The synthesis of $\text{Ag}_3\text{PO}_4$ under graphene oxide and hydroxyapatite aqueous dispersion for enhanced photocatalytic activity

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Abstract. The development of $\text{Ag}_3\text{PO}_4$ photocatalyst for organic pollutant degradation is very challenging due to excellent activity under visible light exposure. The research aims to synthesize $\text{Ag}_3\text{PO}_4$ under graphene oxide (GO) and hydroxyapatite (HA) as a phosphate ion source for Rhodamin B degradation. The $\text{Ag}_3\text{PO}_4$/GO was prepared using the precipitation method with the starting material of graphene oxide aqueous dispersion, $\text{AgNO}_3$, and hydroxyapatite suspension. The structure, absorption, morphology, and element composition of photocatalysts were studied using XRD, DRS, SEM, and EDX. Photocatalytic abilities of the samples were tested using RhB oxidation under blue light exposure. The results exhibited that GO improves the crystallinity and visible absorption spectrum of $\text{Ag}_3\text{PO}_4$. Incorporating GO on $\text{Ag}_3\text{PO}_4$ decreases the ratio of O/Ag and O/P leading to a defect formation. The reaction mechanism on the surface of the photocatalyst was mainly run by holes and superoxide radical ions. The modification of $\text{Ag}_3\text{PO}_4$ using hydroxyapatite and GO improved photocatalytic activity.

1. Introduction

Recently, the utilization of graphene oxide (GO) on the synthesis of silver phosphate-based photocatalyst has greatly developed. This modification has significantly improved the performance of photocatalysts. GO has potential applications due to good thermal stability, flame resistance, and mechanical performance [1]. The application of GO on $\text{Ag}_3\text{PO}_4$ can increase adsorption performance [2,3], expand the visible light absorption [4,5], enhance the photogenerated charge separation efficiency [6–8], and improve the charge collection efficiency [9]. The immobilization of $\text{Ag}_3\text{PO}_4$/GO composite on the nickel foam improves the adsorption ability [2]. This design brings the photogenerated electrons is highly transferred away, leading to a stable and efficient photocatalyst.

The design of $\text{Ag}_3\text{PO}_4$/graphene oxide aerogel composites using the hydrothermal method increases the specific surface area that improves the adsorption performance [3]. The incorporation of GO into $\text{Ag}_3\text{PO}_4$ can influence the adsorption properties, such as redshift absorption [5]. GO can improve both the visible region’s absorption and adsorption properties after coupling with $\text{Ag}_3\text{PO}_4$ [4]. GO is also a good electron acceptor that can capture photoexcited electrons and enhance the electron transfer and charge separation [6]. In the composite of ZnO/GO/$\text{Ag}_3\text{PO}_4$, GO can act as a bridge between ZnO and $\text{Ag}_3\text{PO}_4$ that can increase the transmission rate [7]. This composite showed higher adsorption, a more effective separation of hole and electron, and a higherrate of electron transfer. This phenomenon was
also found in GO-Ag$_3$PO$_4$/Bi$_2$O$_3$. GO can serve as a facilitator to transfer the photoexcited electrons from the CB (conduction band) of Bi$_2$O$_3$ to the VB(valence band) of Ag$_3$PO$_4$ generating the Z-scheme reaction [8].

The improvement of Ag$_3$PO$_4$ photocatalyst can also be supported by hydroxyapatite (HA). The Ag$_3$PO$_4$/HA composite design generated a redshift and high absorption in visible and UV regions that lead to improved catalytic properties [10]. The catalytic improvement was also provided through a synergistic effect of HA, carbon dots, and Ag$_3$PO$_4$ as found in the composite of HA/N-doped carbon dots/Ag$_3$PO$_4$ [11]. This modification successfully increased active sites. Coupling the Ag$_3$PO$_4$ and HA enhanced catalytic performance through a vacancy of HA that was created under irradiation leading to a Z-scheme reaction [12]. Ag$_3$PO$_4$/HA composites can also have adsorption properties for Pb(II) [13]. This phenomenon could be applied for Pb(II) immobilization, which was very beneficial for water treatment. Interestingly the HA can be utilized as a phosphate source of Ag$_3$PO$_4$ [14]. This preparation successfully enhances the absorption spectrum in the visible region, decreases the particle size, and changes the mechanism of active species.

Based on the above reports, coupling GO on Ag$_3$PO$_4$ using hydroxyapatite is very promising. The GO can improve the separation of photoexcited electrons and holes, and hydroxyapatite can enhance absorption in the visible region. The experiment aims to incorporate the graphene oxide on Ag$_3$PO$_4$ that is synthesized under hydroxyapatite suspension. This method is new in the application of GO and hydroxyapatite for Ag$_3$PO$_4$ preparation. It has not yet been reported by other researchers. The results showed that the simultaneous design using GO and hydroxyapatite increased the crystallinity and visible absorption of Ag$_3$PO$_4$. This modification might induce defect formation in Ag$_3$PO$_4$. These phenomena improve the efficiency of separation of hole and electron, leading to high catalytic activity.

2. Materials and Methods

2.1. Materials

The materials of AgNO$_3$ (Merck), CaCl$_2$ (Merck), KH$_2$PO$_4$ (Merck), ethylenediamine (Merck), and graphene oxide aqueous dispersion (5 mg/mL) (Goographene, USA), were used in the synthesis of the photocatalyst. The Rhodamine B (Merck) was used as a dye for the analysis of photocatalytic activity.

2.2. Synthesis

The Ag$_3$PO$_4$/GO was synthesized using the starting material of AgNO$_3$, graphene oxide aqueous dispersion, and hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) as a source of silver and phosphate respectively. The hydroxyapatite (HA) was synthesized using CaCl$_2$ and KH$_2$PO$_4$ at pH 8 adjusted using ethylenediamine [14,15]. The co-precipitation method was applied to prepare the photocatalyst of Ag$_3$PO$_4$/GO. The quantity of 0.45 g of graphene oxide aqueous dispersion (5 mg/mL) was added to the AgNO$_3$ solution (1 g of AgNO$_3$ in 10 mL of water). This mixture was added to the hydroxyapatite suspension (0.3 g of HA in 20 mL of water), mixed under a magnetic stirrer for 30 minutes. The precipitates were filtered, washed with water three times, and dried at 105°C for 5 hours. The Ag$_3$PO$_4$ without graphene oxide was also prepared with a similar procedure.

2.3. Characterization

The structure of Ag$_3$PO$_4$ and Ag$_3$PO$_4$/GO were characterized using the XRD (Rigaku Miniflex 600), operating at 40 kW, 15 mA, using Cu. The morphology and atomic composition were analyzed using SEM-EDX (JEOL, JSM-6510). The morphology magnification of 15000 times was set at 20 kV. The composition was analyzed using ZAF Method Standardless Quantitative Analysis at 20 kV, with a magnification of 3000 times, a counting rate of 3232 cps, and an energy range of 0-20 keV. Absorptions were analyzed using UV-vis DRS (JASCO V-670) with a wavelength range of 320-700 nm.
2.4. Photocatalytic Activity
The photocatalytic ability of Ag$_3$PO$_4$ and Ag$_3$PO$_4$/GO were examined using RhB oxidation under the blue LED lamp (Duralux, 3 Watt) [14,16]. The catalyst (0.1 g) was mixed with RhB solution (100 mL, 10 mg/L). The dark treatment and photocatalytic reactions were set at 10 and 8 minutes, respectively. The solution (5 ml) was taken out every 2 minutes and separated from the catalyst using centrifugation. The RhB concentration was monitored by the spectrophotometer. The catalytic recyclability was evaluated up to 3 cycles of 1$^{st}$, 2$^{nd}$, and 3$^{rd}$ reactions.

3. Results and Discussion
The Ag$_3$PO$_4$ was successfully designed using AgNO$_3$, hydroxyapatite, and graphene oxide. The body-centered cubic structure was created in both Ag$_3$PO$_4$ and Ag$_3$PO$_4$/GO (JCPDS No. 06-0505) [17] (figure 1). Figure 2 showed the absorption of Ag$_3$PO$_4$ and Ag$_3$PO$_4$/GO at 320-700 nm. The broad absorption above 520 nm was observed in Ag$_3$PO$_4$/GO. This phenomenon might be originated from the formation of the defect site. The absorption coefficient and the band-gap can follow the direct transition of Tauc's relation [18,19]:

$$ (ah\nu)^2 = B(\hbar\nu - E_g) $$

where $E_g$, $h$, $\alpha$, $\nu$, and $B$ is a bandgap, Planck constant, absorption coefficient, light frequency, and a constant, respectively. The optical bandgap of the two samples was similar (2.44 eV).

![Figure 1. XRD profile of Ag$_3$PO$_4$ and Ag$_3$PO$_4$/GO](image1.png)

![Figure 2. Absorption spectra of Ag$_3$PO$_4$ and Ag$_3$PO$_4$/GO measured using DRS instrument](image2.png)

The diffraction peak of graphene oxide is not detected due to a very small GO impregnated on the surface of Ag$_3$PO$_4$. The addition of GO did not change the structure, however, it can affect the intensity of diffraction. The higher intensity was observed in Ag$_3$PO$_4$/GO suggested that the GO can improve the crystallinity. It is also found that the FWHM and 2 theta of Ag$_3$PO$_4$/GO are higher than that of Ag$_3$PO$_4$ (Table 1). The three highest peaks at 33.358°, 36.624°, and 55.112° could be found in the sample of Ag$_3$PO$_4$ for (210), (211), and (320) diffractions, respectively. After incorporating the GO, the 2 theta shifted to 33.378°, 36.669°, and 55.130°. The distance of shift was found at 0.020°, 0.045° and 0.018° for (210), (211), and (320) diffractions, respectively. Among these shifts, the crystalline plane of (211) is more affected, suggesting that the defect might be higher created on this plane. This phenomenon occurred because the defect can affect the crystalline planes [20].

The morphology of Ag$_3$PO$_4$ and Ag$_3$PO$_4$/GO were investigated, the results can be seen in figure 3a and figure 3b. The morphology of the two particles was not significantly changed after incorporating
GO. The crystal shape of samples is irregular ranging from 0.42 μm to 2 μm. A thin layer of graphene oxide was observed on the surface of Ag₃PO₄/GO. The GO forms a super thin layer that is strongly attached to the Ag₃PO₄. Due to the hydroxyl and epoxide, a bond bridge between the GO and the cubic Ag₃PO₄ might form [21].

Table 1. Comparison of XRD data from the sample of Ag₃PO₄ and Ag₃PO₄/GO

| Sample       | 2θ     | d (Å)       | FWHM     | Height (Counts) |
|--------------|--------|-------------|----------|-----------------|
| Ag₃PO₄      | 33.358(3) | 2.6839(2)   | 0.2043(19)| 1270(36)        |
| Ag₃PO₄/GO   | 33.378(3) | 2.6823(3)   | 0.2174(17)| 1520(33)        |

The elements of the sample were successfully analyzed using SEM-EDX and the atomic composition can be seen in table 2. A large impurity of carbon was formed in the precipitate of the samples. This impurity might be originated from the carbonate in the solution. Incorporation of GO on Ag₃PO₄ decrease the carbon impurity. Interestingly, the calcium ion from hydroxyapatite was not observed in SEM-EDX, indicating that the Ca²⁺ could not be precipitated and easily dissolved in water, whereas phosphate ion was successfully co-precipitated with silver forming Ag₃PO₄.

Figure 3. SEM images of Ag₃PO₄ (a) and Ag₃PO₄/GO (b)

Table 2. Atomic composition (%) from the SEM-EDX measurement of Ag₃PO₄ and Ag₃PO₄/GO.

| Atom (%) | Ag₃PO₄ | Ag₃PO₄/GO |
|----------|--------|-----------|
| Ag       | 10.35  | 18.78     |
| P        | 3.61   | 6.64      |
| O        | 36.78  | 46.40     |
| C        | 46.43  | 23.01     |
| Cu       | 0.52   | 1.07      |
| Zn       | 0.35   | 0.89      |
| Cd       | 0.82   | 1.28      |
| Ar       | 1.14   | 1.94      |

Due to high carbon impurity, the precise investigation of the sample differences should be in the atomic ratio. The atomic ratios of P/Ag, O/Ag, and O/P in Ag₃PO₄ can be estimated at 0.35, 3.55, 10.2, respectively, whereas in the Ag₃PO₄/GO, they were 0.35, 2.47, and 6.99, respectively. The sample of Ag₃PO₄ and Ag₃PO₄/GO has a similar atomic ratio of P/Ag but the atomic ratio of O/Ag and O/P in Ag₃PO₄/GO is lower than that of Ag₃PO₄, indicating that the incorporation of GO might influence the environment of co-precipitation. The lower ratio of O/P in Ag₃PO₄/GO might be originated from the oxygen vacancy phenomenon.
The photocatalytic abilities of Ag₃PO₄ and Ag₃PO₄/GO were investigated using RhB oxidation. The results can be seen in figure 4a. The pseudo-first-order reaction was utilized to investigate the profile of photocatalytic activity with the equation of \( \ln(C_t/C_0) = kt \), \( C_t \) and \( C_0 \) are concentration at \( t \) time and initial concentration of photocatalytic reaction, \( k \) is the rate constant [16]. The pseudo-first-order reaction occurred in both Ag₃PO₄ and Ag₃PO₄/GO with the rate constant of 0.455 min⁻¹ and 0.670 min⁻¹, respectively. The Ag₃PO₄/GO showed faster reaction activity (1.5 times faster than the Ag₃PO₄). Many results showed that the utilization of GO increased the adsorption [2,3], however, due to the low amount of GO impregnated on Ag₃PO₄, the adsorption in the dark condition is not so high.

![Figure 4. Photocatalytic activity of Ag₃PO₄ and Ag₃PO₄/GO (a), Photocatalytic cycling of Ag₃PO₄/GO (b), the effect of scavenger to photocatalytic in Ag₃PO₄/GO (c) NS=no scavenger, AO=ammonium oxalate, IPA=isopropyl alcohol, BQ=benzoquinone, and the proposed mechanism of photocatalytic activity in Ag₃PO₄/GO (d).](image)

Recycled catalytic activity was also investigated (figure 4b). The catalytic activity decreased after cyclic reaction up to three times. The rates of photocatalytic reaction are 0.684 min⁻¹, 0.377 min⁻¹, and 0.243 min⁻¹ for the reaction of 1st, 2nd, and 3rd, respectively. The decreased activity might be caused by the photoreduction of Ag⁺ to Ag⁰. It suggested that although the photogenerated electrons can be highly separated through the GO, they have still reduced Ag⁺ ions leading to photo-corrosion. Another reason is due to lower adsorption in the 2nd and 3rd reactions. The 1st reaction showed the adsorption in the dark condition, whereas 2nd and 3rd did not show the adsorption. This problem might be generated by the reaction 1st that can break the bond of GO from the Ag₃PO₄ leading to low adsorption on the surface.

The mechanisms of photocatalytic in Ag₃PO₄/GO were studied using BQ (benzoquinone), AO (ammonium oxalate), and IPA (isopropyl alcohol) to scavenge the species of •O₂⁻, h⁺, and •OH.
The proposed mechanism

The role of $\cdot{\text{OH}}$ is not significant in the photocatalytic reaction mechanism. The $\cdot{\text{OH}}$ could be highly produced when water or hydroxyl ion (OH\textsuperscript{−}) adsorbed in the surface and reacted with hole producing $\cdot{\text{OH}}$. However, in this case, the adsorbates (RhB) might stronger be trapped by a hole under irradiation leading to decreased $\cdot{\text{OH}}$ formation on the surface of Ag\textsubscript{3}PO\textsubscript{4}.

4. Conclusion

The co-precipitation of Ag\textsubscript{3}PO\textsubscript{4} using the starting material of AgNO\textsubscript{3}, graphene oxide, and hydroxyapatite was successfully synthesized. The graphene oxide improves the crystallinity, decreases the impurity in the surface of Ag\textsubscript{3}PO\textsubscript{4}. The photocatalytic reaction of Ag\textsubscript{3}PO\textsubscript{4}/GO runs faster than the Ag\textsubscript{3}PO\textsubscript{4}. The enhanced photocatalytic activity was caused by improving the separation of photoexcited electrons and holes in the surface. The mechanism of the photocatalytic reaction was carried out by hole as a main role, and superoxide radical ion as a second role.

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6. References

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