Photocatalytic removal of phenol over titanium dioxide-reduced graphene oxide photocatalyst

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Abstract. Titanium dioxide (TiO₂) has been one of the most investigated semiconductors due to its high activity for the removal of organic pollutants. In order to improve the efficiency of the TiO₂, series of TiO₂-reduced graphene oxide (rGO) composites with various loading amounts of graphene oxide (GO), which were 0.5, 1, 3 and 5 wt% were prepared by UV-assisted photocatalytic reduction method. The X-ray diffraction (XRD) patterns and Fourier transform infrared spectroscopy (FTIR) spectra confirmed that all the TiO₂-rGO composites samples were successfully synthesized without disrupting the structure of the TiO₂. Fluorescence spectroscopy revealed the role of the rGO to reduce the electron-hole recombination on the TiO₂, while the transmission electron microscopy-energy dispersive X-ray spectroscopy (TEM-EDS) confirmed the morphology and the presence of both TiO₂ and rGO. In the photocatalytic removal of phenol, all the TiO₂-rGO composites showed better photocatalytic activities than the TiO₂ under UV light irradiation. The activity of the TiO₂ was enhanced by more than two times with the addition of the GO with the optimum amount (3 wt%). It was proposed that the good photocatalytic performance obtained on the composites were caused by the successful suppression of electron-hole recombination by the rGO on the TiO₂.

1. Introduction
Titanium (IV) oxide (TiO₂) is known to be a good photocatalyst for degradation of environmental contaminants nowadays [1]. Due to its good properties, such as having a wide band gap of (~ 3 eV) and anti-photocorrosion, TiO₂ has been reported to give high photocatalytic activities in degradation of organic pollutants and dyes under UV light irradiation. However, TiO₂ still suffers from high electron-hole recombination rates that result in the low photocatalytic activity. Performing a composite between TiO₂ semiconductor and graphene (TiO₂-GR) has been reported to give a higher photocatalytic activity [2-9].

Graphene is a 2-dimensional graphitic material with abundance of sp² hybridization. It has tremendous unique properties, such as high transport conductivity of ~ 5000 W m⁻¹ K⁻¹, excellent mechanical properties, flexible structure, and large theoretical specific surface area up to 2600 m² g⁻¹ [10]. Due to its outstanding properties, many researchers have used graphene to design novel graphene-based materials for various photocatalytic applications, such as degradation of organic pollutants [2-5] and photocatalytic water splitting [6-9]. These graphene based materials are commonly synthesized from graphite to graphene oxide (GO) followed by reduction process to
produce reduced graphene oxide (rGO). Various methods have been reported in reducing the GO, such as chemical reduction, thermal reduction, and hydrothermal reduction [2,3,6]. However, there are some limitations to these methods, such as the use of hydrazine that is highly toxic and high temperature that will affect the structure of the formed rGO [6]. Recently, Williams et al. discovered a clean method by using TiO\textsubscript{2} as a photocatalyst to convert GO to rGO at room temperature [11]. The advantages of the photocatalytic reduction method are low cost and feasible to form partially reduced graphene oxide, which is favorable for the photocatalytic applications. In this study, UV-assisted photocatalytic reduction method was used to prepare the TiO\textsubscript{2}-rGO composites by using methanol as the reducing agent. The photocatalytic activities of the TiO\textsubscript{2}-rGO composite samples were assessed by examining the degradation of phenol under UV light irradiation.

2. Experimental

2.1 Preparation of TiO\textsubscript{2}-rGO composites
GO was prepared via an improved Hummers’ method [12] by reacting a commercial graphite powder (Sigma-Aldrich) with a mixture of KMnO\textsubscript{4}, H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{3}PO\textsubscript{4}. The GO was centrifuged and washed twice with HCl, followed by double distilled water until pH 7. The obtained solid was dispersed in methanol and ultrasonicated for 1 h. Finally, the solution was evaporated to remove excess solvent and dried at room temperature overnight. The TiO\textsubscript{2}-rGO composites were prepared by UV-assisted photocatalytic reduction method [11] with GO contents of 0.5, 1, 3, and 5 wt %. The composite samples were labelled as TiO\textsubscript{2}-rGO(x), which x shows the GO contents. For a typical synthesis of TiO\textsubscript{2}-rGO(0.5), TiO\textsubscript{2} (1 g, Sigma-Aldrich) and the prepared GO (0.005 g) was dispersed in methanol (60 mL) and sonicated for 30 min. After sonication, the mixture was transferred into a 100 mL jacketed beaker and placed on a stirring plate with a cooling water system to ensure that the reaction could be carried out at room temperature. The synthesis reaction was conducted in a closed box for 24 h under UV light irradiation (\(\lambda = 254\) nm, \(I = 0.32\) mw cm\textsuperscript{-2}). After each reaction, the obtained solid was filtered and washed with distilled water and methanol consecutively. The final product was then dried at room temperature. Similar procedures were used to prepare the other TiO\textsubscript{2}-rGO(x) composite photocatalysts.

2.2 Characterizations of TiO\textsubscript{2}-rGO composites
The prepared composite photocatalysts were characterized using different types of instruments. X-ray diffraction (XRD, D8 Advance, Bruker) was used to record the diffraction patterns of photocatalyst. Fluorescence spectroscopy (FP-8500 JASCO) was used to identify the emission sites in the prepared sample. Fourier transform infrared spectroscopy (FTIR, Nicolet iS50, Thermo Scientific) was used to detect the presence of functional groups in the composite photocatalyst. Transmission electron microscopy equipped with energy dispersive X-ray spectroscopy (TEM-EDS, JEM 2100, JEOL) was used to study the morphology of the selected composite sample.

2.3 Photocatalytic removal of phenol
The photocatalytic removal of phenol was conducted by adding photocatalyst (0.05 g) in 50 mL of 50 ppm phenol aqueous solution in a 100 mL beaker attached to the cooling system. Prior to the reaction, the mixture was placed on a stirring plate in a closed box under dark condition for 30 minutes to reach adsorption equilibrium. The mixture was then put under exposure of UV light irradiation (8 W, \(\lambda = 254\) nm, \(I = 0.32\) mw cm\textsuperscript{-2}) from top of the beaker for 3 h. After reaction, the concentration of the solution was measured by a gas chromatography equipped with a flame ionization detector (GC-FID, 7820A, Agilent Technologies) to determine the percentage removal of phenol.
3. Result and discussions

3.1 Characterizations of the TiO$_2$-rGO composite photocatalysts

The XRD patterns of the GO and the TiO$_2$-rGO composite photocatalysts are shown in Figure 1. As can be seen in Figure 1(a), a weak diffraction peak was observed at a 2$\theta$ value of 10.4° (002), which attributed to the interplanar distance of 0.80 nm and was in good agreement with the previous reported literatures [2,12]. This result indicated that the GO was successfully synthesized from oxidation of graphite via the improved Hummers’ method. Figure 1(b-f) illustrate the XRD patterns of the TiO$_2$-rGO composite photocatalysts. It was clear that all the diffraction peaks matched the standard data for pure anatase and rutile phases of TiO$_2$ (JCPDS 84-1286 and 88-1175, respectively). The diffraction peaks identified at 2$\theta$ values of 25.4, 36.8, 37.7, 38.5, 48.1, 53.9, 55.0, 62.8, and 69.0° can be ascribed as (101), (103), (004), (112), (200), (105), (211), (118) and (220) crystal planes of anatase TiO$_2$. Meanwhile, peaks at 2$\theta$ values of 27.6, 36.2, and 41.2° can be indexed as (110), (101), and (111) for rutile phase of TiO$_2$. Addition of GO did not affect the crystallinity and the structural phases of the TiO$_2$. Notably, the characteristic peak of the GO was disappeared while the rGO could not be detected in the composites, suggesting the low amount or low diffraction intensity of rGO.

The molecular structures of the GO and the TiO$_2$-rGO composite photocatalysts were characterized by FTIR spectroscopy. Figure 2 illustrates the FTIR spectra of the GO, the TiO$_2$ and the TiO$_2$-rGO composites. As can be seen from Figure 2(a), the peak of C=C aromatic bonding at around 1630 cm$^{-1}$ and the broad peak at around 3400 cm$^{-1}$ due to physically adsorbed water molecules on the GO were observed [4]. On the other hand, TiO$_2$ exhibited additional broad peaks below 800 cm$^{-1}$, which corresponded to Ti-O-Ti groups [4]. All the TiO$_2$-rGO composites gave characteristic peaks of both GO and TiO$_2$, in which the peak at around 1630 cm$^{-1}$ became more significant with the increase of GO loading, suggesting the presence of GO in the composite photocatalysts.
**Figure 2.** FTIR spectra of (a) GO, (b) TiO\textsubscript{2}, (c) TiO\textsubscript{2}-rGO(0.5), (d) TiO\textsubscript{2}-rGO(1), (e) TiO\textsubscript{2}-rGO(3), and (f) TiO\textsubscript{2}-rGO(5).

**Figure 3.** Fluorescence spectra (a) TiO\textsubscript{2}, (b) TiO\textsubscript{2}-rGO(0.5), (c) TiO\textsubscript{2}-rGO(1), (d) TiO\textsubscript{2}-rGO(3), and (e) TiO\textsubscript{2}-rGO(5).
The emission sites of TiO$_2$ with different loadings of the GO were studied by fluorescence spectroscopy. Figure 3 illustrates the excitation and emission spectra of TiO$_2$ and TiO$_2$-rGO composite photocatalysts. TiO$_2$ showed strong emission spectrum at 276 nm with excitation wavelength of 218 nm. It was confirmed that the addition of the GO did not give any influences on the excitation and emission wavelengths but the intensity of the spectra was found to be affected by the presence of rGO. The intensity of excitation and emission spectra decreased with the increase of the GO contents (0.5 - 5 wt%). This result suggested that the rGO was able to reduce the electron-hole recombination in the TiO$_2$.

The morphology of the selected TiO$_2$-rGO composite photocatalyst was investigated by TEM. Figure 4 shows the TEM image of TiO$_2$-rGO(3) composite. As can be seen in Figure 4(b), the aggregated TiO$_2$ was retained and unaffected after addition of rGO. Moreover, the rGO sheets with slight aggregation could also be observed, suggesting the presence of rGO on the surface of the composite photocatalysts. The presence of both TiO$_2$ and rGO was also confirmed by EDS as shown in Table 1. The amount of carbon (2.2. wt%) was found to be close to the added GO amount (3 wt%).

![Figure 4. The TEM images of the TiO$_2$-rGO(3) with different magnifications of (a) 10,000 and (b) 250,000 times.](image)

| Table 1 The EDS elemental microanalysis of the TiO$_2$-rGO(3) |
|------------------|------------------|------------------|
| Element | Weight %$^a$ | Atomic %$^b$ |
| C       | 2.2            | 4.9             |
| O       | 35.2           | 59.6            |
| Ti      | 62.7           | 35.5            |

$^a$Weight % shows the ratio percentage between mass of each element and total mass of all elements. $^b$Atomic % shows the ratio percentage between atomic number of each element and total atomic number of all elements.

3.2 Photocatalytic activities of the TiO$_2$-rGO composite photocatalysts

The photocatalytic performances of the TiO$_2$-rGO composite photocatalysts were investigated for the removal of phenol under 3 h UV light irradiation at room temperature. Photolysis and adsorption experiments were also conducted to support that the decrease in the concentration of phenol was contributed by the photocatalytic reaction. After 3 h of UV light irradiation without photocatalyst, the
concentration of phenol was unchanged. This result suggested that phenol was stable under UV light irradiation, and phenol could not be degraded under UV light irradiation without the photocatalyst. On the other hand, adsorption test under dark condition showed that adsorption equilibrium of phenol was achieved after 30 min by stirring phenol solution in the presence of the photocatalyst. It was confirmed that only ca. 3% phenol was adsorbed on the TiO$_2$ photocatalyst. This result suggested that phenol could not be degraded in the presence of photocatalyst without UV light irradiation. Table 2 shows the percentage removal of phenol on the TiO$_2$ and the TiO$_2$-rGO composites with different GO contents. All the TiO$_2$-rGO composites showed higher photocatalytic activity than the unmodified TiO$_2$ sample, which only showed 7% removal of phenol. The photocatalytic activity of the TiO$_2$ was enhanced from 7 to 17% when the amount loading of GO was 3 wt%. This good improvement (2.4 times) would be due to the presence of rGO in the composite that suppressed the electron-hole recombination of TiO$_2$, as supported by the fluorescence spectra.

Table 2 Photocatalytic activity of the TiO$_2$ and the TiO$_2$-rGO composites for phenol removal under UV light irradiation

| Sample | Percentage of phenol removal (%)$^b$ |
|--------|-------------------------------------|
| TiO$_2$ | 7                                   |
| TiO$_2$-rGO(0.5) | 9                               |
| TiO$_2$-rGO(1)  | 11                                 |
| TiO$_2$-rGO(3)  | 17                                 |
| TiO$_2$-rGO(5)  | 15                                 |

$^a$Photocatalyst used was 0.05 g, phenol was 50 mL (50 ppm).
$^b$Percentage of phenol removal was calculated as $(C_o-C_t)/C_o \times 100\%$, where $C_o$ is the initial concentration of phenol and $C_t$ is the concentration of phenol after photocatalytic reaction.

4. Conclusions
The TiO$_2$-rGO composite photocatalysts were successfully prepared via a UV-assisted photocatalytic reduction method. It was revealed that the addition of GO did affect the crystalline structure of TiO$_2$, which was remained to be a mixture of anatase and rutile in the TiO$_2$-rGO composite. The presence of rGO was found to decrease the emission intensity of the TiO$_2$, implying the successful reduced electron-hole recombination. The TiO$_2$-rGO composite photocatalysts showed significantly enhanced photocatalytic activities for the removal of phenol. The TiO$_2$-rGO sample with 3 wt% of GO loading exhibited the highest photocatalytic activity, which was 2.4 times higher than pure TiO$_2$. The efficient suppression of the electron-hole recombination in the TiO$_2$ led to the improvement of the photocatalytic performance.

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