THE ENHANCED PHOTOCATALYTIC PROPERTIES OF SILVER PHOSPHATE SYNTHESIZED UNDER MANGOSTEEN PEEL EXTRACT SOLUTION

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1.0 INTRODUCTION

Today silver orthophosphate has been developed as a photocatalyst for dye removal under visible light exposure due to owning small bandgap energy of 2.43 eV, strong photooxidation, and high quantum yield [1, 2]. This material can be an alternative photocatalyst that is active in visible light in addition to popular photocatalysts such as N-TiO\textsubscript{2} [3-5]. The modifications of morphology in Ag\textsubscript{3}PO\textsubscript{4} photocatalyst have been applied to improve their photocatalytic activity [6]. Morphology of coral-like microspheres [7],...
branched Ag₃PO₄ crystals with porous structure [8] and truncated tetragonal bipyramids [9] had improved the photocatalytic activity of Ag₃PO₄. The changed morphology can influence the activity due to a different facet of Ag₃PO₄. However, design a particular morphology that has high activity is very difficult in Ag₃PO₄.

The impressive improvement of photocatalytic activity can be achieved through dopant incorporation on the surface of Ag₃PO₄. The dopant of sulfate [10], platinum complex [11], bismuth [12], molybdenum [13], nickel [14], and lanthanum [15] could be applied in Ag₃PO₄. The metallic silver dopant on Ag₃PO₄ is the most promising because it can be created through a simple reduction of Ag⁺ ions [16]. This dopant could also generate the surface plasmon resonance that leads to a highly active photocatalyst [17]. However, most of these designs have used large particles of Ag₃PO₄.

Modification of Ag₃PO₄ into composite photocatalysts has also significantly improved photocatalytic activity. Generating electron excitation could effectively be facilitated in a hybrid photocatalyst [18], p-n heterojunction [19], and Z-scheme mechanism [20] which can boost the photocatalytic ability. The formation of g-C₃N₄/Ag₃PO₄ hybrid can maintain the Ag₃PO₄ from dissolution in water [21]. It leads to higher stability of activity. The composite of Ag₃PO₄/CdWO₄ photocatalyst improved the separation of carrier pairs through a p-n junction that increase the efficiency of activity [22]. The p-n junction and piezoelectric effect can also be designed through Ag₃PO₄/ZnO composite [23]. Under this modification, the piezoelectric effect of ZnO can be generated which leads to the improvement of pollutant degradation. The composite can also generate a Z-scheme mechanism, Ag₃PO₄ and C₃N₄ can be a good model of this system [24]. Through this mechanism, the photocatalytic ability can be improved significantly. However, up to now, the large particle of Ag₃PO₄ has been still a problem in the Ag₃PO₄-based composites that lead to limitation of photocatalytic activity.

The photocatalytic activity of Ag₃PO₄ is strongly affected by the size and surface area [25]. The large particle size could have a low surface area that leads to the poor performance of Ag₃PO₄ activity. Therefore, the development of Ag₃PO₄ synthesis to produce a small particle size is very important. Many researchers have developed the high surface area of Ag₃PO₄. Attaching the graphene oxide aerogel on Ag₃PO₄ increased the specific surface area and adsorption ability leading to high photocatalytic activity [26]. The higher content of graphene oxide aerogel showed a higher adsorption capacity. The mesoporous TiO₂ spheres could also be applied to enhance the surface area of Ag₃PO₄ [27]. The large pores and high specific surface area could lead to high photocatalytic activity due to higher adsorption capacity.

Recently, the green synthesis and plant-mediated materials synthesis is very interesting due to the eco-friendly approach that brings to high efficiency [28,29]. Mangosteen peel, a natural dye, might be applied for an agent of synthesis due to containing xanthone [30] that has polyphenol groups. This compound has derivatives of α-mangostin, β-mangostin, γ-mangostin, 3-isomangostin hydrate, 8-deoxygartanin, gartanin, garcinone E, and hydroxycalabaxanthone [31].

Herein, the mangosteen peel extract solution was applied to affect the coprecipitation of Ag₃PO₄ synthesis. A polyphenol of xanthone might control the crystal growth and morphology during the precipitation. This treatment improved the crystallinity, increased the surface area, and lowered the bandgap energy of Ag₃PO₄.

2.0 METHODOLOGY

2.1 Materials

The chemical of disodium hydrogen phosphate dodecahydrate (Na₂HPO₄·12H₂O), silver nitrate (AgNO₃), Rhodamine B, ammonium oxalate, benzoquinone, and isopropanol are pro analysis and purchased from Merck. The mangosteen peel extracts are provided using the extraction of the mangosteen peel using methanol [32].

2.2 Synthesis of Photocatalysts

The silver phosphates were synthesized using simple coprecipitation of AgNO₃ and Na₂HPO₄·12H₂O [18] under mangosteen peel extract solution. To preparing the mangosteen peel extracts, fresh mangosteen peel was washed with water and dried in the open air for 3 days. Dried mangosteen peel (10 gram) was ground and immersed in 1 liter of methanol for 24 h. The filtrate was separated and evaporated under a rotary evaporator at 64.7°C. The mangosteen peel extract solution was prepared by adding 1 gram of extract with water of 100 mL solution (1% of w/v). The sample without and with mangosteen extract solution was named M-0 and M-100, respectively.

The photocatalysts were prepared by mixing two solutions of AgNO₃ and sodium phosphate containing mangosteen peel extract. The AgNO₃ solution was made by dissolving 1.7 g of AgNO₃ in 10 mL of mangosteen peel extract solution, whereas the sodium phosphate solution was prepared by dissolving 1.2 g of Na₂HPO₄·12H₂O in 20 mL of mangosteen peel extract solution. The two solutions were then mixed under stirring at 500 rpm for 10 minutes. The products were filtered and washed with water and dried at 60°C for 3 h.
2.3 Characterization

The sample of pristine Ag₃PO₄ (M-0) and Ag₃PO₄ prepared under mangosteen peel extract (M-100) were studied using XRD (Shimadzu XRD-7000) to investigate the structure of photocatalysts. The peak of XRD was further analyzed by HighScore Plus. The absorption and bandgap energies of photocatalyst were investigated using diffuse reflectance spectroscopy, DRS (Shimadzu UV-2450). The direct transition was applied to estimate the bandgap energy of samples. Morphologies of samples were observed using SEM (JEOL JSM-6510LA). The surface area and pore size were evaluated using the BET analysis (Quantachrome Instruments version 11.0). FTIR (Shimadzu Prestige-21) was used to investigate the functional group of samples.

2.4 Photocatalytic Activity Evaluation

The photocatalytic activity was studied using Rhodamine B (RhB) photodecomposition [16]. Typically, 0.1 g of catalyst was dispersed in 100 mL of 10 mg/L Rhodamine B solution. This solution was irradiated under blue light (LED 3W, Ranpo) irradiation after 10 minutes in dark conditions. The concentration of Rhodamine B was monitored by a UV-Vis spectrophotometer at 554 nm [33].

The photocatalytic reactions were evaluated using the pseudo-first-order kinetic with the rate constant (k) using the equation of ln(C₀/C) = kt, where C₀ is the initial concentration and C is the concentration at t time [34]. Linear relationships between ln(C₀/C) and reaction time (t) implying that the reactions are fit with the pseudo-first-order kinetics.

The mechanism of photocatalytic was investigated using ammonium oxalate, benzoquinone, and isopropanol as a scavenger for holes, superoxide ion radicals, and hydroxyl radicals, respectively [16]. In this experiment, 1 mmol/L of scavenger was applied in Rhodamine B solution. Their effects on photocatalytic activity of RhB degradation in M-0 and M-100, were investigated after 15 minutes of illumination. The RhB degradation (%) was calculated by the equation of \(((\text{C₀} - \text{C₁})/\text{C₀}) \times 100\%\), where \(\text{C₀}\) and \(\text{C₁}\) are the initial concentration and 15 minutes photodegradation, respectively.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Photocatalysts

The photocatalyst of pristine Ag₃PO₄ (M-0) and the Ag₃PO₄ prepared using the mangosteen peel extract (M-100) were characterized using the XRD, SEM, BET, and DRS. Figure 1 shows the XRD profile of M-0 and M-100. These samples were identified as body-centered cubic structures (JCPDS No. 06-0505) [35]. No impurities were observed in both M-0 and M-100, indicating that the catalysts are single phases. However, higher intensities of XRD peaks could be observed in M-100, reflecting that the mangosteen peel extract solution could enhance the crystallinity of the sample. It is similar to the function of surfactants on ZnO nanoparticles that increases the crystallinity of the photocatalyst [36]. The calculated measurement of XRD can be summarized in Table 1. The decreased peak position and lowered full width at half maximum (FWHM) were found in the sample of M-100. The increase of d-space in M-100 indicating the expansion of the crystal occurred. Based on these differences, mangosteen peel extracts significantly affected the crystallite size, lattice strain, and crystallinity of Ag₃PO₄.

![Figure 1](image_url)

**Figure 1** The XRD of pristine Ag₃PO₄ (M-0) (a) and Ag₃PO₄ synthesized under mangosteen peel extract (M-100) (b)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak Position (deg)</th>
<th>Height (counts)</th>
<th>FWHM (deg)</th>
<th>d-space (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-0</td>
<td>33.51842</td>
<td>364.6622</td>
<td>0.44698</td>
<td>2.6714</td>
</tr>
<tr>
<td>M-100</td>
<td>33.47597</td>
<td>1169.762</td>
<td>0.16127</td>
<td>2.6747</td>
</tr>
</tbody>
</table>

Table 1 The characteristics of peak (210) in XRD analysis

Figure 2(a) demonstrated that the pristine Ag₃PO₄ (M-0) possesses an irregular shape of 200–600 nm in diameter with an average of 503 nm. The addition of mangosteen peel extract on the preparation decreases the particle size significantly up to 150–350 nm with an average size of 292 nm (Figure 2(b)). It indicates that the mangosteen peel extract could control the grain growth of particles. The interaction of xanthone and its derivatives from extract solution and silver ion might affect the growth particle of Ag₃PO₄, and inhibit the agglomeration leading to a small particle size formation and more uniform distribution.
The pore size distribution of M-0 revealed mostly centered at 2–15 nm with an average pore size of 4.6 nm, whereas the pore size distribution of M-100 was mostly centered at 2–25 nm with an average pore size of 3.7 nm. The corresponding pore size distribution indicates that the photocatalysts were mesopores. The characterization of BET analysis can be seen in Table 2.

Table 2 The surface area, average pore radius, and total pore of samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>( S_{\text{BE}} ) (m(^2)/g)</th>
<th>Average pore Radius (nm)</th>
<th>Total Pore Volume (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-0</td>
<td>1.42</td>
<td>4.6</td>
<td>0.0033</td>
</tr>
<tr>
<td>M-100</td>
<td>3.39</td>
<td>3.7</td>
<td>0.0063</td>
</tr>
</tbody>
</table>

Figure 4 showed that the absorption of M-100 was higher compared to the M-0, indicating the mangosteen peel extract affected the optical properties of Ag\(_3\)PO\(_4\). The bandgap energy can be calculated using the formula (1):

\[
(ahv)^2 = hv - E_g
\]

where \( E_g \), \( v \), \( h \), and \( A \) were bandgap energy, light frequency, Planck constant, and absorbance, respectively [37]. The bandgap energies of 2.12 eV and 2.00 eV were estimated for the M-0 and M-100, respectively. The lower bandgap energy of M-100 might be the effect of the chemical interaction of functional group from xanthone structure of mangosteen peel extract with the precursors during the coprecipitation of Ag\(_3\)PO\(_4\) that increases the crystallinity. It is reported that the increased crystallinity can lower the bandgap energy [38]. The effect of mangosteen on the bandgap energy is also found in TiO\(_2\) [39].
The FTIR spectra of pristine Ag3PO4 (M-0) and Ag3PO4 prepared under mangosteen peel extract (M-100) were scanned from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\), the results are shown in Figure 5. For pristine Ag3PO4 (M-0), the peaks at 563 cm\(^{-1}\), 1010 cm\(^{-1}\), and 1385 cm\(^{-1}\) are assigned to O=P-O bending vibration, P-O-P asymmetric stretching, and nitrate impurities, respectively [40]. The broad peak at around 3431 cm\(^{-1}\) is attributed to O-H stretching vibration, whereas the peak at 1656 cm\(^{-1}\) is attributed to H-O-H bending vibration from water adsorbed on the surface of Ag3PO4 [41]. The spectrum of M-100 is slightly different from the spectrum of M-0. A slight shift of spectrum in M-100 was found at 3433 cm\(^{-1}\), 1658 cm\(^{-1}\), and 1012 cm\(^{-1}\) that come from the stretching vibration of O-H groups, H-O-H bending vibrations, and asymmetric stretching of P-O-P, respectively. The O-H stretching vibration of M-100 was of higher intensity compared to the M-0, indicating that the extract of mangosteen peel affected the vibration spectrum of the photocatalyst.

However, the vibrations of C-O ester (1027 cm\(^{-1}\)), C=O stretching (1686 cm\(^{-1}\)), CH\(_2\) bending (1363 cm\(^{-1}\)), CH\(_3\) bending (1419 cm\(^{-1}\)), and C-H sp\(^3\) stretching (2938 and 2828 cm\(^{-1}\)) [42] from derivative xanthone were not observed due to releasing the mangosteen peel extract form Ag3PO4 surface due to washing treatment during the synthesis. It indicates the extract might act as a precipitating agent of particle size and crystallinity control, similar to the role of H\(_3\)C\(_6\)O\(_4\) and Na\(_2\)CO\(_3\) for the preparation of bismuth oxide [43].

The samples of Ag3PO4 synthesized under mangosteen peel extract solution showed higher photocatalytic activity. A decrease of photocatalytic activity during the dark reaction of extract-treated samples indicating there is an adsorption phenomenon on the surface of the photocatalyst.

The photocatalytic activity evaluation shows that the rate constant of 0.202, and 0.587 min\(^{-1}\) had been calculated in the sample of M-0 and M-100, respectively. The rate constant increased 2.9 times higher compared to the sample of M-0. The excellent photocatalytic activity of M-100 might be induced by higher surface area, pore volume, and crystallinities.

3.2 Photocatalytic Evaluation

The photocatalytic activities of M-0 and M-100 were investigated under blue light irradiation (Figure 6).

![Figure 5](image1)

**Figure 5** The FTIR of pristine Ag3PO4 (M-0) (a) and Ag3PO4 prepared under mangosteen peel extract solution (M-100) (b)

![Figure 6](image2)

**Figure 6** The photocatalytic activity of pristine Ag3PO4 (M-0) and Ag3PO4 synthesized under mangosteen peel extract (M-100)

![Figure 7](image3)

**Figure 7** Mechanism analysis of the photocatalytic activity of Ag3PO4 (M-0) and Ag3PO4 synthesized under mangosteen peel extract solution (M-100), using (a) control, (b) ammonium oxalate, (c) benzoquinone, and (d) isopropanol scavenger for investigating the holes, superoxide ion (O\(_2^−\)·), and hydroxyl (•OH), respectively

The mechanism of photocatalysis was investigated by adding ammonium oxalate, benzoquinone, and isopropanol in a photocatalytic reaction as a scavenger to investigate the existence of holes (h\(^+\)), superoxide ion (O\(_2^−\)·) radical, and...
hydroxyl (·OH) radical, respectively [16]. The sample of M-0 and M-100 were evaluated in detail, the results can be seen in Figure 7. The ammonium oxalate and benzoquinone addition on the M-0 photocatalyst suppressed the photocatalytic activity, indicating that the holes and superoxide ion radical are significant roles in the M-0, whereas the isopropanol addition did not suppress the reaction reflecting that the reaction was not run via hydroxyl radical. In contrast, the addition of ammonium oxalate, benzoquinone, and isopropanol on M-100 suppressed the reaction significantly, suggesting that the reaction was run via hole, superoxide radical, and hydroxyl radical. It showed that the superoxide radical was the most prominent in the mechanism of the M-100 photocatalyst. The high superoxide radical in M-100 might be generated due to lower bandgap energy. This property increases the photoexcited electron in the conduction band leading to higher oxygen reduction in the surface of Ag3PO4.

4.0 CONCLUSION

The Ag3PO4 was successfully synthesized using coprecipitation of AgNO3 and Na2HPO4.12H2O under mangosteen peel extract solution. The extract has significantly affected the coprecipitation of Ag3PO4 that leads to a higher crystallinity, smaller particle size, and higher surface area. The interaction of xanthone and its derivatives from mangosteen peel extract might affect the growth particle of Ag3PO4 and inhibit the agglomeration leading to small particle size, more uniform distribution, higher crystallinity, and low bandgap energy. The photocatalytic ability of Ag3PO4 can be improved, the rate is 2.9 times higher compared to the pristine Ag3PO4. The enhanced photocatalytic activity might be generated by the higher formation of superoxide ions and hydroxyl radicals in photocatalytic reactions.

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References


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