Reduced Graphene Oxide-TiO$_2$ Nanocomposite Facilitated Visible Light Photodegradation of Gaseous Toluene

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Abstract

The photocatalytic degradation of gaseous toluene was investigated on TiO$_2$ nanoparticles coated on reduced graphene oxide. Reduced graphene oxide-TiO$_2$ composite (RGO-TiO$_2$) was synthesized via two step processes. The prepared RGO-TiO$_2$ composite was characterized using SEM, XRD, and UV-visible spectra. A significant increase in light absorption to visible light was observed by RGO-TiO$_2$ compared with that of pure TiO$_2$ nanoparticles. The photocatalytic degradation efficiency of the RGO-TiO$_2$ composite was much higher than that of the P25 TiO$_2$, 95% and 40% respectively. In our investigated conditions, the initial concentration, flow rate and relative humidity had significant influences on the photocatalytic degradation of gaseous toluene. The most efficiency was recorded at the 0.3 ppm concentration, 1L/min flow rate and 30% relative humidity. We believe that this TiO$_2$ based composite material can be effectively used as a highly active and stable photocatalyst to remove various indoor air pollutants especially gaseous toluene. The photocatalytic degradation efficiencies of toluene increased slowly below 20% relative humidity and then decreased as the relative humidity increased further. The main reason of enhanced photocatalytic property might be the strong electron transfer ability, and the increased adsorption capacity of RGO sheets in the composites as well as the retarded charge recombination rate contributed by the energy level of the two materials. We believe that this TiO$_2$ based composite material can be effectively used as a highly active and stable photocatalyst to remove various gaseous pollutants.

Keywords

Photocatalytic, RGO-TiO$_2$, Nano Particles
1. Introduction

Heterogeneous photocatalytic oxidation has been studied for several decades and shown to be an effective method for dealing with the environmental pollution problems, such as air cleanup, water disinfection, hazardous waste remediation, and water purification [1]-[7]. Among the many types of semiconductors, titanium dioxide (TiO₂) has been received lots of attention due to its high photocatalytic activity as well as the low cost and non-toxicity [8]-[14]. However, the photocatalytic performance of TiO₂ still restricted by the fast electro-hole pair recombination rate [15] [16]. In order to improve the photocatalytic performance of TiO₂, many materials have been studied to couple with TiO₂ for suppressing the charge recombination rate. Recently, studies showed the introduction of carbon materials can effectively decrease the charge recombination rate, thus enhancing the photocatalytic performance of TiO₂ [17].

Among the carbon materials, graphene, a monolayer two-dimensional graphitic carbon system, has attracted much attention since it was isolated in 2004 [18]. The two-dimensional structure, large surface area, outstanding electronic and catalytic properties of graphene make it become a suitable candidate for incorporating with TiO₂. For both graphene and reduced graphene oxide composites, the electrons in TiO₂ generated by photons can be moved across the carbon sheets, which reduce the recombination of photon-generated electron-holes [18]. These kinds of materials have a high adsorption capacity, which enhances the photocatalytic performance of TiO₂ nanoparticles [19].

Moreover, carbon derivatives also behave as impurities, leading to the generation of Ti-O-C bonds which extends light absorption to the visible range [20].

Several studies [21] [22] [23] have utilized RGO-TiO₂ composites for the degradation of water pollutants such as methylene blue, methyl orange, diphenhydramine and rhodamin B. However, to the best of our knowledge, no studies investigate application of RGO-TiO₂ composite to air pollutants. Air applications of such photocatalysts require a supporting material to prevent their blowing away with photocatalytically treated air. Therefore, in this research, a RGO-TiO₂ composite was synthesized using a chemical mixing process and its heterogeneous photocatalytic activity for the degradation of a toxic organic vapor (toluene) under visible-light irradiation was investigated using a cylindrical glass tube as a supporting material. The experiments were conducted under different operation conditions by varying the treatment airflow and initial concentration of toluene, which are two important parameters for photocatalytic processes of vaporous pollutants [24]. In addition, the photocatalytic activity of commercially available P25 TiO₂ was also evaluated.

The target compound, toluene, was chosen as the model VOC because of its prevalence in indoor air and toxic effect [25] [26].

2. Materials and Methods

2.1. Materials and Reagents

Graphite powder, tetrabutyltitanate, ammonium chloride, ammonium hydrox-
ide (28%), ascorbic acid, and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM] [PF6]) were supplied by Sigma-Aldrich (St. Louis, MO, USA). All reagents were of analytical reagent grade and were used without further purification.

2.2. Synthesis of RGO-TiO₂ Composites

Graphite oxide was prepared through a modified Hummers method by the oxidation of graphite powder [27]. RGO-TiO₂ composite was prepared according to Shen et al. 2011 as described below [28].

Solution A: 850 mg of tetrabutyltitanate was added to a mixture of 1 mL of [BMIM] [PF6] and 9 mL of water. The above mixture was stirred for 2 h. Solution B: 100 mg of GO was added to 50 mL of water. The mixture was sonicated for 30 min followed by high-speed stirring for further 1 h. 100 mg of ascorbic acid and 1 mL of ammonium hydroxide solution was added to the GO solution. Subsequently, solutions A and B were mixed. The mixture was put into an autoclave and heated at 160 ℃ for 4 h. When the reduction reaction was finished, the as-synthesized product (RGO-TiO₂) was isolated by centrifugation, washed several times with pure water and ethanol, and dried at 90 ℃ for 12 h.

Prepared RGO-TiO₂ composite was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transforms infrared (FTIR) spectroscopy, ultraviolet (UV)—visible spectroscopy.

2.3. Performance Evaluation

The photocatalytic activities of prepared RGO-TiO₂ composite were investigated for degradation of gaseous toluene under different operational conditions using a glass tube reactor. The inner wall of the photocatalytic reactor was coated with a thin film of the RGO-TiO₂ composites. A visible light lamp was then inserted inside the glass tube, where it served as the inner surface of the annular reactor, through which the gas flowed. The temperature inside the photocatalytic reactor heated by the lamp ranged from 56 ℃ - 63 ℃. Three major parameters, initial concentration (IC), flow rate (FR) and relative humidity were tested for their effects on the degradation efficiency of toluene. The range of FRs investigated ranged from 1 - 4 L·min⁻¹, and the ICs surveyed ranged from 0.1 - 1.0 ppm, which includes typical indoor air quality levels. Visible radiation was supplied by an 8-W fluorescent daylight lamp (F8T5DL, Sunlite Co.) with a full spectrum, and its intensity was measured using a Digital Lux Meter (51021, Yokogawa Co.). Time series of gas samples were collected at the inlet and outlet of the photocatalytic reactor before and after activating the lamp. Air samples were collected directly from rubber septum sampling ports using 10 mL Hamilton gas-tight syringes and were injected immediately into GC unit for analysis. Gaseous toluene was analyzed by using a Varian cp-3800 gas chromatograph (GC) equipped with a flame ionization detector. The quality assurance program for the measurement of gaseous compounds included laboratory blank and spiked samples.
3. Results and Discussion
3.1. Catalyst Characterization
The prepared RGO-TiO₂ composite was characterized using SEM, UV-visible, X-ray diffraction (XRD), and Fourier transforms infrared (FTIR) spectroscopy. Figure 1 shows the SEM images and energy-dispersive X-ray (EDX) spectra of the RGO-TiO₂ composite.

The EDX spectra of the RGO-TiO₂ composite contained peaks corresponding to the Ti, Pt, O, and C atoms, the peaks of Ti and O atoms were likely associated with TiO₂, while the C atom peak may have been related to RGO. The Pt peaks were likely due to Pt coating of the samples for SEM analysis. The UV-visible absorbance spectra of RGO-TiO₂ composite and the P25 TiO₂ powder are shown in Figure 2. The P25 TiO₂ revealed an absorption edge around 410 nm, which
was similar to that reported in previous studies [29] [30]. However, a substantial shift in the absorbance spectrum toward the visible region was observed for the RGO-TiO₂ composite, which was in good agreement with the results of previous studies [29] [31]. The light absorption edge for the RGO-TiO₂ composite was shifted to larger than 800 nm, which was ascribed to the interaction of RGO with TiO₂. These findings indicated that the RGO-TiO₂ composite could function effectively under visible-light irradiation. FTIR is a convenient tool to identify chemical bonds in complex composite materials. The representative absorption peaks of GO (Figure 3), including those at 3400 cm⁻¹ (O-H stretching vibration), 1720 cm⁻¹ (C = O stretching vibration of COOH groups), 1390 cm⁻¹ (tertiary C-OH stretching vibration), and 1052 cm⁻¹ (C-O stretching vibration), decreased dramatically in intensity or even disappeared after hydrothermal preparation, indicating that the oxygen-containing functional groups in GO were decomposed in the hydrothermal environment [32]. In the spectrum of RGO-TiO₂, band at 3250 cm⁻¹ is due to O-H stretching, which means that the TiO₂ nanocrystal will easily absorb water in air. XRD was used to further study the changes in structure. Figure 4 shows powder XRD patterns of raw graphite, GO, RGO, and RGO-TiO₂. For the RGO-TiO₂ sample, the (002) reflection peak was broad and was centered at around 25 degrees.

3.2. Photocatalytic Decomposition

As shown in Figure 5, the photocatalytic degradation efficiency (PDE) of the RGO-TiO₂ composite was much higher than that of the P25 TiO₂. The degradation of possible deactivation, even the time period was short (4 h). This finding is due to the fact that the PDE of the TiO₂ is too low and decreased gradually over the 4h, in disi-
Figure 3. FTIR spectra of GO, RGO and RGO-TiO$_2$ composite.

Figure 4. XRD pattern of raw graphite, GO, RGO and RGO-TiO$_2$ composite.

Similar to other researchers results that the photocatalytic activity of TiO$_2$ decreases dramatically after only a few minutes irradiation [33] [34]. In this study, it was found that photocatalytic activity of the RGO-TiO$_2$ composite was higher than TiO$_2$ powder and this improvement may be attributed to the unique structure of GO sheets in the composite. GO likely acts as an excellent support for adsorption of toluene, enhancing the photocatalytic activity of the RGO-TiO$_2$
composite. GO like other carbon derivatives, has a photosensitizing nature that extends the light absorbance into the visible range, causing the RGO-TiO$_2$ composite to be activated by visible-light irradiation.

### 3.3. Effect of Initial Concentration

In order to discuss the effect of VOCs initial concentration (IC) on photo-catalytic degradation rates, we studied the removal efficiency of toluene under different initial concentrations. The toluene concentrations in the experiment ranged between 0.1 - 1 ppm. The conditions were as follow: gas flow-rate of 1 L/min, relative humidity of 30%, RGO-TiO$_2$ as photo-catalyst, and irradiation time of 4 hr. The results showed that the photo-catalytic degradation rates decreased with increasing toluene initial concentration more than 0.3 ppm, just shown in Figure 6. Based on the Langmuir-Hinshelwood model, which is most commonly used to link the photocatalytic degradation reaction rate of VOCs to their ICs [35], the reaction rate decreased with increasing initial concentration while the absolute amount of degraded pollutants may increase. These findings

![Figure 5](image5.png)

**Figure 5.** Photocatalytic degradation efficiency (PDE, %) of toluene determined using RGO-TiO$_2$ composite and P25 TiO$_2$ powder under visible-light irradiation.

![Figure 6](image6.png)

**Figure 6.** Photocatalytic degradation efficiency (PDE, %) of toluene determined using RGO-TiO$_2$ composite under visible-light irradiation according to initial concentration.
are consistent with those reported in other researches [36] that used undoped TiO₂ under UV irradiation. The IC dependence was ascribed to adsorptive competition between toluene molecules for the active adsorption sites on the surface of the RGO-TiO₂ composite. Regarding higher ICs, the active adsorption sites on the photocatalyst surface might be more limited for adsorption of toluene molecules.

3.4. Effect of Gas Flow Rate

The effect of gas flow rate (FR) on toluene degradation reaction was investigated at an initial concentration of 0.3 ppm and relative humidity of 30 %, just as illustrated in Figure 7. When the flow rate was increased from 1 - 4 L/min, degradation rate of toluene decreased. With a flow rate >1 L/min the reactants have shorter residence time on the photocatalyst surface and consequently do not bind to the active sites. In general, an increase in gas flow rate probably results in two antagonistic effects. These are a decrease in residence time within the photocatalytic reactor, and an increase in the mass transfer rate. Therefore, these

![Figure 7. Photocatalytic degradation efficiency (PDE, %) of toluene determined using RGO-TiO₂ composite under visible-light irradiation according to stream flow rate.](image)

![Figure 8. Photocatalytic degradation efficiency (PDE, %) of toluene determined using RGO-TiO₂ composite under visible-light irradiation according to relative humidity.](image)
results suggested that FR was still a critical factor for the photocatalytic application of the RGO-TiO₂ composite. Decreased FRs would result in a decrease in the bulk mass transport of target compounds from the gas-phase to the surface of the catalyst particle due to convection and diffusion, which is an important heterogeneous catalytic reaction process [30].

### 3.5. Effect of Relative Humidity of Air Stream

The effect of relative humidity (0% - 60% RH) of air stream on toluene decomposition was examined by adding water vapor to a fixed concentration of toluene. RGO-TiO₂ photocatalyst was used in this experiment. Figure 8 showed the experimental results at different relative humidity. The degradation rate increased with increasing relative humidity up to 30% and then started to decrease as the RH goes up, which meant that 30% was the optimal humidity for photo-catalyst process under the experimental conditions. When the reaction time was 4h, the highest removal efficiency of toluene was 95% when RH was 30%. The results revealed that a little water vapor could promote the photocatalytic degradation of VOCs, while excessive water vapor could inhibit the photocatalytic degradation. This phenomenon is in agreement with the observations reported previously [37]. The reason of this phenomenon could be due to more saturation of the surface by RH at higher levels of humidity.

### 4. Conclusion

In this study the RGO-TiO₂ composite was coated on inner wall of the photocatalytic reactor and toluene was chosen as the model VOC. We studied the photocatalytic activities of RGO-TiO₂ composite for the photocatalytic degradation gaseous toluene under different conditions. The RGO-TiO₂ composite exhibited a shift in the absorbance spectrum toward the visible light region when compared to undoped TiO₂ powders, indicating that the as-prepared RGO-TiO₂ composite could be effectively activated by visible-light irradiation. Another major finding was that the RGO-TiO₂ composite photocatalytic system showed superior toluene photocatalytic conversion efficiencies to undoped TiO₂ under visible-light irradiations. Overall, the results indicated that the RGO-TiO₂ composite could be effectively applied for the purification of indoor-level gaseous toluene under optimal operational conditions.

### References


