Boosted Ag/g-C\textsubscript{3}N\textsubscript{4} prepared under microwave irradiation for photocatalytic activity of RhB under visible light

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Abstract. The effluent of Rhodamine B (RhB) from industries causes a high impact toward contamination of the environment. Photocatalytic degradation has become a promising destructive technique to remove those dye from industrial. In this study, Silver/graphitic carbon nitride (Ag/g-C\textsubscript{3}N\textsubscript{4}) prepared using simplistic preparation using microwave irradiation in its place of normal calcination under furnace as heating media. The prepared photocatalyst was characterized by using Fourier transform infrared (FTIR), N\textsubscript{2} adsorption-desorption, ultraviolet-visible diffuse reflectance spectra (UV-VIS/DRS). The deposited of Ag on g-C\textsubscript{3}N\textsubscript{4} surface photocatalyst enhanced capability to extend the adsorption of visible light region. The texture of g-C\textsubscript{3}N\textsubscript{4} affected after deposited with Ag and the bandgap energy of Ag/g-C\textsubscript{3}N\textsubscript{4} narrowed from 2.7 eV to 2.31 eV significantly boosting and improved the efficiency of degradation RhB under visible light irradiation. The additional Ag on g-C\textsubscript{3}N\textsubscript{4} revealed highest performance (98%) using RhB solution after exposed under visible light for 180 min. As a result, this works can give benefit to purify the effluent of toxic dyes as wastewater treatment.

1. Introduction

In recent years, worker have revealed a great interest in removal of dye pollutants from wastewater due to industrial development. The effluents discharged from industries have resulted in increasing wastewater to the environment. This wastewater needs to be treated as it contains highly carcinogenic aromatic amine that can cause a serious environmental pollution and bring negative impacts to all living creatures [1]. The discharged of dye from industries was estimated about over 200,000 tons per year cause by huge scale-production [2]. Rhodamine B (RhB) is one of the recognized dyes as colorant in textile due to its high stability [3]. However, this dye is very harmful to human being which can cause irritation of eyes and respiratory tract [4]. Various effort has been developed to remove this toxic dye including chemical treatment, biological treatment, physical adsorption, ozonation, and membrane filtration [5, 6]. However, these wastewater treatments have becoming less efficient to give complete decolorized of pollutant. Some of these treatment have potential to generate secondary product [7].

Nowadays, Advanced Oxidation process (AOPs) was considered as unique and effective technique in treating chemical dye pollutants. Heterogeneous photocatalysis was employed in AOPs give a
promising destructive method to degrade and mineralize dye pollutant [8]. This method provided a powerful oxidizing agent which can oxidize any organic pollutants into harmless product such as carbon dioxide (CO$_2$) and water [9]. Generally, the most favourable photocatalysts are semiconductor materials (such as TiO$_2$, ZnO, SnO$_2$, g-C$_3$N$_4$) because of their band gap energy ($E_g$) [10].

Particularly, g-C$_3$N$_4$ has intensively becoming one of the most excellent materials which has been utilized by many researchers due to its strong ability to absorb visible light irradiation [11]. Besides, the g-C$_3$N$_4$ has biocompatible, resistant to oxidation and high thermal stability [12]. The constricted band gap of the g-C$_3$N$_4$ around (~2.70 eV) allow this material to penetrate under visible light more than 460 nm. Unfortunately, this carbonaceous also has their own drawbacks. This carbonaceous has great recombination of photogenerated electron-hole. This recombination can limit the productivity of the photocatalytic activity [13,14]. Various approach to modify this carbonaceous have been demonstrated to rise the potential of g-C$_3$N$_4$. One of promising technique by depositing g-C$_3$N$_4$ with noble metal such as Ag which can improve catalytic efficiency [15]. Various procedure have been utilized to synthesis Ag/g-C$_3$N$_4$ such as photodeposition, photo-assisted reduction method and microwave-assisted polyol process which undergoes wet preparation using ethylene glycol [16-18]. Most of these method required a specific equipment and involving a lots of chemical solvent. Thus, to best of our knowledge, there is no works has been done in synthesis Ag/g-C$_3$N$_4$ using dry preparation under microwave irradiation without using any solvent. Subsequently, the modified Ag with g-C$_3$N$_4$ was undergoes visible light irradiation using RhB as model pollutant.

2. Experimental

2.1. Catalyst preparation

Silver loaded on graphitic carbon nitride was prepared using microwave method with varying Ag loadings. 0.3 g of g-C$_3$N$_4$ prepared using pyrolysis was combined with AgNO$_3$ and the mixture was sonicated for 10 minutes [2]. Next, the mixture in the beaker was covered using aluminium foil and heated using microwave at 100 W for 20 minutes. Then, dried using oven for 2 hours.

2.2. Characterizations

Fourier Transform Infrared (FTIR) spectroscopy was used to investigate the catalyst functional group. The surface area of photocatalyst was analyzed via Nitrogen physisorption. The band gap of catalyst was determined using Ultraviolet-Visible Diffuse Reflectance (UV-Vis/DRS).

2.3. Photodegradation of RhB

The photocatalytic performance of RhB was conducted via a photocatalytic batch reactor with a cooling system. 400 W metal halide lamp was used for source of visible light. The reaction was undergoing adsorption for 30 min to achieve the equilibrium of adsorption and then continue the reaction under visible light for 3 hours. Then, the UV-Vis spectrophotometer was utilized to investigate the decolourization of RhB at the absorption band of 567 nm.

3. Result and Discussion

FTIR analysis was used to investigate the chemical structure of the modified catalyst. Figure 1 displays the FTIR spectra of prepared photocatalyst in the region amid 400 and 4000 cm$^{-1}$. For g-C$_3$N$_4$, there is several main characteristic absorption band that usually can be detected in the region of 4000-400 cm$^{-1}$. The signal appear at 3000-3400 cm$^{-1}$ was allocated to the stretching vibration of nitrogen bonded to hydrogen (N-H) and surface adsorbed H$_2$O molecules [19]. Characteristic vibration of aromatic rings was assigned in the absorption signal between 1200 and 1465 cm$^{-1}$ [20]. The signal around 1636 cm$^{-1}$ is recognized to the occurrence of imine bonds [21]. Additionally, the peak at region 808 cm$^{-1}$ is associated to the triazine units with breathing mode [19]. The depositing Ag on g-C$_3$N$_4$ might not influence the g-C$_3$N$_4$ structure but intensity Ag/g-C$_3$N$_4$ was decreased with additional of Ag. This probably the surface of g-C$_3$N$_4$ is directly deposited with Ag during synthesis. Therefore, the result demonstrated the
preparation of catalyst using microwave was successful. This reduction intensity show similar behaviour by previous study on Ag loaded on g-C₃N₄ as indicated that Ag⁺ could anchored on the amino group of g-C₃N₄ [22].

![Figure 1. FTIR spectra of the catalysts](image)

The UV-VIS/DRS spectroscopy was utilized measure the optical properties of prepared photocatalyst as depicted in Figure 2. The optical absorption of photocatalyst was converted into function of Kubelka-Munk in order to determine the bandgap of photocatalyst. Based on Figure 2 shows the bandgap of unmodified catalyst (g-C₃N₄) was measured exactly at 2.70 eV reliable with the preceding study [23]. The broad absorption band of Ag/g-C₃N₄ showed a drastically shift to lower energies from 2.70 eV to 2.31 eV after additional of Ag. This result suggested that the reduction in bandgap with introduce Ag in g-C₃N₄ led to increasing the utilization rate in visible light with efficient generation of electron-hole pairs which improve the ability of photocatalyst to harvest which favors the higher photocatalytic performance.
Figure 2. Kubelka-Munk function of the catalysts

The N\textsubscript{2} adsorption-desorption isotherm curve of prepared photocatalyst are depicted in Figure 3. Based on IUPAC classification, both catalyst demonstrated a typical type IV isotherm with hysteresis loop H3 which corresponds to the slit-like mesopores [16].

Figure 3. N\textsubscript{2} physisorption isotherm of the catalysts

Table 1 shows the information related with the surface area and pore catalyst. The surface area of Ag/g-C\textsubscript{3}N\textsubscript{4} possesses a lower surface when comparing with g-C\textsubscript{3}N\textsubscript{4}. This phenomenon was corresponded to the g-C\textsubscript{3}N\textsubscript{4} has been deposited by Ag. This deposition Ag might obstruction some of the mesopores in g-C\textsubscript{3}N\textsubscript{4} [24]. Thus, the result significant to the high interface contact between both materials in the composite and subsequently improve the photocatalytic performance. The result also has similar behavior with previous studies observed when introduced Ag on carbonaceous [25].

| sample       | S\textsubscript{BET} (m\textsuperscript{2}/g) | V\textsubscript{pore} (cm\textsuperscript{3}/g) | Micropore volume (cm\textsuperscript{3}/g) | Mesopore volume (cm\textsuperscript{3}/g) |
|--------------|-------------------------------------------|------------------------------------------|----------------------------------------|-------------------------------------------|
| g-C\textsubscript{3}N\textsubscript{4} | 49.4                                      | 0.185                                    | 0                                      | 0.185                                    |
| Ag/g-C\textsubscript{3}N\textsubscript{4} | 3.2                                       | 0.088                                    | 0.012                                  | 0.076                                    |

The photodegradation of the prepared photocatalyst was determined using RhB solution under visible light irradiation for 180 min. Figure 4 shows irradiation time versus of degradation rate of RhB using prepared photocatalyst. The adsorption behaviour of photocatalyst was investigated for 1 hr before visible light irradiation. After undergoes adsorption under dark for 60 min, g-C\textsubscript{3}N\textsubscript{4} shows a high adsorption capacity (~21%) comparing with Ag/g-C\textsubscript{3}N\textsubscript{4} (7%). The adsorption capacities of Ag/g-C\textsubscript{3}N\textsubscript{4} was reduced comparing with g-C\textsubscript{3}N\textsubscript{4}. This might be owing to the smaller specific surface area [16]. In contrast, the degradation of g-C\textsubscript{3}N\textsubscript{4} was exhibited with degradation rate 66.8% for 90 min and 84.8% for 180 min. The degradation of g-C\textsubscript{3}N\textsubscript{4} might be accredited to its own strong absorption properties of visible-light. The photodegradation of RhB drastically improved after additional of Ag on g-C\textsubscript{3}N\textsubscript{4} surface with degradation rate 97.1% for 90 min and 98.3% for 180 min. The Ag play a main factor for
higher performance reaction of RhB. Thus, Ag/g-C$_3$N$_4$ demonstrated outstanding performance due to the additional Ag in g-C$_3$N$_4$ extend the absorption toward visible region as can be seen in Figure 2.

![Graph showing degradation of RhB over time](image)

**Figure 4.** Photocatalytic performance on degradation of RhB using prepared photocatalyst using visible light irradiation

4. Conclusion

As conclusion, the composite of Ag/g-C$_3$N$_4$ was successfully prepared under facile preparation using microwave irradiation and characterized by FTIR, UV-VIS/DRS and N$_2$ physisorption. The FTIR and N$_2$ physisorption results proved the presence of Ag in g-C$_3$N$_4$. The bandgap of modified catalyst reduced from 2.70 eV to 2.31 eV significantly improved the performance of degradation RhB (98%) after exposed under visible light for 180 min. Thus, the synthesis of modified photocatalyst provided an excellent potential to be a promising photocatalyst for pollutants purifications.

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