Synthesis of TiO$_2$/GO nanocomposite for Methylene Blue Degradation

L. D. Kasmiarno$^1$, D. Floresyona$^1$, R. Raissa$^2$, N. S. Pambudi$^3$

$^1$Department of Chemical Engineering, Faculty of Industrial Engineering, Universitas Pertamina, 12220, DKI Jakarta, Indonesia
$^2$Department of Chemistry, Faculty of Industrial Engineering, Universitas Pertamina, 12220, DKI Jakarta, Indonesia
$^3$Department of Chemical Engineering, Universiti Teknologi Petronas, Seri Iskandar, Perak 32610, Malaysia
*e-mail: laksmi.dewi@universitaspertamina.ac.id.

Abstract
In using visible light for commercially available photocatalytic TiO$_2$ powder, the alteration of its chemical structure is required in which a metal or non metal ion is introduced to the naturally TiO$_2$ compound in a process called doping. In this study, a graphene oxide is chosen as composite that can be functioned under visible light irradiation since it can extended light absorption range and can improved activity of TiO$_2$/GO nanocomposite for enhancing charge separation. The TiO$_2$/GO nanocomposite were characterized by SEM, TEM, XRD, and FT-IR. The TiO$_2$/GO nanocomposites was active for reduction of Methylene Blue in aqueous media.

Keywords: TiO$_2$/GO synthesis; Degradation; Photocatalytic Reduction

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Introduction
Recently, Water is the most essential resources for the existence of all beings. Nevertheless nowadays, water poses a serious threat to all beings, from aquatic to human. Serious environmental pollution problem has arouses due to the increase of organic waste induced by industrial and human activitie [1].

Photocatalyst have shown great potential in water treatment. Photocatalyst such as TiO$_2$, ZnO, CdS have applied for the degradation of organic pollutants in aqueous solution. Among the several researchs, TiO$_2$ is the most active and stable photocatalyst based on photochemical stability, non-toxicity, and affordable price to process [2]. Many researchers had been made using TiO$_2$ based photocatalytic oxidation to photocatalytic decomposition and invactivation of bacteria and viruses. But TiO$_2$ has major drawbacks including rapid charge recombination and absorpt a small portion of solar spectrum since TiO$_2$ has relatively large band gap. [3]–[5]

Photocatalysts are semiconducting material. ZnO, TiO$_2$, BiOCl, CdS, etc, are several examples of semiconducting materials which are commonly used in photocatalysis. Among those semiconductors, TiO$_2$ is the most commonly used semiconductor for application in photocatalysis because of its strong photocatalytic performance, availability, long-term stability, non-toxicity, chemical inertness, and low cost [6]. However, the fast electron-hole pairs recombination after excitation process of TiO$_2$ significantly limits the efficiency of the photocatalytic reaction. In addition, due to its large band gap (@ 3.2 eV), TiO$_2$ will only active under UV light irradation, while the solar spectrum mainly consists...
of visible light (44 %) and infra-red (53 %), with a small proportion of UV radiation (4 %). Thus the utilization of solar light as the source of energy for photocatalysis on TiO₂ appears to be not efficient.

The modification of TiO₂ with metal plasmonic nanoparticles is expected can enhance the absorption of TiO₂ towards visible light. While, combining TiO₂ with reduced graphene oxide can effectively suppressed the electron – holes recombination, thus increase the catalytic activity. To the best of our knowledge, the composites of plasmonic metal nanoparticles-reduced Graphene oxide-TiO₂ which are used as photocatalysts for organic pollutant degradation under visible light have not been explored.

Material and Methods

Materials
Graphite fine powder, Titanium (IV) isopropoxide, Sulfuric acid, Phosphoric acid were purchased from merck. Kalium permanganate and Methylene blue were purchased from SAP and sigma aldrich respectively.

Methods
Synthesis of Graphene Oxide
Graphene Oxide was synthesized using modified Hummer methods [7]. The mixture of H₂SO₄, H₃PO₄, and KMnO₄ was added to a mixture of graphite and heated to 50 °C and stirred for 12 hours. The mixture is centrifuged and dried to get the solid precipitation.

Synthesis of Graphene Oxide-TiO₂ nanocomposite
The procedure was modified from [8]. Graphene Oxide-TiO₂ was prepared via sol gel at low pH. Graphene oxide solid was diluted in DI water and isopropanol alcohol then put in bath sonicator for 1 hour. titanium isopropoxide (TTIP) was added in solution under stirring condition. The pH solution was adjusted to pH 2 using HCl the continuously stirred overnight. The precipitation was separated using centrifuge and dried in vacuum oven for 12 h.

Characterization of samples
FTIR (Fourier Transform Infrared Spectroscopy) spectra were obtained using Thermo scientific iS 5 with infrared scan from 4000 to 400 cm⁻¹. X-ray Diffractmeter (XRD) were conducted using X’Pert³ Powder abd Empyrean Panalytical with Cu Kα irradiation (λ=1.54) range of diffraction angles (2θ) from 10 to 70° with with step size of 0.01°/step and exposure time of 1s/step. Different phases were determined by using JCPDS library in X’Pert High Scope Plus software.

Photocatalytic Degradation of methylene blue under UV radiation
The photocatalytic performance was evaluated by photodegradation activity of methylene blue experiment. Various concentration of methylene blue were investigated of photodegradation under UV condition. 2 g of TiO₂/GO with different GO ratios are individually selected and mixed with the 40 ppm of methylene blue mixture in the dark without providing any illumination. After 1 hour, the 10 UV lamp with 9 watt each is turned on to provide light source. The experiment is then continued for 6 hours with samples taken at interval 1 hours. Lastly, the samples taken is measured for its absorbance value using a UV-VIS spectrophotometer and the decreasing value in absorbance value represents the degradation of the methylene blue solution. A standard calibration curve for methylene blue is made beforehand so that any changes in absorbance value, we are able to determine the concentration of methylene blue at the absorbance value obtained from the UV-VIS spectrophotometer.

Result and Discussion

Characterization of TiO₂-GO composites
FTIR (Fourier Transform Infrared Spectroscopy) was employed to identify the Graphene oxide content in TiO₂-GO composites. The range for an infrared region within the electromagnetic spectrum falls between wavenumber 12800 ~ 10 cm⁻¹, in which can be further categorized into three different
classes which are near-infrared (12800 ~ 4000 cm\(^{-1}\)), mid-infrared (4000 ~ 2000 cm\(^{-1}\)), and far-infrared (50 ~ 1000 cm\(^{-1}\)) regions. As samples are exposed to infrared radiation, they absorb specific wavelengths of incoming radiation resulting in the generation of peaks as shown in Figure 1.

The FTIR spectra show the existence of Ti-O bond at around 596.89 cm\(^{-1}\), the peak at around 1038 cm\(^{-1}\) shows the appearance of C-O bond, while the C=C bond can be seen around 1614 cm\(^{-1}\). The broad peak around 3200 cm\(^{-1}\) is due to the O-H bending and stretching vibration of surface adsorbed water [9], [10].

Figure 1. FTIR image of a. Graphene Oxide (GO), b. TiO\(_2\) P25, c. TiO\(_2\) 30%/GO, d. TiO\(_2\) 50%/GO, and e. TiO\(_2\) 80%/GO

Figure 2. shows the result for XRD analysis for samples TiO\(_2\) and TiO\(_2\)-GO with different GO concentration ratio. The X-Ray diffraction characterizations provides information of the developed catalysts phase and crystal structure for the determination on the degree of structural order in solid phase, arrangement of atoms and molecules as well as the physical structure which are influenced by factors such as hardness, density, transparency, and diffusivity.

By analysis the XRD pattern of TiO\(_2\)-GO, it can be observed that similar XRD patterns are shown for all samples containing GO and TiO\(_2\). However the pure TiO\(_2\) XRD pattern have a slight pattern difference from the other TiO\(_2\)-GO samples due to an extra diffraction peak at 2\(\theta\) = 10.57\(^\circ\). TiO\(_2\)/GO
photocatalysts as well as TiO$_2$ has major diffraction peak which is located at $2\theta = 25.3$ and 25.6 for samples TiO$_2$ and TiO$_2$-GO respectively.

![XRD Spectra of TiO$_2$ and TiO$_2$/GO with various TiO$_2$ variable](image)

**Figure 2.** XRD Spectra of TiO$_2$ and TiO$_2$/GO with various TiO$_2$ variable

Figure 3. shows a SEM and EDX spectrum of the GO after added with TiO$_2$. The size of TiO$_2$ crystallites was ~ 10 $\mu$m. The EDX spectrum shows distinct peaks attributed to Ti, strong peak from C and O since amount of GO was used in synthesis.

![SEM image and EDX spectrum of TiO$_2$/GO](image)

**Figure 3.** SEM image and EDX spectrum of TiO$_2$/GO

Figure 4. shows the percentage degradation curve for all photocatalyst samples synthesized. It can be seen that the photocatalyst with the highest percentage degradation obtained it TiO$_2$/GO with 80% TiO$_2$, followed by TiO$_2$/GO with 50% GO and 30% GO. The highest percentage degradation of methylene blue is achieved from the photocatalyst sample TiO$_2$ 80%/GO at time 24 hours is 89.18% degradation of methylene blue from its original concentration.

![Percentage degradation curve of photocatalysts](image)
Figure 4 Methylene Blue Percentage Degradation Curve using 10x 9W UV lamp for 24 hours

Conclusion

This study presents the effect of the Graphene Oxide doping on photocatalyst TiO$_2$ performance for photoreaction under visible light irradiation that will enable a sustainable and cheap wastewater treatment method. The highest percentage of methylene blue degradation is at 89.18% by using TiO$_2$ 80%/GO photocatalyst, followed by TiO$_2$ 50%/GO with degradation 71% by using low wattage UV lamp (90 W). Further investigation on recyclability needs to be performed in the future to reveal the effectiveness of photocatalyst composite to overcome the secondary pollutant problem.

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