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Preliminary studies of the impact of synthesis method on Reduced Graphene Oxide-Titanium Composite

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ABSTRACT There are two current major challenges aroused by the continued usage of fossil fuels as the energy source, which are the production of high levels of carbon dioxide (CO_2), resulting in global warming, and concerning the use of energy resources. There is a clear need to explore new prospects for CO_2 capture to prevent it from penetrating into the atmosphere. Carbon Capture and Conversion (CCC) method is one of the alternative solutions in carbon management. The synthesized reduced graphene oxide-Titanium (rGO-TiO_2) composites used in this preliminary study is the CCC material which will potentially capture the carbon dioxide (CO_2) and convert it into a hydrocarbon fuel such as methane. The aim of this preliminary study is to examine the impact of synthesis method and raw material to synthesize the rGO-TiO_2 composite. The photocatalytic activity was measured by using the Gas Chromatograph (GC) while the optical properties were measured by using Electrochemical Impedance Spectroscopy (EIS) and fluorescent spectrometer (PL). The EIS, PL and GC results confirms that the synthesize method and raw materials were affect the optical properties and the photocatalytic performance of the rGO-TiO_2. The rGO-TiO_2(H1) which was synthesized using the TBT powder via Hydrothermal method shows the best electrical properties and lowest recombination rate of the photogenerated electron-hole pairs compared to the other samples. The rGO-TiO_2(H1) also shows the highest photoreduction performance with 0.722 $ų_{mol}/g_{cat}$ methane yield.

KEYWORDS: Titanium Dioxide; Reduced Graphene Oxide; Photocatalyst; Carbon dioxide; Methane.
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INTRODUCTION

The reduction of CO_2 via photochemical technology using heterostructure photocatalyst may become a critical step to produce solar fuels (Tahir & Amin, 2013). More progress needs to be accomplished before this technology can be effectively implemented on an industrial scale. Excessive quantities of CO_2 will therefore be eliminated from the environment and a low-pollution energy supply will be supplied to society, emphasizing the production of energy systems that are reliable, economical, and clean.

Titanium Dioxide (TiO_2) is the metal oxide which is most widely being studied in classical photocatalyst. The photocatalytic properties of TiO_2 are attributed to the production of photogenerated electrons in the conduction band (CB) and holes in the valence band (VB), which can only absorb short wavelength light, which falls in the UV region (10-400 nm) due to the relatively large band gap (3.0-3.2 eV) of TiO_2 (Mustafa *et al*., 2020). The carbon-based nanomaterials such as graphene, graphene oxide (GO), reduced graphene oxide (rGO) and Graphene Carbon Nitride were employed in various energy and environment applications (Han *et al*., 2016). The addition of small percent carbon nanomaterial in metal oxide TiO_2 photocatalysts can enhance the photoactive nature, increase the recombination time of charge carriers, and show a superior electron capturing and transportation properties (Wang *et al*., 2014).

Fast charge recombination rate and limited spectral response are the two common issues in photocatalyst which hindered their commercial applications. The heterojunctions photocatalyst strategy can combine the advantages of the coupled semiconductors and effectively facilitate the charge transport (Low *et al*., 2017). The alignment of the crystal phase, band structures, and interfacial contact of the contacted materials are essential for the successful construction of heterojunctions (Tahir *et al*., 2019). Therefore, the coupled semiconductors using Titanium dioxide and carbon based photocatalyst was synthesized in this study. The impact of its synthesis method and raw material was examine. The Electrochemical Impedance Spectroscopy (EIS) and fluorescent spectrometer (PL) were examined to analyze its electrical and optical properties while the Gas Chromatograph (GC) testing to confirm and measure its photoreduction activity.

BACKGROUND THEORY

CO_2 methanation, known as Sabatier reaction, generates methane (CH_4) through CO_2 hydrogenation is shown in Equation (1) (Shen *et al*., 2020). Reducing CO_2 to CH_4 involves a transfer of eight electrons and thus high kinetic barrier exists. The H_2, CH_4 and H_2O are the primary reductants used in CO_2 reduction process. The total yield of methane (CH_4) gas can be calculated by using Equation (2) (Tan *et al*., 2014). In an aqueous environment, pure TiO_2 can only generate CH_4 and CO under simulated sunlight irradiation, with a very high CO_2 reduction rate to CH_4 and CO at room temperature (Wang *et al*., 2017). The generation rate of CH_4 and CO for graphene-based photocatalysts is about 9 times higher compared to pure TiO_2, such as CH_3OH, CH_3COH and HCOOH (Han *et al*., 2016).

$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O \tag{1}$$

$$\text{Total } CH_4 \text{ yield} = \frac{\text{total amount of } CH_4 \text{ produced } (\mu\text{mol})}{\text{amount of photocatalyst used (g-catalyst)}} \tag{2}$$

METHODOLOGY

Graphite Oxide (GO) powder, Tetrabutyl Titanate powder (TBT), Anatase P90 TiO_2 powder, ethylene glycol (EG), acetic acid (HAc) and Ammonium hydroxide (NaOH) are the raw material used to prepare the rGO-TiO_2 composites. There are 4 samples had been synthesized and characterized in this preliminary study. The pure titanium, denoted as TiO_2 while the rGO-TiO_2 synthesized via solvothermal method denoted as rGO-TiO_2(S). The rGO-TiO_2 (H1) and rGO-TiO_2 (H2) were synthesized via hydrothermal method by using different titanium raw material. The chemical properties of these four samples were characterized and tested using electrochemical impedance analysis (EIS), photoluminescence (PL) and gas chromatography (GC).

Figure 1 shows the flow chart of Graphene Oxide preparation via Hummer's method. The graphite powder undergoes the stir, wash, filter, dry and centrifuge process to produce the Graphene Oxide powder as the source of Reduced Graphene Oxide (rGO).

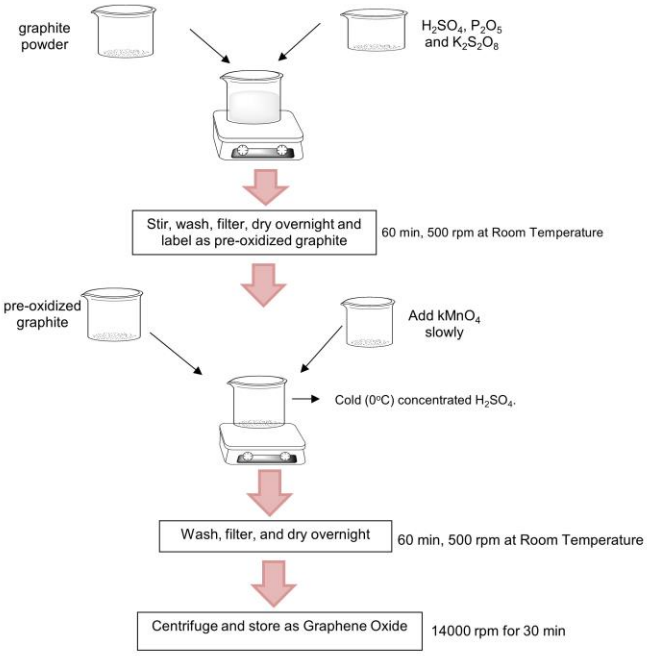

Figure 1. Preparation of Graphene Oxide via Hummers method

Figure 2 shows the flow chart of rGO-TiO2(H1) and rGO-TiO2(H2) preparation via hydrothermal method. The rGO-TiO2 (H1) was synthesized using the TBT powder as the raw material while the rGO-TiO2 (H2) were using the anatase P90 TiO2 powder. The distilled water and the Ammonium hydroxide (NaOH) were the solvent used in this hydrothermal method.

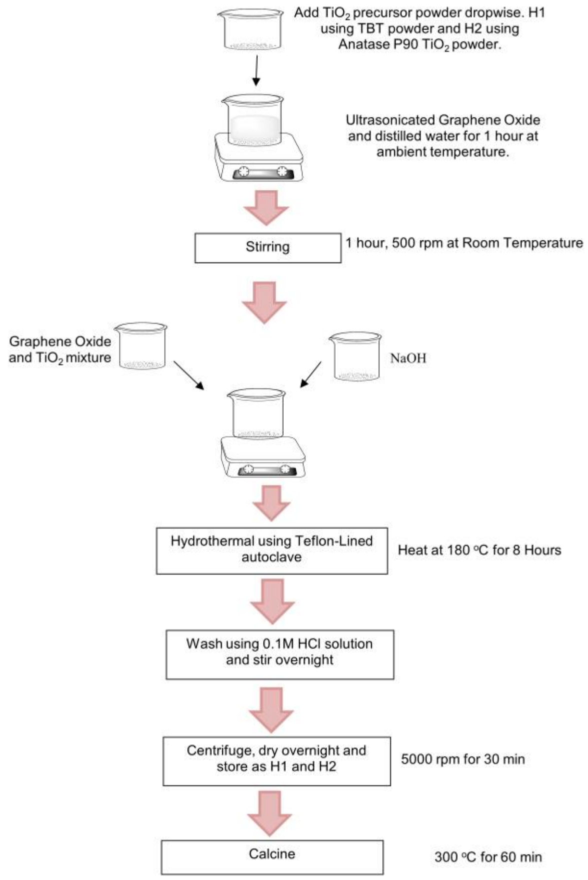

Figure 2. rGO-TiO2 (H1) and rGO-Anatase TiO2 (H2) preparations via hydrothermal method

Figure 3 shows the flow chart of rGO-TiO_2(S) preparation via solvothermal method. The rGO-TiO_2 (S) was synthesized using the TBT powder as the raw material and ethylene glycol (EG) and acetic acid (HAc) were used as the solvent in this solvothermal method.

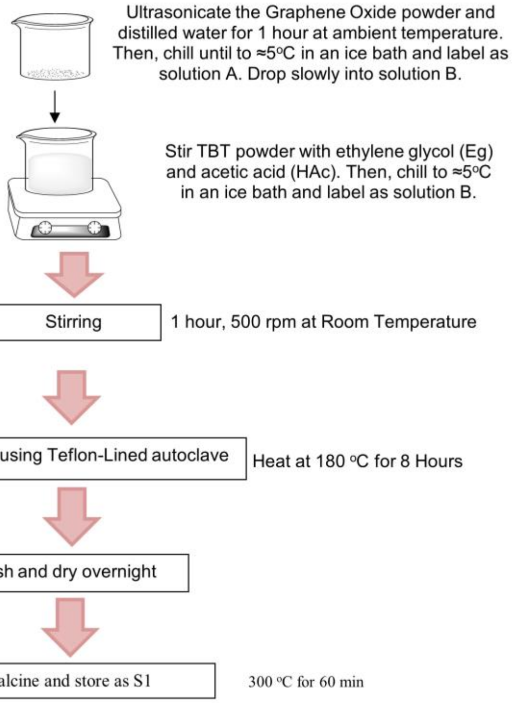

Figure 3. rGO-TiO_2 (S) preparation via solvothermal method

RESULT AND DISCUSSION

The four samples were successfully synthesized and characterized using SEM, EDX, XRD EIS, and PL measurements. In this research paper, the data obtained from EIS, PL and GC will be reported and discussed. The Nyquist Plot (NP) in EIS result can be used to determine the electrical properties of the four samples as shown in Figure 4. The recombination rate of the photogenerated electron-hole pairs can be interpreted using the PL spectrum as shown in Figure 5 and 6. Finally, the photoreduction and conversion activity was interpreted from the GC results as shown in Figure 7.

The electrical resistance of material can be measured directly from the NP spectrum in Figure 4. The lower the intensity of NP spectrum, the higher the resistance on that composite which leads to decelerating its recombination rate. The rGO-TiO_2(H1) shows the lowest intensity of NP spectrum, indicating that it has the lowest recombination rate compared rGO-TiO_2 (H2) and rGO-TiO_2(S) composites. Besides that, the three rGO-TiO_2 composites show a lower intensity of NP spectrum compared to the pure Titanium, TiO_2. The uniqueness transport properties of rGO occurred due to its two-dimensional π-conjugation structure (zero bandgap) and the massless fermions of its electron holes (Wang *et al.*, 2014). From this analysis, we can conclude that the recombination rate of electrons and holes pairs were depends on the synthesis methods and raw material. The recombination rate was decreased as the following order TiO_2> H2 > S > H1 which led to the increase of their photoreduction and conversion performance. This NP results successfully support the PL as discussed in the following.

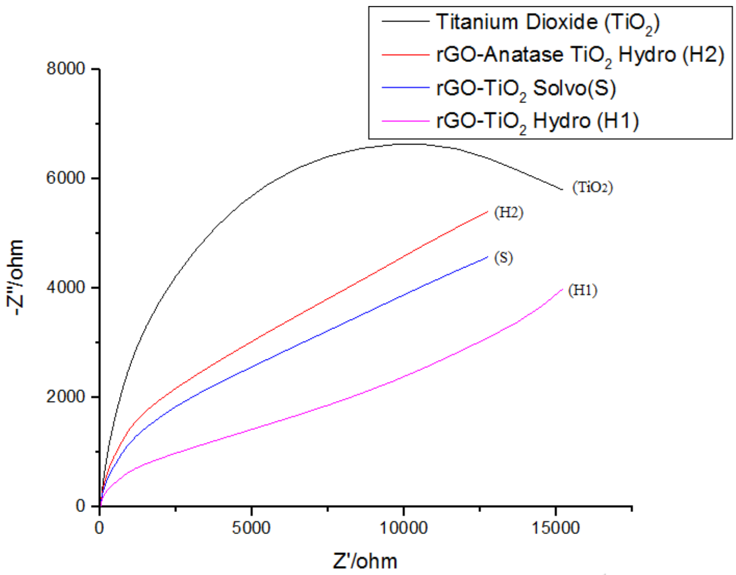

Figure 4. Nyquist Plots of TiO_2, rGO-TiO_2(H1), rGO-TiO_2 (H2) and rGO-TiO_2(S).

The photocurrent versus time (I-t) curves of composites are shown in Figure 5. The transient photocurrent response was performed to determine the quantity and quality of active electron on composite which enhance their photocatalytic performance. The higher the intensity of PC spectrum, the higher the active electron detected on that composite. The results clearly show that, the rGO-TiO_2(H1) has the highest intensity of PC spectrum indicate its most active electron compared to rGO-TiO_2(H2) and rGO-TiO_2(S). Therefore, it can be concluded that, the synthesis methods and raw material were affecting the production of active electron in composite. Besides that, the rGO-TiO_2(H1) showed the highest anodic PC density which was around 0.7ųA/cm^2 when the light source was switched on. The zero detected current was negligible when the light source was switched off. The rapid, steady, prompt, and reproducible transient PC spectra during several times switched on and off the cycles of the visible light irradiation, indicating that the photogenerated electrons from the TiO_2 were collected efficiently. In addition, the three rGO-TiO_2 photocatalyst shows an increasing intensity of PC spectrum compared to pure titanium, TiO_2. The total active electron detected has increased as the following order: TiO_2 with 0.25ųA/cm^2 > rGO-TiO_2(H2) with 0.35 ųA/cm^2 > rGO-TiO_2(S) with 0.4ųA/cm^2 > rGO-TiO_2(H1) with 0.6 ųA/cm^2.

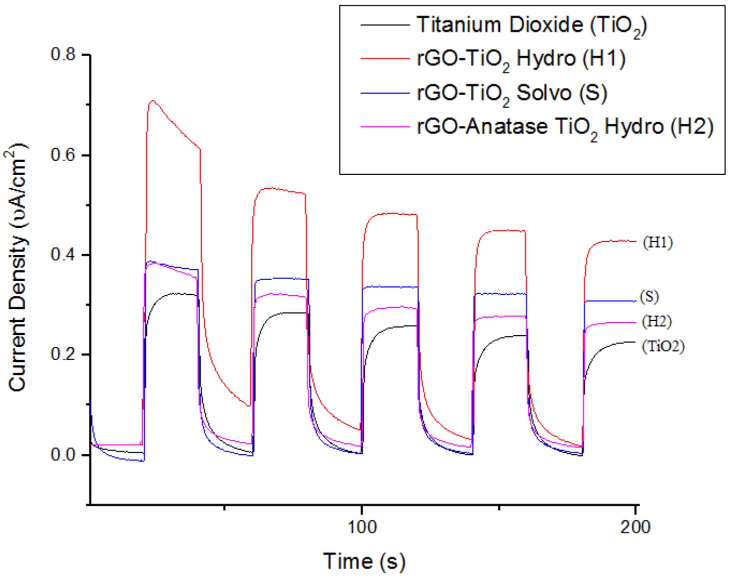

Figure 5. Photocurrent versus time (I-t) curves of TiO_2, rGO-TiO_2(H1), rGO-TiO_2 (H2) and rGO-TiO_2(S).

The intensity of PL spectrum for all samples are shown in Figure 6. The PL quenching effect is the efficient method to understand the emission mechanism and charge transfer in the composite. The intensity of PL spectrum illustrates the recombination rate of the photogenerated electron-hole pairs. The higher the intensity of PL spectrum, the faster the recombination rate perform in that composite. As clearly shown in Figure 6, the intensity of PL spectrum was decreasing from TiO_2, rGO-TiO_2(H2), rGO-TiO_2(S) and rGO-TiO_2(H1) composite, indicating that the recombination rate is getting slower. The rGO-TiO_2(H1) shows the lowest intensity of PL spectrum compared the other samples. The presence of the Schottky barriers at the interface of rGO were collected and they trapped the excites electron which help to decelerate the electron holes recombination rate (Tan *et al.*, 2014). The accuracy of this PL data was supported by the NP plot results in Figure 4 and the photocatalytic testing results in Figure 7.

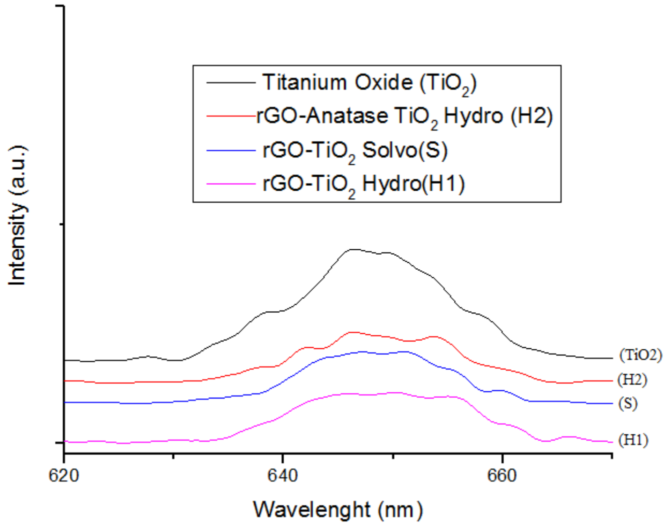

Figure 6. PL spectrum intensity of TiO_2, rGO-TiO_2(H1), rGO-TiO_2(H2) and rGO-TiO_2(S).

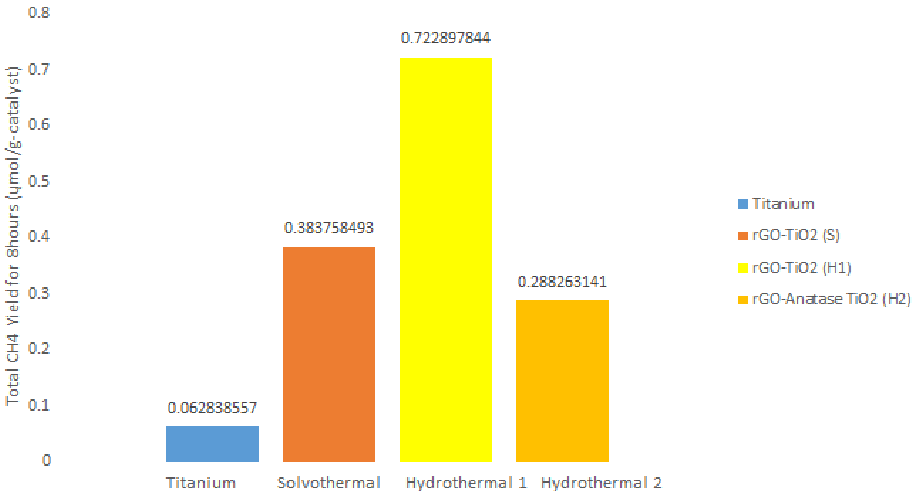

Figure 7. Photocatalytic testing over TiO_2, rGO-TiO_2(H1), rGO-TiO_2(H2) and rGO-TiO_2(S) under visible light irradiation

The photoreduction activity was tested using the GC for all four samples under visible light irradiation for 8 hours. Figure 7 shows the total methane gas yields of methane which was calculated by using equation 2 and plotted. The rGO-TiO_2(H1) photocatalyst has the highest CH_4 yield with 0.722 ɥ$_{mol}$/g$_{cat}$ compared to TiO_2, rGO-TiO_2(H2) and rGO-TiO_2(S) composite with 0.06 ɥ$_{mol}$/g$_{cat}$, 0.28

ų$_{mol}$/g$_{cat}$ and 0.38 ų$_{mol}$/g$_{cat}$ respectively. These results prove that the manipulation of synthesize method and raw material were affect the photoreduction activity of composite. Besides that, it can be concluded that, the intimate contact between this couple semiconductor, TiO_2 and rGO were successfully enhance the photoreduction activity. Their intimate contact was accelerating the transfer of photogenerated electrons on TiO_2 to rGO and decelerate the recombination rate of charge carrier which aligns with the results and statement reported by previous researchers (Chen *et al*., 2014; Liu *et al*., 2017; Shavanova *et al*., 2016).

CONCLUSION

The impact of synthesis method and raw material were study and examine in our reduced graphene oxide-Titanium (rGO-TiO_2) composites. This preliminary data to confirm the relation between synthesize method and the electrical, optical and photoreduction activity of the composite. The electrical properties were measured by using Electrochemical Impedance Spectroscopy (EIS), the optical properties were illustrated via fluorescent spectrometer (PL) and the photoreduction activity was measured by using the Gas Chromatograph (GC) result. In Conclusion, the synthesize method and raw materials were affect the properties and the photocatalytic performance of the rGO-TiO_2. The rGO-TiO_2(H1) which was synthesized using the TBT powder via Hydrothermal method shows the best properties and lowest recombination rate compared to the other samples. The rGO-TiO_2(H1) also shows the highest photoreduction performance with 0.722 ų$_{mol}$/gcat methane yield. The success in synthesizing the couple semiconductor based on TiO_2 and carbon-based photocatalyst via simple and green method are the other beneficial in this preliminary works. This synthesize method is potentially used to produce a high grade of rGO–TiO_2 at the large scale in the future due to its environmentally friendly raw material, low equipment cost and efficient experimental works.

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