



In-Situ Sol-Gel Method of TiO₂-reduced Graphene Oxide as Photocatalyst

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Abstract. Nanocomposites of TiO₂-reduced Graphene Oxide were synthesized with graphene oxide (GO) loadings of 4, 8, 12, and 16 mg via in situ sol-gel method. The raw material of graphene oxide was coconut shell charcoal which was processed using a modified Hummer's method by dissolving the graphite into the acid mixture of H₂SO₄ and H₃PO₄. The rGO-TiO₂ composites were characterized by X-ray Diffraction (XRD), Inductance, Capacitance & Resistance Meter (LCR-Meter), and UV-Vis. LCR-meter results revealed that the highest electrical conductivity of the sample is $5.37 \times 10^{-6} \text{ Scm}^{-1}$ with a GO composition of 4 mg. XRD analysis results show that the sample was having both anatase and rutile phases with anatase as the dominant phase. The photocatalytic activity of the sample was investigated using a photocatalytic reactor under UV exposure using methylene blue as a pollutant. Composite with GO loading 4 mg resulted in the best percentage of degradation reaching 81.37% in 15 min.

Keywords: rGO · TiO₂ · Composite · Photocatalytic activity

1 Introduction

Nowadays nanocrystals have become a special concern among researchers, because of their extraordinary physicochemical properties and have great potential to be applied such as energy conversion prototypes, supercapacitors, and photocatalysts [1, 2]. Among them, TiO₂ with outstanding photocatalytic properties is easy to obtain and nontoxicity [3]. TiO₂ has been thought of as one of the most encouraging materials [4]. The photocatalytic activity of TiO₂ is limited by the large energy gap (3.2 and 3.0 eV for the anatase and rutile phases), which limits the absorption capacity and causes only absorption in the Ultra-Violet spectrum [5]. Various procedures have been proposed to challenge these limits. One significant methodology is to utilize metal-particle or nonmetal doping to the TiO₂. This technique can decrease the electron – hole pair recombination rate, which significantly improves the interfacial charge-transfer response rate [6–8]. In several studies, TiO₂ has been successfully composited with metal oxides, such as WO₃,

SnO₂, MoO₃, and Fe₂O₃ [9–12]. Although photocatalytic activity is more efficient, there are problems such as the composite begins to lose photocatalytic activity due to the loss of photocatalyst active surface [13].

Recently, graphene become popular among researchers because of its extraordinary physical properties, such as high chemical reaction, especially very high surface area, an excellent charge carrying (20,000 m² V⁻¹ s⁻¹), and great transparent optical properties [14–16]. However, it is quite difficult to produce high pure graphene. One of the derivatives of graphene is reduced graphene oxide (rGO) which is easy to synthesize, making it possible to produce it in large quantities. In addition, rGO is also widely composited with other materials, one of which is TiO₂. In some cases, graphene in rGO-TiO₂ composites has shown a favorable increase in photocatalytic activity, because graphene facilitates the charge separation process and performs functions when used as electron carriers in composite materials [17–20].

There have been many kinds of research on the development of rGO-TiO₂ composite materials, such as sol-gel [21], hydrothermal reduction [22], solvothermal method, sonochemical method, and in situ reduction method [23, 24]. In this research, rGO-TiO₂ from coconut charcoal shell was synthesized using the in-situ sol-gel method. The obtained rGO-TiO₂ was investigated using XRD (X-Ray Diffraction) and analyzed by the Rietveld method with the help of MAUD (Materials Analysis Using Diffraction) software [25] to determine the crystallite size, crystal structure, and phases quantitatively [26]. The photocatalytic activity of the sample was observed under UV exposure to methylene blue.

2 Material and Method

2.1 Material

The materials that have been used to prepare the rGO-TiO₂ composites are coconut shell charcoal as raw material to produce graphene oxide (GO), Isopropanol, and Titanium Tetra Isopropoxide (TTIP). Graphene oxide (GO) was prepared by Hummer's modified method using chloride acid (HCl), sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), and hydrogen peroxide (H₂O₂) 98%, ammonium hydroxide (NaOH), potassium permanganate (KMnO₄) and Distilled Water. Methylene blue (MB) was used as a pollutant to investigate the photocatalytic activity of rGO-TiO₂.

2.2 Synthesis of Graphite from Coconut Shell

Graphite powder is obtained by dissolving coconut shell charcoal powder into an HCl 0.4 M solution and stirring for 5 h. The graphite was washed with Distilled water and alcohol until neutral and dried at 150 °C. Then the powder is sieved through a 62-micron sieve.

2.3 Synthesis of Graphene Oxide (GO)

Graphene oxide (GO) was synthesized from coconut shell charcoal using a modified Hummer's method. Initially, 1 g of graphite was added to 23 ml of H₂SO₄ and 2.55 ml

of H_3PO_4 then stirred at 900 rpm. The solution was put in an ice bath to control the temperature of not more than $20\text{ }^\circ\text{C}$ while dripped with 3 g of KMnO_4 . After that, the solution was stirred at $50\text{ }^\circ\text{C}$ for 40 min. Further 46 ml of Distilled Water was added to the solution which was still in an ice bath condition and kept the temperature below $50\text{ }^\circ\text{C}$, to conduct the oxidation process. The hydrogen peroxide (H_2O_2) was added to stop the oxidation process. Graphene oxide solution was washed with 0.4 M HCl three times and washed with NaOH, distilled water, and alcohol until the concentration solution is neutral. Then the solution was heated at $60\text{ }^\circ\text{C}$ for 12 h.

2.4 Synthesis of rGO-TiO₂ Composites

The rGO-TiO₂ composite was synthesized using the sol-gel method. In the first step, 1.47 mL TTIP was added to 5.15 mL Isopropanol and then stirred for 30 min at room temperature. Followed by adding graphene oxide (GO) which has been varied (4, 8, 12, and 16 mg) while stirred for 30 min, then 2.94 mL of water was added and stirred for 1 h until the gel is formed. The next step is the oxygen-containing functional group reduced process using microwave irradiation for 10 min. Samples were heated for the drying process at $80\text{ }^\circ\text{C}$ for 12 h. And the corresponding products were denoted as TiO₂/rGO-4, TiO₂/rGO-8, TiO₂/rGO-12, and TiO₂/rGO-16.

2.5 Characterization

Powder X-ray diffraction (XRD) patterns were obtained (PHILLIPS-Xpert MPD) with Cu K α radiation ($\lambda = 1.5406\text{ \AA}$) in the 2θ range from 5 to 60° with a step size of $0.016^\circ\text{ s}^{-1}$ and all samples will be characterized to identify the phases, crystal structure, and crystallite size. The electrical conductivity value of the sample was carried out by measuring it using LCR Meter, and a photocatalytic activity test was carried out using 8 ppm methylene blue solution as a pollutant. The photocatalytic test was carried out in a UV reactor, the samples were irradiated for 15 min using UV exposure with a power of 170–240 V then measured the absorbance using UV-Vis to estimate the percentage degradation of methylene blue solution.

3 Results and Discussion

3.1 Synthesis of RGO-TiO₂ Composite

The synthesis procedure is schematically presented in Fig. 1. Graphite from coconut shell charcoal was oxidized and dispersed using modified Hummer's method to obtain graphene oxide. The graphene oxide was mixed up with TTIP as a TiO₂ precursor using the sol-gel method, followed by a reducing process using microwave irradiation. The final product, rGO-TiO₂ was tested for photocatalyst material for methylene blue solution as pollution. The degraded solution shows that rGO-TiO₂ has good photocatalyst properties.

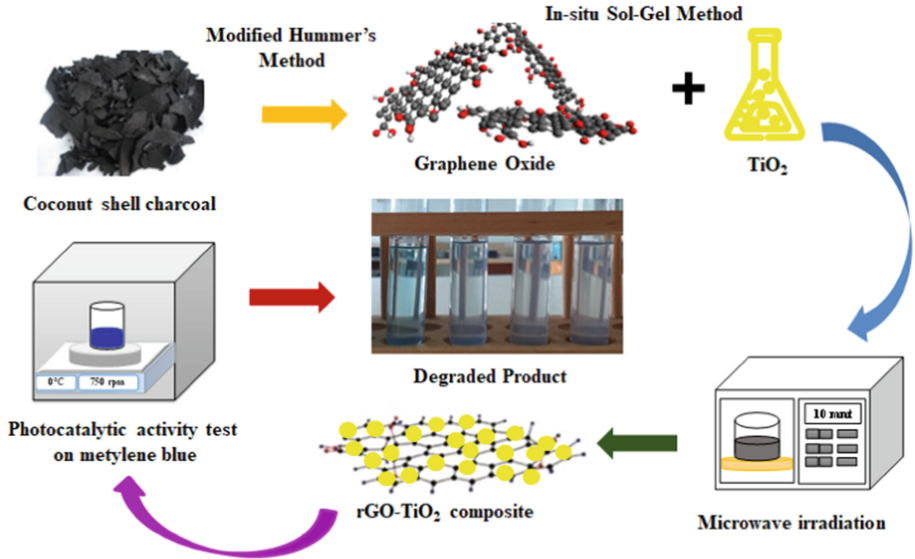


Fig. 1. Schematic illustration for fabrication of rGO-TiO₂ composite. The 8 ppm methylene blue degradation by rGO-TiO₂ composite under UV exposure.

3.2 LCR Meter Result

Before the electric conductivity test using LCR-meter, the rGO-TiO₂ powder had to be pelletized using Polyvinylidene fluoride (PVDF) as a binder to compact the powder. PVDF is in the form of large granules that need to be dissolved with N-Methylpyrrolidone (NMP). The ratio used in this study was 0.08 g of PVDF and 2 mL of NMP. After the powder is formed into pellets, it is heated at a temperature of 100 °C to evaporate the NMP.

This characterization was carried out to determine the electrical conductivity value of the samples. Theoretically, the electrical conductivity of the sample is directly proportional to the performance of the photocatalytic activity. As shown in Fig. 2 the addition of the ratio does not make the conductivity value higher, and the highest electrical conductivity reaches $5.37 \times 10^{-6} \text{ Scm}^{-1}$ for the TiO₂/rGO-4 sample. The results of this study have similarities with the results of research conducted by Selim (2012) in which the photocatalytic activity of the rGO-TiO₂ composite increased with the decrease in the amount of rGO in the composite [28].

3.3 XRD Analysis

XRD analysis has been successfully carried out using the Rietveld method with the help of MAUD software. As shown in Fig. 3, several peaks at 2θ values of 25.1°, 37.7°, 47.7°, and 56.7° can be indexed to (101), (004), (200), and (204) planes of anatase titania, respectively [27], and peak at 2θ values of 28.5° can be indexed to (110) plane of rutile titania. It ought to be noticed that there is no different peak for rGO in the rGO-TiO₂ composite, potentially because of the low amount of rGO [28]. Moreover, the diffraction

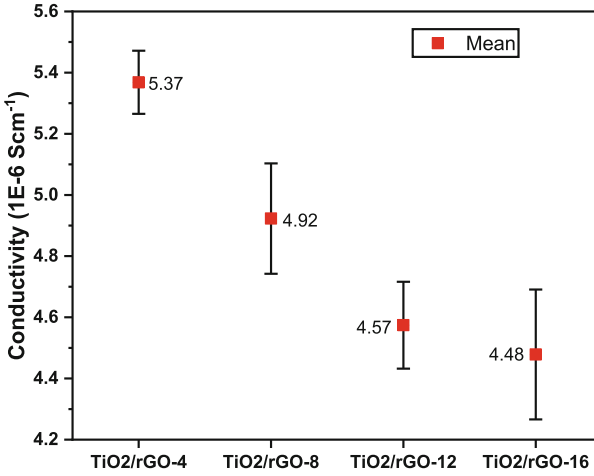


Fig. 2. GO-TiO₂ conductivity value

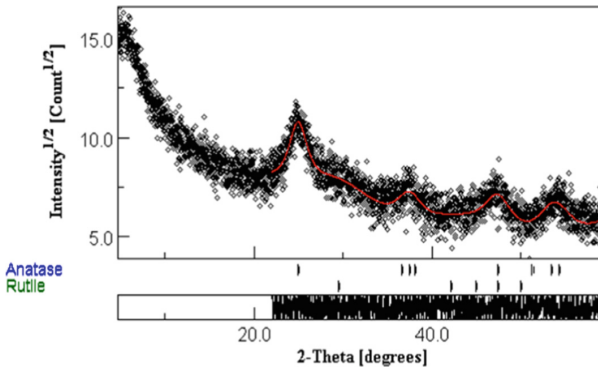


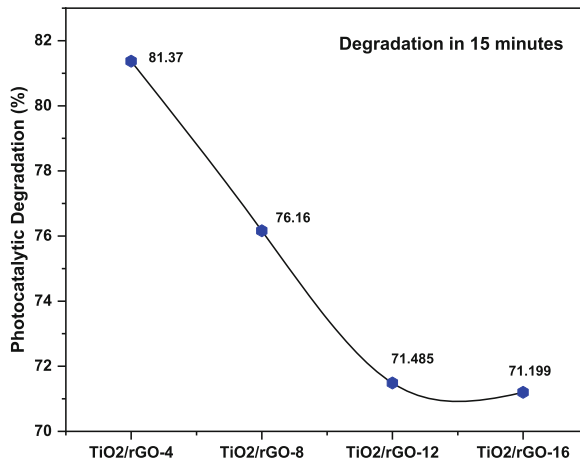
Fig. 3. Refined TiO₂/rGO-4 diffractography

peak of rGO at 24.5° may be covered or over-lapping with the main peak of the anatase phase at 25.1° [29].

Table 1 showed that anatase is more dominant than rutile quantitatively. Moreover, the anatase phase had better photocatalytic activity than the rutile phase. This is due to the anatase phase having a wider surface area than the rutile phase surface area, thus the active surface (defect sites) of each catalytic phase unit is wider than the rutile phase. This can be seen from the energy gap between the anatase phase (3.2 eV) which is larger than the rutile phase (3.0 eV) where the reduction potential value is higher, meaning that the anatase phase is more reactive in absorbing energy from photons [30]. Either way, a blend of anatase and rutile phases causes a high photoactivity, as the consequence of advancing of charge pair partition [31]. On other hand, the anatase phase of TiO₂/rGO-4 has 5.1 nm and the rutile phase has a 4.9 nm crystallite size. According to size and

Table 1. Refinement output from MAUD

Sample	Phases	Crystallite Size (nm)	Rwp
TiO ₂ /rGO-4	Anatase ± 64%	5.1	15.6%
	Rutile ± 36%	4.9	

**Fig. 4.** Photocatalytic degradation of the sample

thermodynamics, anatase is long-term stability in crystal form that has sizes less than 11 nm, brookite between 11 and 35 nm, and rutile more than 35 nm [32].

3.4 Photocatalytic Activity

Finally, to evaluate the photocatalytic degradation of rGO-TiO₂ composites obtained in this work, a model reaction of methylene blue is employed for photodegradation experiments under ultra-violet exposure for 15 min. Before the photocatalytic test, the dye solution with the catalyst was kept in the dark to attain the absorption – desorption equilibrium of the dye with the catalyst.

As can be seen from Fig. 4 the higher percentage degradation in 8 ppm methylene blue solution was in with 81.37% for TiO₂/rGO-4 followed by TiO₂/rGO-8 with 76.16%, TiO₂/rGO-12 with 71.485%, and TiO₂/rGO-16 with 71.199%. This degradation value shows that the photocatalytic activity increased with the decrease in the amount of rGO. Moreover, the sample which has the highest electrical conductivity has the highest percentage of photocatalytic degradation in the methylene blue solution.

4 Conclusion

The rGO-TiO₂ composites are successfully synthesized by a straightforward and naturally harmless few-stage in-situ sol-gel technique. TiO₂ is available in both anatase and rutile phases in the composites. Notably, rGO-TiO₂ composites show good photocatalytic activity toward the degradation of methylene blue under irradiation of UV light. The photocatalytic activity increments with diminishing concentrations of rGO in composites and also the electrical conductivity increases with the same pattern. The best photocatalytic activity is observed with TiO₂/rGO-4, resulting in methylene blue degradation of 81.37% after 15 min under UV light.

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