]. In addition, the recombination of electrons with holes is also minimized by the composite as the conduction electrons from TiO<sub>2</sub> move to the graphene surface [23–26]. Graphene oxide (GO) is structurally the same material as graphene apart from the presence of abundant functional oxygen groups (e.g., mainly hydroxyl and carboxyl groups), making it more reactive and hydrophilic in nature [18,26]. Therefore, GO has a great potential to form composites with TiO<sub>2</sub> particles. For example, Wang et al. reported the efficiency of a nano-TiO<sub>2</sub>/functionalized GO composite in the photocatalytic degradation of methylene blue [18]. However, the performance of a TiO<sub>2</sub> composite in phenolic wastewater has not yet been established.

In this study, we systematically analyze and report the performance of a titania@graphene oxide (TGO) composite photocatalyst prepared by the hydrothermal method for the decomposition of phenolic compounds using a pseudo-first order kinetic model. The present work reveals how the presence of GO sheets affects the photocatalytic activity of phenol compounds and how the design of a TGO composite catalyst improves the photodegradation and adsorption performance in liquid phase.

## 2. Materials and methods

### 2.1. Preparation of graphene oxide

Deionized water produced with the Milli-Q water purification system (Millipore Co.) was used to prepare all aqueous solutions. GO sheets were chemically exfoliated from carbon black (CB) by the modified Hummers' method [27]. Briefly, CB powders (5 g) were mixed with 1 M KMnO<sub>4</sub> and 120 ml of concentrated H<sub>2</sub>SO<sub>4</sub> in an ice bath. The slurry was stirred continuously for 2 h. Next, the solution mixture was slowly heated to 98 °C. Then, the slurry was neutralized by washing with distilled water. The resulting GO powders were then dried at 80 °C in a vacuum oven overnight. Prior to the deposition of GO sheets, GO powders were well-dispersed in water, forming a GO colloidal suspension.

### 2.2. Synthesis of TGO composite

The TGO composite was synthesized by the hydrothermal method. Briefly, GO powder (2.85 g) and titanium dioxide (0.15 g, Degussa P-25, ca. 70% anatase and 30% rutile) were mixed with 70 ml of ethanol. Then, the slurry was stirred for 2 h to obtain a homogeneous suspension. Afterwards, the solution was placed in a Teflonclave and kept at 160 °C for 8 h. The system was then cooled to room temperature, and the TGO powders were filtered out of the suspension and washed several times with an ethanol solution. Finally, the powders were dried at 80 °C in an oven overnight.

### 2.3. Material characterization

The crystalline structure of the photocatalyst powders were characterized by X-ray diffraction (XRD) spectroscopy using Cu-K $\alpha$  radiation ( $\lambda=0.15418$  nm) within  $2\theta$  ranging from 8 to 80°. The morphology of the photocatalyst powders were observed by field emission scanning electron microscopy (FE-SEM, JEOL JSM 7500F) with an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-1230 transmission electron microscope operated at 100 kV.

### 2.4. Adsorption and degradation analysis

Three materials (T, GO, and TGO samples) were tested for the photodegradation of phenol (Sigma–Aldrich, 98%, USA). The adsorption temperature was set at 35 °C. The initial pH of the solution was adjusted to be 7.50 by adding 0.1 M NaOH, which was reported to be suitable for the photodegradation of phenols over titania [1]. The photocatalytic reactor consisted of a cylindrical 1.0-l Pyrex-glass cell (10 cm I.D. and 10 cm height) [1]. A 100-W water-cooled, high-pressure mercury lamp (HL100CH-5, SEN Japan) was located in the center of the reactor within a 5-cm diameter double-walled cooling tube. The lamp and tube were immersed in the reactor vessel, and the light path was 80 mm. The amount of tested solution was 800 ml, with a phenol concentration of 100 and 500 mg/l. After adding 1 g of catalyst to the reactor, the solution was agitated with a magnetic stirrer at 120 rpm in darkness for 3 h, ensuring adsorption equilibrium. The UV lamp was then turned on to initiate the photocatalytic reaction at 35 °C. The whole system was maintained a constant voltage by a voltage stabilizer (input 140 V, output 110 V).

Liquid samples (1 ml at each time) were regularly collected at every 30-min interval. The sample was filtered through a 0.22  $\mu$ m syringe filter (Millipore) to remove any TiO<sub>2</sub> particles and the concentration of phenol was analyzed by HPLC (Jasco, Japan). The column was a Merck LiChroCART® 250-4.6 (250 mm length, 4.6 mm diameter), packed with Purospher® STAR RP-18 end-capped (5  $\mu$ m). A mixture of acetonitrile (50%, v/v) and deionized water was used as the mobile phase at 1.0 ml/min. An aliquot of the sample (10  $\mu$ l) was injected to HPLC using the auto-sampler (Jasco, Japan) for analysis at a wavelength of 280 nm. The data were fitted to Langmuir equilibrium and kinetic models to determine the maximal adsorption capacity and the apparent rate constant, respectively.

### 2.5. Liquid chromatography–mass spectrometry (LC–MS) analysis

The aromatic intermediates were identified using an ultra-performance liquid chromatography (UPLC) system coupled with time-of-flight mass spectrometry (TOF-MS) (Waters, USA). Chromatographic separation was performed on a C18 column (Phenomenex; 5  $\mu$ m, 4.6 mm  $\times$  250 mm). Column temperature was maintained at 30 °C. The mobile phase consisted of 50% acetonitrile and 50% deionized water.

Mass spectrometric analysis was performed using the Waters Synapt HDMS system, which was equipped with the electrospray ionization (ESI) operating at a negative-ion mode. The capillary and cone voltages were set at 2000 V in ESI mode and 35 V, respectively. The de-solvation gas flow rate was set at 700 l/h, and gas flow was maintained at 25 l/h. The de-solvation and source temperatures were set at 300 °C and 80 °C, respectively. MS data were acquired over a range of  $m/z$  of 20–990 at a rate of 0.1 scan per second. Data were collected in centroid mode. Sulfadimethoxine (Sigma–Aldrich, USA) was used as a reference compound ( $m/z$  of 309.0658 in ESI mode). LockSpray frequency was set at 0.5 s and was averaged over 10 scans for correction.

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