The Starting Material Concentration Dependence of Ag₃PO₄ Synthesis for Rhodamine B Photodegradation under Visible Light Irradiation

Febiyanto and Uyi Sulaeman

Department of Chemistry Faculty of Mathematics and Natural Sciences Universitas Jenderal Soedirman
Jl. Dr. Soeparno No. 61 Karangwangkal Purwokerto Central Java Indonesia 53123

Corresponding author: uyi_sulaeman@yahoo.com

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Abstract

Synthesis of Ag₃PO₄ photocatalyst under the varied concentrations of AgNO₃ and Na₂HPO₄·12H₂O as starting material has been successfully synthesized using the co-precipitation method. The concentration of AgNO₃ is 0.1; 0.5; 1.0; and 2.0 M, whereas Na₂HPO₄·12H₂O is 0.03; 0.17; 0.33; and 0.67 M, respectively. The co-precipitations were carried out under aqueous solution. As-synthesized photocatalysts were examined to degrade Rhodamine B (RhB) under blue light irradiation. The results showed that varying concentrations of starting materials affect the photocatalytic activities, the intensity ratio of [110]/[200] facet plane, and their bandgap energies of Ag₃PO₄ photocatalyst. The highest photocatalytic activity of the sample was obtained by synthesized using the 1.0 M of AgNO₃ and 0.33 M of Na₂HPO₄·12H₂O (AP-1.0). This is due to the high [110] facet plane and increased absorption along the visible region of AP-1.0 photocatalyst. Therefore, this result could be a consideration for the improvement of Ag₃PO₄ photocatalyst.

Keywords: Ag₃PO₄, co-precipitation method, photocatalytic activity, Rhodamine B.

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1. INTRODUCTION

To date, silver orthophosphate or Ag₃PO₄ photocatalyst has been promising visible light-activated photocatalyst material. This because of their small bandgap energy (~2.40 eV) and their quantum efficiency of nearly ~90% under visible light or above 520 nm (Yi et al., 2010). In addition, it has greater photocatalytic efficiency than well-known traditional photocatalyst like doped-TiO₂ (Katsumata et al., 2013), TiO₂ commercial (P25) (Liu et al., 2012), and ZnO (Khan et al., 2012).

To enhancing their photocatalytic activities, some modifications have been prepared and investigated. They were doping (Song et al., 2017; Xie and Wang, 2014; Yu et al., 2015), composite fabrication (Chen et al., 2013; Zhankui et al., 2013) and morphology design (Dong et al., 2014; Guo et al., 2015; Sulaeman et al., 2016; Vu et al., 2013). The modifications were also carried out by using the addition of complex solution (Wang et al., 2012; Xu and Zhang, 2013), the hydrophilic polymer (Yang et al., 2014), various reactant composition (Bozetine et al., 2013), stirring time (Yan et al., 2013) and temperature (Wang et al., 2015). These modifications showed a significant effect on the photocatalytic activities of Ag₃PO₄ photocatalyst.

Recently, the different morphology, particle size, crystallinity, and absorption profiles could be resulted in the different concentrations of KH₂PO₄ as starting material in the Ag₃PO₄ synthesis. This might be due to the different concentration influenced the nucleation and crystal growth during photocatalyst synthesis. However, the high photocatalytic activity of Ag₃PO₄ photocatalyst can be found in the sample with smaller particle size, higher crystallinity, and UV-Vis absorption ability of Ag₃PO₄ (Afifah et al., 2019). Besides KH₂PO₄, the reactant of Na₂HPO₄·12H₂O as a source of phosphate has been applied for Ag₃PO₄ design synthesis (Chen, Dai, Guo, Bu, & Wang, 2016; Wang et al., 2015; Wu et al., 2013). Nevertheless, the investigation using the variation of
Na$_2$HPO$_4$·12H$_2$O concentration has not been reported. Based on these reports, it is a good idea to obtain high photocatalytic activity by using Na$_2$HPO$_4$·12H$_2$O. Therefore, we have tried to observe the effect of the varied concentration of AgNO$_3$ and Na$_2$HPO$_4$·12H$_2$O as starting material for Ag$_3$PO$_4$ co-precipitation. The activities of the products were investigated using the Rhodamine B (RhB) photodecomposition under blue light irradiation.

2. MATERIALS AND METHODS

Materials

Materials were used without further purification, such as a commercial textile dye of RhB, distilled water (DW), AgNO$_3$ (Merck), and Na$_2$HPO$_4$·12H$_2$O (Merck).

Photocatalyst Characterization

Determination of crystallinity and purity of samples was done using X-ray diffraction (XRD) Bruker AXS D2 Phaser. UV and visible light absorption profiles were conducted using Diffuse Reflectance Spectroscopy (DRS) JASCO V-670. Photocatalyst samples were examined under blue light irradiation of LED Skyled (3W/220V) for RhB photodegradation. Lamp-suspension surface distance was adjusted at 10 cm. The absorbance of filtrate after the photodegradation process was analyzed using UV-Visible spectroscopy Shimadzu 1800.

Synthesis of Ag$_3$PO$_4$ Photocatalyst with The Varied Concentration of Reactants

Photocatalyst was synthesized using the co-precipitation method by reacting AgNO$_3$ and Na$_2$HPO$_4$·12H$_2$O with various concentrations of reactants. The concentration of Na$_2$HPO$_4$·12H$_2$O was 0.03, 0.17, 0.33, and 0.67 M were slowly mixed drop by drop in room temperature into 0.1, 0.5, 1.0, and 2.0 M of AgNO$_3$, respectively. The reactants of AgNO$_3$ and Na$_2$HPO$_4$·12H$_2$O were stoichiometrically synthesized following the reaction as shown in Eq. 1 (molar concentration ratio of Ag$^+$ to HPO$_4^{2-}$ is 3:1) (Vogel, 1990) and separately dissolved in 25 mL volumetric flask using DW. Samples were stirred, and as-resulted yellow precipitates were collected, washed several times, and dried in the oven at 105 °C for 5-10 hours. Samples were labeled as AP-0.1, AP-0.5, AP-1.0, and AP-2.0, respectively.

$$3\text{Ag}^+ + \text{HPO}_4^{2-} \rightarrow \text{Ag}_3\text{PO}_4 + \text{H}^+$$ (1)

3Ag$^+$ + HPO$_4^{2-}$ → Ag$_3$PO$_4$ + H$^+$

Photocatalytic Activity Analysis

An amount of 0.2 g of Ag$_3$PO$_4$ photocatalyst was poured into 100 mL of 10 mg/L RhB under stirring condition. Initially, the reaction was carried out under the dark condition for 20 minutes to ensure the adsorption-desorption of dye and Ag$_3$PO$_4$ photocatalyst. After that, the suspension was irradiated under blue light, and the sample was drawn ±5 mL at a certain time. The suspension was centrifuged at 1,500 rpm, and the absorbance of the filtrate was measured (Febiyanto et al., 2016).

3. RESULTS AND DISCUSSION

XRD Analysis of Ag$_3$PO$_4$ Photocatalyst

The XRD profile of as-synthesized Ag$_3$PO$_4$ was shown in Fig. 2. The diffraction of AP-0.1; AP-0.5; AP-1.0; and AP-2.0 are similar. As shown in Fig. 1, the photocatalysts synthesized under the varied concentration have a body-centered cubic of Ag$_3$PO$_4$. It is suitable with the JCPD #06-0505 (Huang et al., 2019; Yan et al., 2014). High intensities of peaks and no others peak except Ag$_3$PO$_4$, suggesting that the samples are highly crystalline and high purity (Ge, 2014).

The crystallite size of samples was calculated using the Debye-Scherrer equation as follow (Bozetine et al., 2013):

$$D = \frac{K\lambda}{\beta\cos\theta}$$ (2)

where $D$, $K$, $\lambda$, $\beta$, and $\theta$ were crystallite size (nm), Scherrer constant (~0.9), a wavelength of X-ray sources (Cu $K_{\alpha}$=0.15406 nm), FWHM (radians), and peak position (radians). Relatively, the same average diameter of crystallite was observed in all samples. Further, the ratio intensity of [110]/[200] was also investigated and summarized in Table 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$D_{\text{average}}$ (nm)</th>
<th>Intensity ratio of [110]/[200]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP-0.1</td>
<td>52.02</td>
<td>0.93</td>
</tr>
<tr>
<td>AP-0.5</td>
<td>46.86</td>
<td>1.67</td>
</tr>
<tr>
<td>AP-1.0</td>
<td>46.96</td>
<td>2.02</td>
</tr>
<tr>
<td>AP-2.0</td>
<td>46.16</td>
<td>1.50</td>
</tr>
</tbody>
</table>
According to Table 1, the intensity ratio of facet planes was affected by the varied molar concentrations of reactants. The highest intensity ratio of [110]/[200] was observed in the sample of AP-1.0, suggesting that their surfaces are dominated by the [110] facet plane. This facet plane is similar to the tetrapod and rhombic dodecahedron morphology types (Martin et al., 2013; Wang et al., 2014). Moreover, the highest [110] dominated-facet surfaces could contribute to the improvement of the photocatalysis activity of Ag₃PO₄ photocatalyst (Bi et al., 2012). Previously, the [110] facet plane of photocatalyst shows a high photocatalytic activity in the dye removal (Wang et al., 2012; Zheng et al., 2013).

### Band gap energy analysis of Ag₃PO₄ photocatalyst

Analysis of UV-Vis absorption profiles of as-synthesized Ag₃PO₄ photocatalyst was analyzed using DRS and depicted in Fig. 2 (A-B). Based on Fig. 2 (A), samples have a good-absorption ability on the UV up to visible light (<600 nm). In addition, the difference in absorption ability could also be found in the visible wavelength at around 400-500 nm. The sample of AP-1.0 showed the highest absorption in the visible region (540-800 nm).

Fig. 2 (B) showed the band gap energy profiles of AP-0.1, AP-0.5, AP-1.0, and AP-2.0, respectively. The band energy of samples can be estimated using the formula as follows (Eq. 3) (Rawal et al., 2012):

\[
\alpha h v = A(h v - E_g)^{n/2}
\]

where \(\alpha\), \(h\), \(v\), \(A\), \(E_g\), and \(n\) are absorption coefficient, Planck’s constant, light frequency, a constant number, band gap energy, and value depend on the direct \((n=1)\) and indirect \((n=4)\) characteristics of nature semiconductor transition. According to Eq. 3, the \((\alpha h v)^2\) plot as a function of \(hv\) where the band gap energy of each sample was resulted using extrapolation of a straight line towards the axis \((x)\)-direction. The direct band gap energy of samples was summarized in Table 2. According to Table 2, the varied molar concentrations slightly affect the light absorption as same as the band gap energy of photocatalyst samples.
is no apparent concentration changing compared to the RhB photodecomposition with the addition of Ag₃PO₄ photocatalyst. However, the dye photodegradation using radical species that is resulted from light-activated photocatalyst was a plausible mechanism to decrease the absorbance or dye concentration than photolysis reaction (Febiyanto et al., 2019).

### Table 2. Sample characteristics of Ag₃PO₄ photocatalyst

<table>
<thead>
<tr>
<th>Samples</th>
<th>Band gap energy (eV)</th>
<th>Linearity (R²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP-0.1</td>
<td>2.38</td>
<td>0.987</td>
</tr>
<tr>
<td>AP-0.5</td>
<td>2.36</td>
<td>0.896</td>
</tr>
<tr>
<td>AP-1.0</td>
<td>2.36</td>
<td>0.960</td>
</tr>
<tr>
<td>AP-2.0</td>
<td>2.35</td>
<td>0.915</td>
</tr>
</tbody>
</table>

### Photocatalytic activity examination of Ag₃PO₄ photocatalyst

Photocatalytic activity of as-synthesized Ag₃PO₄ photocatalyst under the varied molar concentration of reactants was performed in Fig. 3. Based on Fig. 3 (A), the control or RhB photolysis process without the addition of photocatalyst material showed a small decrease in RhB concentration under blue light irradiation. The percent RhB degradation using photolysis reaction over 80 minutes of light exposure was less than 6% (yellow color). The slight decrease in RhB photodegradation without catalyst addition could be explained by Wilhelm and Stephan (Wilhelm and Stephan, 2007) as follows: the excitation of RhB compounds (Eq. 4) is followed by O₂ reduction to be O₂⁻• and photogenerated RhB⁺• (Eq. 5) under the light irradiation. The O₂⁻• radicals react with H⁺ from H₂O autoprotolysis, and then OOH• was resulted (Eq. 6). Subsequently, RhB cationic was degraded, resulting in CO₂, H₂O, and acid minerals (Eq. 7). Qu and Zhao reported that these reaction mechanisms are a very slow reaction, and the photocatalysis reaction using a catalyst is the best reason to explain a significant decrease in RhB photodecomposition (Qu and Zhao, 1998).

\[
\begin{align*}
\text{RhB} + h\nu & \rightarrow \text{RhB}^+ \quad (4) \\
\text{RhB}^+ + \text{O}_2 & \rightarrow \text{RhB}^{+•} + \text{O}_2^{-•} \quad (5) \\
\text{O}_2^{-•} + \text{H}^+ & \rightarrow \text{OOH}^• \quad (6) \\
\text{RhB}^{+•} + \text{O}_2 & \rightarrow \text{products} \quad (7)
\end{align*}
\]

In addition, the same trends were also observed in the adsorption ability of photocatalysts under the dark condition, with a percent decrease of less than 10%, as shown in Fig. 3 (A) (green color). It concluded that RhB photodecomposition under blue light irradiation or photolysis and adsorption process at least could be neglected since there

![Figure 3. Photocatalytic activities of RhB over 80 minutes of light exposure under blue light (red color) and adsorption ability (green color) over 20 min in the dark condition (A), and their pseudo-first-order rate constant (B).](image-url)
A significant decrease in RhB concentration was found when the RhB sample was mixed with Ag₃PO₄ photocatalyst, as shown in Fig. 3 (A). Fig. 3 (A) (red color) showed that all samples could effectively degrade the RhB dyes. The high photocatalytic activity can be found in the AP-1.0 sample, with the percent degradation of 82.5%. The high photocatalytic activity might be induced by the highest intensity of [110] facet plane and different properties obtained by co-precipitation under the starting material of AP-1.0 photocatalyst. This preparation generates high absorption along the visible region, as shown in Fig. 2 (A). The AP-1.0 is the high absorption in the visible region. This phenomenon increases the photogenerated electron and holes that lead to improving the photocatalytic activity. The percent degradation of 69.2, 57.4, and 54.3% could be observed in AP-0.1, AP-0.5, and AP-2.0, respectively. These photocatalytic activities were relatively similar and highly different from the AP-1.0 sample.

Photocatalytic kinetic analysis of Ag₃PO₄ photocatalyst with varied molar concentrations was performed in Fig. 3 (B). Rate constant can be determined from a slope that is resulted from linear regression. These can be determined using a formula as follows (Eq. 8):

\[ \ln(C_0/C) = kt \]  

where \( C_0 \), \( C \), \( t \), and \( k \) are initial concentration, the concentration at a certain time, irradiation time, and a rate constant of pseudo-first-order kinetic (Yan et al., 2014). Based on Fig. 3 (B) and Table 2, the rate constant of samples shows a good-linearity and following the pseudo-first-order rate kinetic (Pradhan et al., 2014). However, the sample with AP-1.0 showed a high photocatalytic rate kinetic of 0.0218 min⁻¹, whereas samples of AP-0.1, AP-0.5, and AP-2.0 were 0.0147, 0.0107, and 0.0098 min⁻¹, respectively. The results showed that varying molar concentrations affect the rate constant, as same as photocatalytic activities of Ag₃PO₄ photocatalyst.

The RhB oxidation and reduction mechanism chain of photocatalyst generally might be happened on the photocatalyst surfaces of Ag₃PO₄ under visible light irradiation. This following the photodegradation mechanisms below (Guo et al., 2015):

\[ \text{Ag}_3\text{PO}_4 + \text{hv} \rightarrow \text{Ag}_3\text{PO}_4 (e^-_{\text{CB}} + h^+_{\text{VB}}) \]  
\[ \text{Ag}_3\text{PO}_4(h^+_{\text{VB}}) + \text{H}_2\text{O} \rightarrow \text{Ag}_3\text{PO}_4 + \text{H}^+ + \cdot\text{OH} \]  
\[ \text{Ag}_3\text{PO}_4(h^+_{\text{VB}}) + \text{OH} \rightarrow \text{Ag}_3\text{PO}_4 + \cdot\text{OH} \]  
\[ \text{Ag}_3\text{PO}_4(e^-_{\text{CB}}) + \text{O}_2 \rightarrow \text{Ag}_3\text{PO}_4 + \cdot\text{O}_2 \]  
\[ \text{Organic compounds} + \cdot\text{O}_2 + \cdot\text{OH} \rightarrow \text{CO}_2 \text{ and H}_2\text{O (acid minerals)} \]  

Photocatalyst under blue light excites electron (\( e^+ \)) from valence band (VB) to the conduction band (CB) resulted in electron (\( e^-_{\text{CB}} \)) and hole (\( h^+_{\text{VB}} \)) (Eq. 9). The electron-hole pairs transferred to the Ag₃PO₄ surfaces and oxidation/reduction of water molecules (\( \text{H}_2\text{O} \)) (Eq. 10) and \( \text{OH}^- \) ions or dissolved oxygen (\( \text{O}_2 \)) (Eq. 11-12) can take place. Subsequently, this can produce a radical species of hydroxyl (•OH) and superoxide (•O₂⁻). The benefits of this chemical radical decompose the RhB dye structures to be small molecules such as \( \text{H}_2\text{O} \), \( \text{CO}_2 \), and acid minerals (Eq. 13).

4. CONCLUSION

The photocatalyst of Ag₃PO₄ under the varied concentration of starting materials have been successfully synthesized using the co-precipitation method. The results showed that the varied concentrations of starting materials affect the photocatalytic activities, the intensity ratio of [110]/[200] facet plane, and their bandgap energies of Ag₃PO₄ photocatalyst. Photocatalyst synthesized using 1.0 M of AgNO₃, and 0.33 M of Na₂HPO₄/12H₂O (AP-1.0) showed the highest photocatalytic activity with the percent photodegradation of 82.5%. This is due to the high [110] facet plane and the absorption along a visible region of AP-1.0 photocatalyst. However, the [110] dominated-facet plane which is similar to the tetrapod or dodecahedron morphology structure could contribute to the improvement of photocatalysis reaction of Ag₃PO₄ photocatalyst in the RhB photodegradation.

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