Graphene/TiO₂ hydrogel: a potential catalyst to hydrogen evolution reaction

VIRGIL CHRISTIAN CASTILLO¹ and JULIET Q DALAGAN^{2,*}

¹Department of Chemistry, Ateneo de Manila University, Loyola Heights, Quezon City 1108, Philippines

²Chemistry Department, Xavier University, Corrales Avenue, Cagayan de Oro City 9000, Philippines

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Abstract. In this study, graphene was synthesized from graphite. Graphite was oxidized via modified Hummer's method and sonicated to form graphene oxide (GO). Infrared spectroscopy revealed the successful oxidation of graphite by the emergence of oxygen functionalities. The spectrum of GO showed peaks at 3270, 1629, 1227 and 1096 cm⁻¹, indicating O–H, C=O, C–OH and C–O–C functional groups, respectively. Graphene hydrogels were prepared by the addition of L-ascorbic acid to GO suspensions and subsequent heating at 90°C. Composite hydrogels of graphene and titanium (IV) oxide (TiO₂) were synthesized with various TiO₂ to GO mass ratios. Composites were applied to photocatalytic hydrogen evolution reaction (HER) and the hydrogen gas produced was analysed by gas chromatography with thermal conductivity detector. Highest HER yield was 66.00% H₂.

Keywords. Graphene; hydrogen evolution reaction; photocatalyst; titanium oxide.

1. Introduction

In 2010, the world's main sources of energy was oil, electricity and natural gas [1]. Oil and natural gas, in particular, are not only nonrenewable but using them also emits harmful substances [2]. On the other hand, hydrogen gas is an alternative fuel with zero emissions. Combustion of hydrogen or usage in fuel cells produces heat or electricity, respectively, with water as by-product [3,4]. Hydrogen is an excellent substitute for current fuels. Hydrogen fuel with the same mass as gasoline can produce three times more energy [5]. However, certain challenges must be overcome before hydrogen fuel can be widespread. Compared by mass, hydrogen has the highest energy output but extremely low density. This causes problems for storage. Since high pressures and low temperatures are needed to store more hydrogen per volume, the net energy output of hydrogen is decreased [5]. This storage problem also limits the mileage of vehicles [3,4]. Another problem is the production of hydrogen gas. Methane is the main source of hydrogen through steam-methane reforming. This is an efficient way of producing hydrogen, but methane is a nonrenewable resource. Hydrogen can be found in a vast number of compounds, but separating hydrogen from these compounds requires energy. Hydrogen can be found in water and organic matters, such as glucose, methane and ethanol [3,5]. Water is very abundant in resource, which makes it suitable for hydrogen gas production if an efficient method of extracting hydrogen is developed.

The objective of this study was to evaluate titanium (IV) oxide/graphene (TiO₂/G) composite as a photocatalyst in

hydrogen evolution reaction (HER). The study is an inquiry into the production of one of the most probable fuels of the future—hydrogen fuel. Production of hydrogen fuel is one of the challenges of the present day. In this study, a very abundant resource was used as a source of hydrogen—water. In addition, the energy input to produce hydrogen was significantly less. The source was only a violet lamp, used to create electron–hole pairs in the semiconductor.

Graphene composite as a photocatalyst has been explored recently due to its excellent electronic properties. Higher photodegradation rates of organic pollutants have been reported for graphene and semiconductor composite, such as on Cu₂O/G composites, in the study by Gao *et al* [6]. Under visible-light illumination, Cu₂O/G composites exhibited higher photodegradation rate of methylene blue (MB), which was attributed to the transfer of excited electrons in the conduction band of Cu₂O to graphene [6]. Fan *et al* [7] also observed an increase in the photodegradation property of ZnO/G composites. Photodegradation of MB using ZnO/G and ZnO demonstrated higher photodegradation using ZnO/G with the highest from a ZnO:G ratio of 50:1 [7]. A study by Wang *et al* [8] used CdS/G composite. The optimum CdS/G for photocatalytic degradation of MB was CdS/G with 5 wt% graphene, due to the uniform dispersion of CdS and just the right distance between CdS particles, which was not achieved with lower graphene content. Higher wt% graphene only decreased the CdS content and increased the scattering of light, which lead to the shielding of the active sites of CdS [8]. Min *et al* [9] created a TiO₂ and graphene composite for MB photodegradation, using a more oxidized graphene oxide (improved graphene oxide or IGO) as precursor. The photoresponse and photocatalytic activity of reduced IGO/TiO₂(IG/TiO₂) composite was approximately

* Author for correspondence (jdalagan@xu.edu.ph)

just the same with G/TiO₂ composite under UV light illumination. However, under visible light, the two IG/TiO₂ composites exhibited higher photoresponse and photocatalytic activity [9]. More efficient photocatalytic hydrogen evolution has also been reported with TiO₂/G composites with the same reasons and limitation discussed above [10,11]. Graphene enhances the photocatalytic activity of semiconductors. The reasons can be summarized into the following; limiting the recombination of photogenerated electron-hole pairs, providing adsorption and catalytic sites, photosensitizing the semiconductor (i.e., narrowing the bandgap size of the semiconductor) and acting as a co-catalyst in the HER [12]. Graphene hydrogel (GH) 3D network is formed by the conjugation of the π - π interaction during the loss of polar groups when GO is reduced [13–15]. In the synthesis of GH, the dispersion of GO is important to create uniform aquatic gels. For this reason, L-ascorbic acid (AA) is usually used as reducing agent, as it produces no gaseous products compared to hydrazine, NaBH₄ and LiAlH₄ [14]. Sonication also produces a well-dispersed solution of GO.

2. Experimental

2.1 Preparation of GO hydrogel

GO was prepared by modified Hummer's method. In brief, 5 g of graphite powder was added with concentrated H₂SO₄ and heated in an oil bath at 80°C for 4.5 h. The mixture was cooled with H₂O, left overnight, filtered and washed with H₂O. The pre-oxidized graphite was added with concentrated H₂SO₄, placed in an ice bath and stirred. Potassium permanganate was added to the solution, stirred and added with H₂O. Hydrogen peroxide was added to the mixture, diluted with H₂O, left overnight and filtered under vacuum the next day.

About 100 mg of dried GO was added to 20 ml of distilled H₂O and sonicated using Branson Ultrasonic Cleaner 5510 (40 kHz). Five hundred (500) mg of AA was dissolved in the aqueous GO by sonication and it was heated in a 90°C water bath for 4 h. The resulting GO hydrogels were left undisturbed overnight at room temperature and evaluated by inversion method. The hydrogels were then filtered, washed, dried in an oven at 50°C and analysed by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM).

2.2 Preparation of TiO₂/G composite hydrogel

Approximately 100 mg of GO was placed in four vials and 20 ml of distilled H₂O was added. The vials were sonicated for 3 h. A quantity of 200, 300, 400 and 500 mg of TiO₂ was added to different vials followed by 250 mg of AA. The vials were then sonicated for 5 min and heated at 90°C for 4 h. The composites were labelled 2TiO₂/G, 3TiO₂/G, 4TiO₂/G and 5TiO₂/G. The TiO₂ to GO mass ratios were 2:1, 3:1, 4:1 and 5:1.

2.3 Instrumental characterizations

FTIR spectroscopy was done on graphite, GO and TiO₂/G hydrogel to determine the functional groups present using Perkin-Elmer Spectrum 100. Morphology was examined by SEM in the Physics Department of De La Salle University.

2.4 Swelling tests

Approximately 20 mg of a composite was placed in a pre-weighed 50-ml beaker. Twenty (20) ml H₂O was added and left for 48 h at room temperature in the locker. Excess water was decanted. The beaker was air-dried for 2 h, then weighed. Percent swelling ratio was calculated as shown in equation 1, where m_s and m_d stand for the mass of the swollen and dry hydrogel, respectively. This was compared to the % swelling of rGO.

$$\% \text{ Swelling} = \frac{m_s - m_d}{m_d} \times 100\%. \quad (1)$$

2.5 Photocatalytic HER

Photocatalytic tests were done in stoppered Erlenmeyer flasks connected to Tedlar gas sampling bags. One hundred (100) mg of TiO₂/G was dispersed in a mixture of 150 ml of distilled H₂O and 50 ml of ethanol (96%, v/v). The solution was magnetically stirred while being irradiated with a violet lamp (420 nm) for 10 h. The sampling bags were then inflated with helium. Gas samples had to be forced into a sampling loop, which required inflated bags to be pressured into the sampling loop. The content of the bags were analysed by Agilent 7820A gas chromatograph with thermal conductivity detector (GC-TCD) (Pilipinas Kao Inc., Jasaan, Misamis Oriental). Blank tests were also conducted, wherein the same procedure was followed but no photocatalyst was added.

3. Results and discussion

3.1 Preparation of GO

GO was synthesized from graphite through oxidation. The infrared (IR) spectra overlay of GO and graphite are shown in figure 1. The IR spectrum of graphite shows no IR active groups. Graphite does not have polar groups and is symmetrical, as pi electrons are delocalized. The IR spectrum of GO shows a broad peak at 3270 cm⁻¹, sharp peak at 1629 cm⁻¹, weak bands at 1489, 1227 and 1096 cm⁻¹, which indicate O-H stretching, C=O stretching, O-H deformation of C-OH groups, C-OH stretching and C-O-C stretching, respectively. The presence of oxygen functional groups indicates that graphite has been oxidized to GO [6,8,16,17].

Scanning electron micrographs in supplementary figure S1 revealed the difference in the morphology of graphite and GO. Graphite appeared as flat and smooth thick sheets, while GO looked soft. GO does not have surfaces as smooth as

graphite due to the oxygen functionalities. The thickness of graphite is due to the stacked graphite layers [18].

3.2 Optimization of GH synthesis

The optimum sonication time was 3 h. Sonication is the exfoliation step in the synthesis of GO. The longer the GO is sonicated, the more the layers separate and the more layers are fractured [19]. Separation of GO layers is also dependent on the type of sonicator. A probe sonicator disperses GO better than a bath sonicator, which was used in this study. The properties of graphene depend on the number of layers [20,21]. Hydrogels produced from 1 and 2 h of sonication were broken by inverting the vial, as shown in supplementary figure S2.

Heating for 1, 2 and 3 h produced hydrogels that were broken, as depicted in supplementary figure S3; thus, the optimum heating time was 4 h. Heating is needed to increase the

rate of GO reduction. As GO is reduced to graphene, pi bonds are regained and interact in between layers. This interaction is what links graphene layers into a GH. Supplementary figure S3a shows an incomplete reaction. The hydrogel has not even taken form yet. As shown in supplementary figure S3b and c, hydrogels have formed but was broken indicating incomplete gelation. This means not all graphene layers have been linked, as not all have been reduced to graphene.

Supplementary figure S4 shows the hydrogels formed with different AA masses. IR spectroscopy was needed to confirm the reduction of GO when AA mass was optimized. AA reduces GO; unreacted AA helps in the uniformity of the dispersion of reduced GO (rGO). GO reduction restores π - π interactions, which attract rGO layers and causes assembly of 3D rGO sheets [22]. Supplementary figure S5 reveals that all AA masses were enough to reduce GO. This was proven by the significantly decreased 3270, 1629, 1489, 1227 and 1096 cm^{-1} peak intensity as compared to GO, and the emergence of weak peaks at 1585 cm^{-1} attributed to the C=C skeleton of rGO [6,8,17]. However, the hydrogel from 125 mg of AA was broken by the vial inversion as shown in supplementary figure S4. The optimum AA mass is 250 mg, as no difference could be observed between 250 and 375 mg.

3.3 Preparation and characterization of TiO₂/G composite hydrogels

Figure 2 shows the IR spectra of the photocatalysts contrasted to TiO₂ and GO. The spectra show that GO has been reduced in the photocatalysts, as 3270, 1629, 1489, 1227 and 1096 cm^{-1} peaks are diminished. TiO₂ spectrum shows a peak centred near 500 cm^{-1} , which is attributed to the Ti-O-Ti vibration. Higher peaks near 500 cm^{-1} in the composites are attributed to Ti-O-C [22] but the shift to left (blue shift) of these peaks compared to Ti-O-Ti is not very pronounced. However, the evident C=C stretching peak of the composites

Figure 1. IR spectra of graphite and GO.

Figure 2. IR spectra of TiO₂, 2TiO₂/G, 3TiO₂/G, 4TiO₂/G, 5TiO₂/G and GO.

at 1581 cm^{-1} means Ti-O-C bonds have been formed. C=C bonds connected to other C=C such as in GH or graphite do not produce IR peaks, because vibration is symmetrical.

C=C bonds connected to Ti-O would produce asymmetrical stretching vibration giving rise to a band at 1581 cm^{-1} [6,8,17].

Figure 3. Micrographs of (a) $2\text{TiO}_2/\text{G}$, (b) $3\text{TiO}_2/\text{G}$, (c) $4\text{TiO}_2/\text{G}$, (d) $5\text{TiO}_2/\text{G}$, (e) and (f) higher magnifications.

The hydrogel structure of the composites was proven by SEM and swelling tests. Figure 3 reveals the interconnected graphene layers. This is clearer in 3TiO₂/G. Some of the hydrogel pores are encircled in figure 3; graphene sheets appear as flat surfaces and TiO₂ particles appear as deformed spheres. Interconnected layers are not very evident because the hydrogels were oven-dried at 50°C. Drying the hydrogels when H₂O was in liquid state created menisci, which exerted pressure on the hydrogel. Pressure was relieved by shrinkage [23], i.e., bringing of the rGO sheets closer together. Preventing shrinkage of hydrogel could be done by avoiding a meniscus such as freeze drying and supercritical CO₂ exchange [23].

In addition, compared to micrographs of other studies [13,14,22], the GH in figure 3e and f appeared too flat and smooth as compared to being soft. This may indicate too many layers of graphene stacked. The stacking of the rGO may have been due to van der Waals forces and π - π stacking interaction [24]. The stacking may also have occurred due to the collapse of the GH structure because of the drying method employed. However, with the addition of TiO₂ inside the GH, the composite did not collapse. Swelling was enhanced as revealed by the swelling test. The TiO₂ in graphene has a greater swelling compared to the GH [23].

Swelling tests were conducted to investigate the primary attribute of hydrogels, which is to retain water. Swelling tests revealed a significant difference in the swelling property between the hydrogel composites and rGO. Swelling percentages are shown in supplementary figure S6. The composites retained more water than rGO due to the pores in the hydrogel. Pores are sites in which water can be absorbed; these bound waters are called free water [25]. This is a proof of the hydrogel structure of the composites.

3.4 Hydrogen evolution reaction

Hydrogen evolution reaction happens by photocatalysis. UV light excites electrons in TiO₂, which creates free electrons and holes. The electron reduces H⁺ ions into H₂ gas, while the hole oxidizes H₂O into O₂ [26]. The hydrogen gas yield of the photocatalysts with different mass ratios of GO and TiO₂ is shown in figure 4. The addition of rGO to TiO₂ increases the H₂ yield only when the ratio was 5 times (5TiO₂/G). At this ratio, the composite hydrogel must have attained a uniformly dispersed graphene/TiO₂ for a typical 3D network structure, where TiO₂ is evenly distributed in the graphene matrix [24]. This could have ensured transfer of electrons stereoscopically through the 3D network, leading to an improvement in the photocatalytic activity. Zhang *et al* [27] reported an enhanced photocatalytic activity with an increasing ratio of TiO₂ to graphene. The other mass ratios may have been too low which caused shielding. This is even more significant with the thickness of graphene conjectured in figure 3. A higher number of layers would allow less light to pass through graphene [20,21], which would prevent electron from being photoexcited.

Figure 4. Hydrogen yields of TiO₂, 2TiO₂/G, 3TiO₂/G, 4TiO₂/G and 5TiO₂/G.

4. Conclusions

GO was synthesized by modified Hummer's method and was used as starting material in fabricating GHs. Optimum conditions for GH synthesis were 3 h of sonication, 4 h of heating and 250 mg AA. TiO₂/G composite hydrogels were synthesized with 2:1, 3:1, 4:1 and 5:1 TiO₂ to GO mass ratio. Synthesis of the composites was confirmed by FTIR analysis while the hydrogel structure of the composites was established by SEM and swelling tests. Monitoring of the amounts of hydrogen gas was done by GC-TCD. The ratio 5TiO₂:1GO yielded the highest amount of H₂ gas.

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Electronic Supplementary Material

Supplementary material pertaining to this article is available on the Bulletin of Materials Science Website (www.ias.ac.in/matursci).

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