The influence of Ag in TiO$_2$/NGP composites as a high performance photocatalyst under UV and visible light irradiation

M Fauzian$^{1,2}$, A Taufik$^{1,2}$ and R Saleh$^{1,2}$

$^1$Department of Physics, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia
$^2$Integrated Laboratory of Energy and Environment, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia

Corresponding author’s email: rosari.saleh@ui.ac.id

Abstract. Ag/TiO$_2$ nanocomposites were synthesized using a sol-gel method, and Ag/TiO$_2$/NGP composites were synthesized using a co-precipitation method. X-ray diffraction (XRD), UV-Vis absorbance, Raman spectometry, and thermogravimetric analysis (TGA) were used for the characterization of prepared samples. The photocatalytic performance of all prepared samples was tested by removing methylene blue (MB) dyes. Photocatalytic activity using UV and visible light irradiation. The photocatalytic performance of all Ag/TiO$_2$/NGP composites was much higher than pure TiO$_2$ and TiO$_2$/NGP composites. The enhanced photocatalytic ability is predominantly due to the properties of NGP and the surface plasmon resonance (SPR) of Ag nanoparticles (NP). The NGP acted as an electron transporter and acceptor in composites and inhibited electron–hole recombination. The Ag NPs acted as an electron trap, making the separation of photo-generated electron–hole pairs easier. The best condition for the photocatalytic activity of Ag/TiO$_2$/NGP composites was pH 13. Holes were the major radicals involved in the photocatalytic process of Ag/TiO$_2$/NGP composites.

Keywords: TiO$_2$/NGP, photocatalytic, methylene blue

1. Introduction

Over the past decade, environmental issues have been the main topic for all researchers. Dye wastewater is mainly from the textile and food industries, and contains very hazardous compounds. Thus, it is important to treat dye wastewater before discharging it into the environment. The photocatalytic degradation of dye wastewater has become very familiar in recent decades [1, 2]. The TiO$_2$ semiconductor is the most familiar photocatalyst in the field of dye wastewater photodegradation because it is nontoxic, has high chemical stability, and is low cost. However, TiO$_2$ has a high energy band gap (±3.2 eV) and can only absorb the UV light region of sunlight [3, 4]. Reducing the band gap of TiO$_2$ so that it can absorb visible light will significantly increase its photocatalytic performance.

Improving TiO$_2$ photocatalytic efficiency can be achieved by incorporating Ag in the TiO$_2$ structure. The existence of the effect of surface plasmon resonance (SPR) of Ag may cause a shift in the absorption into the range of visible light [5, 6]. Furthermore, Ag nanoparticles (NP) have strong
oxidation and a strong ability to absorb photo-generated electrons, thus restraining the recombination of electron–hole pairs and enhancing photocatalytic ability under visible light irradiation [7].

Graphene is the main single layer graphitic carbon material; it has unique properties such as good absorbance, high chemical stability, and good electrical stability. For these reasons, graphene is a good material for photocatalytic activity [8-10]. However, graphene has high electron mobility, which reduces electron–hole recombination. Graphene acts as the base of the photocatalyst, creating a large surface area that provides large active sites for interaction with dyes [11].

In this report, Ag/TiO$_2$/NGP composites were synthesized using a co-precipitation method. The effect of weight percent of Ag (wt.%) on the structures, optic, and thermal properties, and the photocatalytic activity of Ag/TiO$_2$/NGP composites was investigated. The photocatalytic activity of Ag/TiO$_2$/NGP composites were tested through the degradation of methylene blue (MB). The results showed that the photocatalytic activity of Ag/TiO$_2$/NGP composites was significantly enhanced compared to pure TiO$_2$ NPs and TiO$_2$/NGP composites. Enhanced photocatalytic activity was related to increased wt.% of Ag. Furthermore, in this report, scavenger experiments were also conducted to find the mechanism of the photocatalytic process. The results showed that the hole was the major radical involved in the photocatalytic process of Ag/TiO$_2$/NGP composites.

2. Experimental detail

2.1. Materials

Titanium dioxide (TiO$_2$, 99 %), silver nitrate (AgNO$_3$), sodium hydroxide (NaOH), and sodium carbonate (NaCO$_3$) were purchased from Merck, and nanographene platelet (NGP) was purchased from Angstrom Materials. Other materials are ethanol, ethylene glycol, distilled water, and MB. All reagents were used without purification.

2.2. Preparation of Ag nanoparticles (NP)

First, AgNO$_3$ and SDS were dissolved separately into ethylene glycol by magnetic stirring for 30 minutes. Meanwhile, NaCO$_3$ was dissolved using distilled water. The SDS solution was first added with NaCO$_3$ solution, and then followed by the addition of AgNO$_3$ solution. Stirring the mix with a magnetic stirrer was carried out for 10 minutes, then the mixture was put into a microwave oven with a power of 800 W for 1 min, followed by another stirring for 10 min with a magnetic stirrer. The result of Ag nanoparticle precipitation is obtained after the mixture is separated from its solution using a centrifuge, then washed with distilled water and ethanol several times, and through a drying process at a temperature of 80 ºC for 12 hours.

2.3. Preparation of Ag/TiO$_2$ nanocomposites

First, distilled water is used to dissolve TiO$_2$ and NaOH mixture. A magnetic stirrer was used to stir the mixture at 80 ºC. Then ethanol and distilled water were used to dispersed the Ag NPs. The Ag solution is then added to the above mix in a particular proportion. It is stirred and heated continuously for 2 h. After that, it is collected then rinsed and aged. The Ag/TiO$_2$ composite were then obtained after drying it in a vacuum for 1 h and temperature of 125 125 ºC. Samples of Ag/TiO$_2$ nanocomposites were varied as 5, 15, and 25 wt.% Ag of the weight of TiO$_2$ NPs.

2.4. Preparation of Ag/TiO$_2$/NGP composites

The process of mixing NGP Ag/TiO$_2$ nanocomposites was done by dissolving and sonication of the NGP first. The solvents used were ethanol and distilled water. The sonication of the NGP solution was carried out for 2 h. Then the Ag/TiO$_2$ nanocomposites was added to the NGP solution together with NaOH. The mixture then stirred for 1 h using a magnetic stirrer. After that, it was heated for 3 h at a temperature of 125 ºC. Powdered Ag/TiO$_2$/NGP was obtained from centrifugation, followed by drying the precipitate in a vacuum for 12 h at a temperature of 70 ºC. The composition of the NGP in the
composite is 10 wt.% by weight of the Ag/TiO2 nanocomposite. Thus, in this experiment, four samples were tested for photocatalytic activity that degrades MB. They were TiO2/NGP and 5, 15, and 25 wt.% Ag/TiO2/NGP composites.

2.5. Characterization and photocatalytic measurement
All prepared samples were characterized using X-ray diffraction (XRD), UV-Vis absorbance spectroscopy, Raman spectroscopy, and thermogravimetric analysis (TGA). These were used to find structure and phase, optic, vibration molecule, and the thermal properties of all prepared samples. TEM and EDX measurements were made using an FEI Tecnai G2 Super Twin.

Photocatalytic activity was tested through the degradation of MB in the presence of Ag/TiO2/NGP composites under UV and/or Visible light irradiation for 2 h. For first step, MB was dissolved in distilled water; the initial concentration of MB was 20 mg/L. Then 10–40 g/L of photocatalyst was added to the MB solution. The solution was then stirred using magnetic stirring for 30 min in the “dark time” to establish desorption–adsorption equilibrium between solution and photocatalyst. Then, the exposure to the light for 2 h using a UV source in the form of 40 W UV-C lamp or a visible light source using a 50 W halogen lamp. Every 15 min, 5–6 mL of suspension was collected and centrifuged to separate the photocatalyst. The absorption intensity measurement using a UV-Vis Spectrophotometer was carried out to determine the concentration of MB at its maximum characteristic absorbance wavelength at 663 nm.

3. Results and discussion

The photocatalytic activities of samples with a dosage of 0.3 g/L were evaluated by the degradation of MB under UV or visible light irradiation. Figure 1 shows the photocatalytic activity of Ag/TiO2/NGP with the variation of Ag. The blank test is the degradation of MB without catalyst; the degradation shows only a slight decline and photolysis can be ignored. The figure shows that 25 wt.% Ag/TiO2/NGP composites was able to remove 90 % and 95 % of MB for UV and visible light irradiation, respectively. The results indicated that a sample of 25 wt.% Ag/TiO2/NGP showed excellent photocatalytic performance under UV light or visible light irradiation. The addition of Ag and NGP to TiO2 NPs improves the photocatalytic efficiency of samples; this may be due to excess Ag acting as a recombination center, or covering the active sites on the NGP surface, which can reduce the efficiency of charge separation. The comparison of the degradation efficiency of 25 wt.% Ag/TiO2/NGP under UV and visible light irradiation in the figure shows that the degradation of MB using visible light is more effective than UV light. It is caused 25 wt.% Ag/TiO2/NGP active under visible light irradiation and SPR of Ag.

Figure 2 shows the photocatalytic activity of 25 wt.% Ag/TiO2/NGP composites degrading MB as a function of the initial concentration of MB under UV and visible light irradiation. An increase in the initial concentration of MB decreases the photocatalytic performance under UV or visible light irradiation. This can be because the samples have an important role in reducing the penetration of light into a solution with an increased concentration of MB. The influence of the dosage of photocatalyst concentration in photocatalytic performance for 25 wt.% Ag/TiO2/NGP composites when degrading MB, with an initial concentration of 20 mg/L, was also investigated, and the result is plotted in figure 3. In this study, the dosage of photocatalyst was varied from 0.1–0.4 g/L. The increase in dosage of photocatalyst from 0.1 to 0.3 g/L, the degradation efficiency of MB also increases. This may be due to an enlargement of the surface area involved in process. However, at a photocatalyst dosage of 0.4 g/L, the photocatalytic efficiency of the samples decreases due to increased turbidity in the solution, which prevents the entry of light and consequently increases the screening effect and light scattering [12]. A photocatalyst dosage of 0.3 g/L has better photocatalytic efficiency than other variations in dosage under both UV and visible light irradiation.
Based on the effect of initial concentration and the catalyst dosage experiments, a catalyst dosage of 0.3 g/L and an initial concentration of 20 mg/L were chosen as the optimum experimental conditions for the study of other parameters.

The stability of the photocatalyst in photocatalytic activity was tested using a four time cycling process; the results are plotted in figure 4. In this study, 25 wt.% Ag/TiO2/NGP composites were used. The results show that after the fourth cycle of the process, the degradation of MB had only slightly declined. It can be concluded that 25 wt.% Ag/TiO2/NGP composites used as photocatalysts have good stability in photocatalytic activity under UV and visible light irradiation.

In this study, various scavengers were added to understand the photocatalytic mechanism. Scavengers such as sodium sulfate, ammonium oxalate, and tert-butyl alcohol act in three ways—as electron, hole, and hydroxyl radical scavengers, respectively. The effect of the addition of a scavenger on photocatalytic activity under UV or visible light irradiation is plotted in figure 5. It can be seen that
the addition of electron, hole, and hydroxyl radical scavengers can reduce photocatalytic performance. The addition of scavengers can trap active species in photocatalytic activity so that active species cannot interact with MB, therefore reducing photocatalytic performance. Hole and hydroxyl radicals are the main active species in the degradation process because with their addition, scavengers exhibit the lowest photocatalytic performance.

The crystalline structure of all samples was tested using X-ray diffraction spectroscopy. The diffraction pattern of all samples was plotted in figure 6. It can be seen that the diffraction peaks of Ag/TiO$_2$/NGP composites are located at 20 = 25.3°, 38.0°, 48.0°, 53.9°, 55.1°, 62.9°, 69.0°, 70.1°, and 75.4°, which are assigned to the anatase TiO$_2$ crystal planes of (101), (004), (200), (105), (211), (204), (116), (220), and (215), respectively and the graphitic-like structure of NGP is located at 20 = 26.49°, which associated to the (002) crystal plane. Ag diffraction peak was not detected in the samples with 5–15 wt.% of Ag because the amount of Ag is low. Diffraction peaks of Ag were detected at 20 = 37.52° and 44.61°, related to the (100) and (004) crystal planes of the cubic structure of Ag.

The EDX spectra of Ag/TiO$_2$/NGP and TiO$_2$ are plotted in figure 7. The results show that the EDX spectra of TiO$_2$ NPs consist of Ti atoms and oxygen atoms. Moreover, the incorporation of Ag and NGP materials result in additional EDX peaks, which could be attributed to the existence of Ag and carbon (C) atoms. The existence of Ag and C atoms indicates the Ag and NGP materials. No undesired peaks were detected indicating that the samples were of good quality.

TGA curves for TiO$_2$ NPs, TiO$_2$/NGP, and 25 wt.% Ag/TiO$_2$/NGP composites are shown in figure 8. The figure shows that TiO$_2$ NPs do not decompose until reaching 800 °C, showing that TiO$_2$ NPs have good thermal stability. NGP is present in both TiO$_2$/NGP and 25 wt.% Ag/TiO$_2$/NGP composites, and the composites decompose at 600 °C. This is due to the combustion process of material carbon in the samples.

The HRTEM image of Ag/TiO$_2$/NGP is shown in figure 9. The figure shows that in the HRTEM image of Ag/TiO$_2$/NGP composites, lattice fringes of TiO$_2$ were detected with d-spacing around 0.32 nm, which could be attributed to the (101) plane of anatase structure; lattice fringes of Ag were detected at 0.23 nm, which could be attributed to the (111) plane of the cubic structure of Ag.

Figure 10 shows the UV-Vis absorption spectra of TiO$_2$ NPs, TiO$_2$/NGP composites and 25 wt.% Ag/TiO$_2$/NGP composite. The absorption edge at around 330 nm is shown by the curve of TiO$_2$ NPs. The enhanced absorption peaks both of TiO$_2$/NGP and Ag/TiO$_2$/NGP composites in whole visible light region can be attributed to the presence of NGP in the sample. The absorption peak of Ag NPs in Ag/TiO$_2$/NGP composites is at around 450 nm [13], which indicates a redshift compared to
pure Ag NPs, which have an absorption peak around 400 nm because of Ag binding with the NGP sheets. Thus, all variations of Ag/TiO$_2$/NGP composites are expected to improve the efficient utilization of solar energy for photocatalysis.

4. Conclusion
In summary, Ag/TiO$_2$/NGP composites with various wt.% of Ag were successfully synthesized using a co-precipitation method, and their photocatalytic activity observed using UV and visible light to degrade MB. All prepared samples were confirmed by XRD, UV-Vis absorbance, and TGA measurements. Samples with 25 wt.% Ag/TiO$_2$/NGP had the best photocatalytic performance. Hole and hydroxyl radicals are active species in the photocatalytic process. Samples of 25 wt.% Ag/TiO$_2$/NGP could be reused in photocatalytic activity for a fourth time.
References

[1] Seabra M P, Pires R R and Labrincha J A 2011 Chem. Eng. J. 171 692-702
[2] Silva S S, Magalhães F and Sansiviero M T C 2010 Quim. Nova [online] 33 85-189
[3] Min L Y, He G Q, Li R B, Zhao W and Chen Y C 2012 Sep. Purif. Technol. 106 97-104
[4] Fujishima A, Zhang X and Tryk D A 2008 Surf. Sci. Rep. 63 515-82
[5] Yang Y, Zhang G and Xu W 2012 J. Colloid Interface Sci. 376 217-23
[6] Majumder S, Naskar B, Ghosh S, Lee C H, Chang C H, Moulik S P and Panda A K 2014
  Colloid. Surf. A 443 156-60
[7] Kowalska E, Mahaney O O P, Abe R and Ohtani B 2010 Phys. Chem. Chem. Phys. 12 2344-55
[8] Geim A K and Novoselov K S 2007 Nature Mater. 6 183-93
[9] Katsnelson M I and Novoselov K S 2007 Solid State Commun. 143 3-13
[10] Boruah P K, Borthakur P, Darabdhara G, Kamaja C K, Karbhal I, Shelke M V, Phukan P, Saikia D and Das M R 2016 RSC Adv. 6 11049-63
[11] Lu C and Chiu H 2006 Chem. Eng. Sci. 61 1138-45
[12] Pardhesi S K and Patil A B 2009 J. Mol. Catal. A Chem. 308 32-40
[13] Fauzian M, Taufik A and Saleh R 2017 IOP Conf. Ser.: Mater. Sci. Eng. 204 012009