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Improving the Activity of Rutile Titanium Dioxide with Reduced Graphene Oxide

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Abstract. Among titanium dioxide (TiO₂), rutile is the most stable polymorph of TiO₂ at all temperatures. However, its application as photocatalyst is less explored since generally anatase and anatase-rutile mixture show better photocatalytic activity than the rutile structure. In this study, we successfully improved the photocatalytic 7 vity of rutile up to four times higher when it was modified with reduced graphene oxide (rGO). The rGO-TiO₂ co 37 sites were prepared by photocatalytic reduction of graphene oxide (GO 36 room temperature under ultraviolet (UV) light irradiation in the presence of rutile TiO₂. The amount of GO which was prepared by oxidation of graphite flakes via the Hummers' method was varie 1 rom 0.5 to 5 wt%. The properties of the obtained composites were investigated by several characterization methods. X-ray diffraction (1 D) and Fourier transform infrared (FTIR) spectroscopies revealed that the rGO-TiO₂ composites could be prepared without disrupting the structure of rutile TiO₂. The fluorescence spectroscopy confirmed that the presence of rGO decreased the emission 1 tensity of rutile TiO₂, suggesting that the int 12 tions between the rGO and the rutile TiO₂ might cause the decrease in electron-hole recombination on the

INTRODUCTION

evaluated for degradation of phenol under UV light irradiation for 3 h. It was observed that the addition of small amount

of rGO (1 wt% GO) significantly improved the photocatalytic activity of rutile TiO2.

In the point of view of sustainable energy, heterogeneous photocatalysis is one important approach to degrade organic pollutants, such as phenol and its derivatives [1-3] as it offers an environmentally safe process and provides an alternative way to utilize solar light in the future. Since titanium dioxide (TiO₂) shows excellent activity for such degradation reactions, TiO₂ has been recognized as one of the mos 35 plored photocatalysts. TiO₂ has various polymorphs, which anatase and rutile are the common or 34 listructures. Anatase is generally known to be more active than rutile [4]. In add 28 n, anatase TiO₂ containing a small amount of rutile phase gave better photocatal 16: performance than the pure anatase TiO₂ for photocatalytic decomposition of phenol and salicylic acid [5], 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid [6]. Owing to its high activity, the TiO₂ P25 consisting anatase-rutile mixture with ratio of about 3:1 has been usually used as a standard material [7]. Therefore, more modifications have been explored to further improve the photocatalytic activity of anatase and anatase-rutile mixture than that of rutile, such as by introduction of reduced graphene oxide (rGO) [8-12].

The rGO is a single-atomic-layered material that can be synthesized from reduction of oxidized graphite crystal. The basic skeletal of rGO is in hexagonal pattern of carbon arranged with densely packed in honeycomb lattice sites consists of sp² – bonded carbon atoms in planar sheet. The distance between carbon atoms is determined to be around

0.142 nm with an inter-planar spacing of each monolayer graphene is around 0.335 nm [13]. The rGO is also known as a building block for carbon structure, such as wrapping in fullerenes, rollin 38) nanotubes and stacking in graphite. Graphene and rGO have a 33 thtly different structure from each other due 26 the oxygen functional groups existed in the rGO. It was reported that the oxygen functional groups in rGO makes them excellent supports to anchor semiconductor nanocrystal for synthesis of photocatalyst composites [14].

The rGO can be synthesized via several methods such as chemical, thermal, electrochemical and UV reduction methods [15-17]. Particular attention has been made for UV reduction method since it does not require high temperature or the presence of strong reducing agents [15, 16], which is very important and considered as a green technique. Moreover, this method only involves mild reaction condition that leads to the formation of p 33 llly reduced GO [15]. GO can be also reduced by photochemical reaction with the assistance of active photocatalyst in the presence of a sacrificial a [4]. A successful reduction of GO was reported to occur on the TiO2 photocatalyst u [3] er UV light irradiation [17]. Upon UV light irradiation, charge separation occurs on the surface of TiO2 particles. The holes are scavenged to produce ethoxy radicals, thus leaving the electrons to accumulate within the TiO2 particles. The accumulated electrons then interact with GO sheets to reduce the functional group [15]. The enhancements of photocatalytic activity in the presence of rGO were observed on anatase TiO2 for decomposition of sarin in gas phase [8], degradation of phenol [9], and hydrogen production [10]. Such enhanceme [32] were also observed on mixture anatase-rutile TiO2 for degradation of phenol [11] and hydrogen production [12]. In this study, we demonstrated that the activity of rutile TiO2 for photocatalytic degradation of phenol could be also improved in the presence of rGO.

EXPERIMENTAL METHODS

Materials

The materials used were graphite flake (Sigma Adrich), potassium permanganate (KMnO₄, Fisher Scientific), sulphuric acid (H₂SO₄, > 95%, Fisher Scientific), hydrochloric acid (HCl, 37%, QRëc), phosphoric acid (H₃PO₄, 85%, Merck), hydrogen peroxide (H₂O₂, > 30%, Fisher Scientific), methanol (CH₃OH, 99.99%, Fisher Scientific), rutile TiO₂ nanoparticles (99.5%, Sigma Adrich 25 100 nm), phenol (C₆H₅OH, 99.5%, Scharlau), acetonitrile (CH₃CN, 99.9%, Merck), and double-distilled water. All the chemicals were used as received without any purification steps.

Preparation of GO

Graphite flake was used as the flature to synthesize the GO by employing the improved Hummers' method [13]. Graphite (1 g) and KMnO₄ (6 g) were added into a 500 mL round bottom flask, followed by addition of solution mixtu 24 containing of H₂SO₄ (135 mL) and H₃PO₄ (15 mL). The mixture was then stirred and heated up to 323 K for 24 h. When the reaction was completed, the mixture was naturally cooled to room temperature 23 efore pouring into ice water (400 mL). Further oxidation was quenched by addition of H₂O₂ (5 mL). The solution was then centrifuged for 10 min (3500 rpm) to discard the super 3 atant. 30% HCl solution (200 mL) was used to wash the obtained solid by centrifugation for two times. Distilled water was then used to further wash the solid until pH of filtrate was near to neutral, the remaining solid was dispersed into methanol followed by sonication for 1 h. After sonication, evaporation of solvent was carried out followed by drying for an overnight at room temperature.

Preparation of rGO-TiO₂

Various rGO-TiO₂ composites were synthesized by a photocatalytic reduction process with the help of UV light irradiation [9, 11, 18]. Various GO contents (x) of 0.5, 1, 3, and 5 weight percentage (wt%) were used to produce rGO(x)-TiO₂ composites. In order to synthesize rGO(0.5)-TiO₂ composite, the TiO₂ (1 g) and GO (0.005 g) was mixed and put in a 100 mL jacketed beaker containing methanol (60 mL). After sonication process for 30 min, the mixture was stirred in a closed box under 8 W UV light irradiation. The synthesis process was carried out for 24 h and the light intensity was 0.32 mW1 m⁻² at wavelength of 254 nm. After the synthesis reaction, the mixture was filtered to obtain the solid composite. Distilled water and methanol were used to consecutively wash the solid product, which was then allowed to dry at room temperature.

Characterizations of GO, TiO2, and rGO-TiO2

Charact 3 zations of the prepared samples were carried out by using X-ray Diffraction, XRD (Bruker, D8 Advance), Fourier transform infrared, FTIR (Thermo Scientific, Nicolet iS50) and fluorescence spectroscopies (JASCO, FP-8500). X-ray diffractometer was used to identify the structure, FTIR 31 ectrophotometer was used to investigate the functional groups, while fluorescence spectrophotometer was used to investigate the excitation and emission properties of the prepared samples. All measurements were carried out at room temperature.

Photocatalytic Degradation of Phenol

Photocatalyst (0.05 g) was dispersed in a 100 mL beaker co 22 ning 50 mL of phenol (50 ppm). The beaker was placed in a closed box to facilitate dark condition. In order to determine the required time for the photocatalyst to achieve equilibrium of adsorption, the dark reaction was conducted for 3 h continuously. The photocatalyst was filtered 10 h the solution by using membrane filter for every 30 min. Gas chromatography, GC (Agilent Technologies 7820A) w a flame ionization detector (FID) was used to analyze the remaining phenol concentration after each sampling. It was found that the p 4 ocatalyst required 30 min to achieve equilibrium in adsorption of phenol. For photocatalytic test, the composite (0.05 g) was dispersed in a 100 mL 18 keted-beaker containing 50 mL of phenol (50 ppm). Based on the adsorption test, the photocatalyst and phenol was stirred in the dark for 30 min before the photocatalytic rea 21 h. The photocatalytic degradation of phenol was carried out for 3 h under 8 W UV light. The UV light intensity was measured to be 0.32 mW cm⁻² by a light meter at wavelength of 254 nm. The concentration of the phenol after each reaction was analyzed by the GC-FID to calculate the percentage degradation of phenol.

RESULTS AND DISCUSSION

XRD was used to reveal the structure of the prepared GO, TiO₂, and rGO-TiO₂ composites. As shown in Fig. 1(a), GO showed a sharp and strong diffraction peak at 10.40° (002) that could be associated to the interplanar distance of the GO. This result agreed well with the reported literature [13]. The XRD pattern clearly indicated the successful formation of GO that was prepared through the current employed method. Displayed in Fig. 1(b)-(f) are the diffraction patterns of TiO₂ and rGO-TiO₂ composites. All samples showed similar diffraction peaks, suggesting that all samples have similar structure to each other. The diffraction peaks appeared at 20 of 27.4, 36.1, 39.1, 41.2, 44, 54.4, 56.6, 62.9, 64.1 and 69.1° could be denoted as (110), (101), (200), (111), (210), (211), (220), (002), (310), and (301) crystal planes of rutile phase, according to the PDF file (JCPDS 88-1175) [19]. The observed diffraction peaks showed that the crystal structure of TiO₂ was maintained to have rutile structure even with the addition of GO. Since no shifting in the diffraction peaks was detected on the rGO-TiO₂ composites, it could be suggested that the addition of GO did not affect the structural property of the rutile TiO₂. Besides the diffraction peaks of rutile TiO₂, there was no other diffraction peak that could be observed for all the rGO-TiO₂ composites. The diffraction peak of rGO was also not detected in all rGO-TiO₂ composites. This might be due to the low amount of rGO or the rGO was well dispersed on the rutile TiO₂.

In order to reveal the functional groups present in the prepared samples, FTIR spectroscopy was used in this study. Can be seen from Fig. 2(a), the C=O stretching peak of carboxyl group at 1628 cm⁻¹ was detected in GO sample [20]. The detection of this peak is also one indicator that the GO was successfully synthesized in this work, as also supported by the aforementioned XRD pattern. Broad peak observed at around 3410 cm⁻¹ could be corresponded to the presence of water which could be adsorbed physically on the GO, which was also observable on all rGO-TiO₂ composites. On the other hand, the rutile TiO₂ and all rGO-TiO₂ composites shown in Fig. 2(b)-(f) exhibited broad peaks below 800 cm⁻¹, which could be associated with the presence of Ti-O-Ti groups [20]. It was obvious that the characteristic peaks of rutile TiO₂ still could be observed in the spectra of all the composites, suggesting that the crystal planes of rutile TiO₂ were not affected by the addition of GO. With the increase of GO loading, the pe 5 around 1628 cm⁻¹ also became more pronounced, which showed that the amount of rGO in the composites was truly increased with the increase in the added amount of GO. Both XRD patterns and FTIR spectra suggested the successful preparation of rGO-TiO₂ composites.

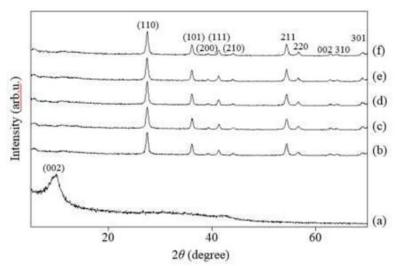


FIGURE 1. XRD patterns of (a) GO, (b) TiO₂, (c) rGO(0.5)-TiO₂, (d) rGO(1)-TiO₂, (e) rGO(3)-TiO₂, and (f) rGO(5)-TiO₂ composites

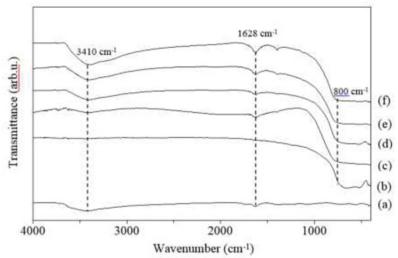


FIGURE 2. FTIR spectra of (a) GO, (b) TiO₂, (c) rGO(0.5)-TiO₂, (d) rGO(1)-TiO₂, (e) rGO(3)-TiO₂, and (f) rGO(5)-TiO₂ composites

Fluorescence spectroscopy was used to examine the interactions between the rutile TiO₂ and different amounts of added GO. As depicted in Fig. 3, rutile TiO₂ exhibited a strong fluorescence property with excitation and emission wavelengths at 218 and 276 nm, respectively. It was obvious that both excitation and emission wavelengths of the rGO-TiO₂ were not changed with the addition of GO. However, the excitation and emission intensities were found to be decreased as the result of GO addition. The reduced intensity was observed in all rGO-TiO₂ composites, suggesting that there were certain interactions between rGO and rutile TiO₂. The decrease in the emission intensity has been generally related to the reduced electron-hole recombination on the TiO₂. However, no clear relationship was observed between the reduced intensity and the amount of GO loading.

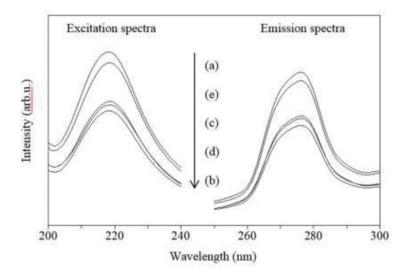


FIGURE 3. Excitation and emission spectra of (a) TiO₂, (b) rGO(0.5)-TiO₂, (c) rGO(1)-TiO₂, (d) rGO(3)-TiO₂, and (e) rGO(5)-TiO₂ composites

As for the photocatalytic activity tests, it was confirmed that phenol retained in the solution and no degradation occurred without UV light irradiation and photocatalyst. GO did not give photocatalytic activity for degradation of phenol. On the other hand, TiO₂ and rGO-TiO₂ composites showed photocatalytic activities for degradation of phenol as shown in Fig. 4. Rutile TiO₂ only gave a low photocatalytic activity, which was 2% degradation. The addition of GO up to 1 wt% increased the activity of bare TiO₂ from 29 8%. The four times higher photocatalytic activity strongly showed the important contribution of rGO in improving the photocatalytic activity of rutile TiO₂. Further increase in the loading amount of GO did not change much the photocatalytic activity. Even slightly lower photocatalytic activity (7%) was observed when the amount of GO was increased to 5 wt%. Therefore, the required optimum amount of GO to achieve optimum photocatalytic activity was 1 wt%. Even though further increase 19 GO amount did not give a positive effect on the photocatalytic performance, all the rGO-TiO₂ composites gave higher photocatalytic activity than that of bare rutile TiO₂. This result suggested the important role of rGO in reducing the electron-hole recombination on the rutile TiO₂, as discussed above.

The possible mechanism for phenol degradation can be described as followed. Under exposure of \overline{UV} light irradiation, electrons in the valence band of rutile TiO_2 would be excited to the conduction band. The excited electrons could react with dissolved oxygen to produce superoxide radical that could oxidize phenol. The electrons could be also shuttled by the rGO so that fast charge recombination on the TiO_2 could be reduced. It has been reported that rGO would help to avoid the charge recombination in various semiconductors due to its ability to transport electrons, which can facilitate the interface charge transfer [21, 22]. Holes that were photogenerated in the valence band of rutile TiO_2 would directly oxidize phenol as well. Since phenol was not prepared as aqueous solution, the possibility to create hydroxyl and hydroperoxyl radical could be excluded and thus, these active species would not contribute in the photocatalytic activity.

CONCLUSIONS

Reduced graphene oxide-rutile TiO_2 composites were successfully prepared by a mild reduction of graphene oxide as the precursor using rutile TiO_2 as the photocatalyst with the assistance of UV light irradiation. The composites showed significantly better photocatalytic performance than the bare rutile TiO_2 for photocatalytic degradation of phenol. Four times enhanced photocatalytic activity was observed on the rGO(I)- TiO_2 composite as the best sample. The rGO contributed to suppress the fast charge recombination on the rutile TiO_2 , which in turn resulted in the improved photocatalytic activity.

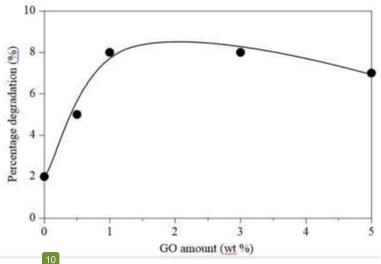


FIGURE 4. Photocatalytic degradation of phenol over rutile TiO2 and rGO-TiO2 composites

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