The Surface Modification of Ag₃PO₄ using Tetrachloroaurate(III) and Metallic Au for Enhanced Photocatalytic Activity

Uyi Sulaeman¹,*, Richo Dwi Permadi¹, Alfa Marcorius¹, Hartiwi Diastuti¹, Anung Riapanitra¹, Shu Yin²

¹Department of Chemistry, Jenderal Soedirman University, Purwokerto, 53123, Indonesia.
²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, 980-8577, Japan.

Abstract

The improvement of Ag₃PO₄ photocatalytic activity was successful by incorporating tetrachloroaurate(III) (AuCl₄⁻) and metallic Au on the surface of Ag₃PO₄. The photocatalysts were synthesized using the coprecipitation and chemisorption method. Coprecipitation of Ag₃PO₄ was carried out under ethanol-water solution using the starting material of AgNO₃ and Na₂HPO₄·12H₂O. AuCl₄⁻ ion and metallic Au were incorporated on the surface of Ag₃PO₄ using a chemisorption method under auric acid solution. The photocatalysts were characterized using XRD, DRS, SEM, and XPS. The AuCl₄⁻ ion and metallic Au were simultaneously incorporated on the Ag₃PO₄ surface. The high photocatalytic activity might be caused by increasing the separation of hole and electron due to capturing photo-generated electrons by metallic Au and Au(III) as electron acceptors.

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1. Introduction

Recently, the Au dopant-modified photocatalysts have a tremendous great attention for improving the photocatalytic properties. The photocatalyst of Au/TiO₂ [1–3], Au/ZnO [4,5], Au/WO₃ [6], Au/SmTiO₃ [7], Au/γ-Fe₂O₃ [8], Au/CdS [9] has been successfully designed for improvement the photocatalytic properties. The incorporation of Au in TiO₂ can reduce Ti⁴⁺ to Ti³⁺ that effectively enhances the stability and activity [3]. This design also generates a strong plasmon resonance absorption and improves photocatalytic activities. The metallic and ionic Au can be incorporated on the surface of TiO₂. The metallic Au can produce the highest Schottky barrier which facilitates the electron capture, whereas the ionic Au (Au⁺ and Au³⁺) can facilitate electron transfer [10]. Both metallic and ionic Au dopants in TiO₂ inhibit the recombination of electron and hole pairs. The Schottky barrier in the interfacial of metal-ZnO can also be formed by Au, this mechanism can enhance the separation of photogenerated carriers at the ZnO surface [11]. Schottky barriers can increase photoreaction through trapping and prolonging the life of the electrons [12]. However, these
modifications have still drawbacks of photogenerated electron and holes recombination. Therefore, many researchers have developed the synthesis into a multi-component design such as a ternary composite of Au dopant in a photocatalyst.

The ternary composite of Au dopant, such as Au-CoFe$_2$O$_4$/MoS$_2$ [13], g-C$_3$N$_4$/Au/ZnIn$_2$S$_4$ [14], rGO/NiWO$_4$@Au [15], Au/CuO/CoO$_3$ [16], and Au/TiO$_2$@CNTs [17], have been successfully synthesized. The Au has a significant role in the improvement of photocatalytic in these composites. The Au in the Au-CoFe$_2$O$_4$/MoS$_2$ and g-C$_3$N$_4$/Au/ZnIn$_2$S$_4$ can effectively act as a facilitator of the Z-scheme mechanism [13,14]. This mechanism maximizes the reaction in the valence band and conduction band, hence improving the photocatalytic activity. The electrons on the surface of Au in the composite of rGO/NiWO$_4$@Au can also act as electron donors, increase the electron transfer and the quantum efficiency leading to high catalytic activity [15]. The Au in Au/CuO/CoO$_3$ effectively mediates an electron trapping that improves the O$_2$ generation [16]. Plasmonic resonance, the powerful properties of metallic Au, can also be designed in Au/TiO$_2$@CNTs [17]. This plasmon can have a synergetic effect with CNTs that enhances the transport rates of electrons and holes. However, these multi-components of Au-based photocatalysts have still produced a low quantum efficiency. Therefore, an alternative photocatalyst should be expected.

Ag$_3$PO$_4$ is a new photocatalyst that has high quantum efficiency and narrow bandgap energy [18], could be promising as a highly active photocatalyst. Many researchers have focused on modifying this catalyst to improve its properties. The surface modification of the Ag$_3$PO$_4$ using Au has been reported [19–21]. Au in the Ag$_3$PO$_4$ inhibited the recombination of photogenerated electrons and holes and decreased the photo-corrosion of the Ag$_3$PO$_4$ [19]. The Au-incorporated Ag$_3$PO$_4$ heterostructure showed highly productive photocatalytic activities [20]. These properties might be induced by the double effect of plasmonic Au nanoparticles and Ag$_3$PO$_4$ photoexcitation that generate converting hydroxyl groups into hydroxyl radicals [20]. The Au nanoparticle incorporated on Ag$_3$PO$_4$/TiO$_2$ heterojunctions showed an excellent activity of 10.2 times higher improvement [21]. Based on the literature reports above, both metallic Au and ionic Au have been shown to increase photocatalytic activity. Therefore, it is promising to modify the surface of Ag$_3$PO$_4$ using the mixed Au states of metallic Au and ionic Au.

Besides the incorporation of Au on the surface of Ag$_3$PO$_4$, the defect formation on Ag$_3$PO$_4$ can enhance the photocatalytic properties. The defect sites on Ag$_3$PO$_4$ can be initiated under ethanol-water coprecipitation [22]. These defects lead to enhance absorption in the visible region resulting in high photocatalytic activity. A combination of this preparation with Au incorporating might improve the photocatalytic activity significantly.

Herein, the incorporation of AuCl$_4^−$ and metallic Au on the surface of Ag$_3$PO$_4$ has been successfully created using the coprecipitation and chemisorption method. The first step is the coprecipitation of Ag$_3$PO$_4$ under ethanol-water solution using the material of AgNO$_3$ and Na$_3$HPO$_4$.12H$_2$O, and the second step is the chemisorption of AuCl$_4^−$ ion on Ag$_3$PO$_4$ under sonication. This design aims to improve the photocatalytic activity of Ag$_3$PO$_4$ through an Au and AuCl$_4^−$. Incorporation of these species on the Ag$_3$PO$_4$ surface can increase the electron capture and prevent photogenerated electron-hole recombination, leading to high photocatalytic activity.

### 2. Materials and Methods

#### 2.1 Synthesis of Photocatalysts

The chemicals of AgNO$_3$ (ACS, ISO, Reag. Ph Eur; Merck), Na$_3$HPO$_4$.12H$_2$O (ISO, Reag. Ph Eur, Merck), HAuCl$_4$.4H$_2$O (purity: 99.9%, Shandong Honrel Co. Ltd), and ethanol (absolute for analysis, Merck), were used for the synthesis of samples. The samples of APO (Ag$_3$PO$_4$) and E-APO (Ag$_3$PO$_4$ prepared under ethanol solution) were synthesized using the coprecipitation method [22,23]. To prepare the E-APO sample, the AgNO$_3$ (0.85 g) was dissolved in 200 mL of ethanol solution (50% of ethanol in water). The Na$_3$HPO$_4$ solution was prepared by dissolving 1.8 g of Na$_3$HPO$_4$.12H$_2$O in 50 mL of deionized water. AgNO$_3$ in ethanol solution was slowly added (dropwise) by Na$_3$HPO$_4$ solution. The precipitate of E-APO was filtered and washed with deionized water and subsequently dried in an oven at 60 °C for 4 h. The sample of APO as control was synthesized with a similar procedure but without ethanol. The APO/Au (Au in Ag$_3$PO$_4$) and E-APO/Au (Au in Ag$_3$PO$_4$ prepared under ethanol solution) were synthesized using the chemisorption method. Firstly, the Au solutions were prepared using HAuCl$_4$.4H$_2$O dissolved in water with a concentration of 1 mg/mL. The 0.5 gram of APO and E-APO powder were each mixed with 10 mL of water to obtain the suspension. The Au solu-
tions (10 mL) were added to the suspension and sonicated for 15 minutes. The products were filtered and washed with water and dried in an oven at 60 °C for 4 h.

2.2 Catalysts Characterizations

All samples were characterized using X-ray diffraction (XRD, Bruker D2 Phaser) with Cu Kα radiation, λ=1.5418 Å. Absorption spectra were measured using diffuse reflectance spectroscopy (DRS, JASCO V-670). Morphology and particle size of E-APO/Au were investigated using SEM. The binding energies of Ag3d, P2p, O1s, and Au4f of E-APO/Au were investigated using XPS (ULVAC PHI 5600, ULVAC PHI Co., Ltd), calibrated by internal reference of the adventitious carbon.

2.3 Photocatalytic Activities

The photocatalytic activities were evaluated under visible light irradiation (Ranpo, LED Spotlight 3 W, blue light) [23]. The catalysts of 0.1 g were added to 100 mL of RhB solution (10 mg/L) then equilibrated for 20 minutes. The sample of RhB solution (5 mL) was withdrawn and centrifuged at 5000 rpm to separate the solution from the catalyst and the concentration was measured using the spectrophotometer. The mechanism of photocatalyst in the surface of E-APO/Au was investigated using benzoquinone (BQ), ammonium oxalate (AO), and isopropyl alcohol (IPA) as a scavenger of O₂•−, h⁺, and •OH, respectively [22].

3. Results and discussion

3.1 Characterization of Photocatalysts

The structure of photocatalysts was investigated using the XRD and the results are displayed in Figure 1A. All samples showed a similar structure of body-centered cubic Ag₃PO₄ (JCPDS no.06-0505) [24]. Due to a very small concentration of Au, the (111) plane of Au was not observed in the XRD. The doublet peak was observed at (210) plane at the highest peak (2θ) of 33.4074°, 33.4479°, 33.3668°, 33.3668° for APO, E-APO, APO/Au, and E-APO/Au, respectively (Figure 1B). The shift of (210) peaks was observed after incorporating the Au into the Ag₃PO₄. Both APO/Au and E-APO/Au exhibited a lower 2θ compared to the Au-untreated photocatalysts. The d-space (Å) of the (210) plane can be measured from the XRD data, resulting in 2.6821, 2.6790, 2.6853, and 2.6853 for APO, E-APO, APO/Au, and E-APO/Au, respectively. The d-space of E-APO is slightly lower than APO, indicating that the preparation with ethanol-water might form a silver vacancy. The changed polarity of solvent can affect the coprecipitation of Ag₃PO₄ leading

Table 1. The characterization of Ag₃PO₄ synthesized under different preparation.

| Samples  | Preparation     | Peaks of (210) (2θ) | d-space of (210) plane (Å) | The intensity ratio of (210)/(110) | Bandgap energy (eV) |
|----------|-----------------|---------------------|----------------------------|-----------------------------------|---------------------|
| APO      | water           | 33.4074             | 2.6821                     | 7.2                               | 2.40                |
| E-APO    | ethanol-water   | 33.4479             | 2.6790                     | 7.6                               | 2.37                |
| APO/Au   | water, HAuCl₄·4H₂O | 33.3668             | 2.6853                     | 8.4                               | 2.42                |
| E-APO/Au | ethanol-water, HAu-Cl₄·4H₂O | 33.3668 | 2.6853 | 8.0 | 2.42 |

Figure 1. (A) XRD profile of APO (a), E-APO (b), APO/Au (c), E-APO/Au (d), and (B) their shifts of (210) Miller indices.
to a defect formation of silver vacancy. This phenomenon can lead to a shrinkage of the lattice. In contrast, incorporating Au on the Ag₃PO₄ slightly increases the d-space, indicating that the Au was successfully incorporated in Ag₃PO₄ leading to the expansion of the lattice.

The (210)/(110) intensity ratio of 7.2, 7.6, 8.4, 8.0 can be found in the samples of APO, E-APO, APO/Au, and E-APO/Au, respectively. The Au-treated samples showed a higher intensity ratio of (210)/(110) plane, indicating that the incorporation of Au might change the plane atomic composition of the crystal. The XRD data of Ag₃PO₄ prepared under different treatments can be summarized in Table 1. The morphology of E-APO/Au was also investigated under SEM, showing that a spherical and irregular shape with the particle size distribution of 100-400 nm was created (Figure 2).

To investigating the effect of different preparation, the spectra absorptions of APO, E-APO, APO/Au, and E-APO/Au are scanned and the results are displayed in Figure 3. The absorption of E-APO along the visible region has higher than that of APO, indicating the defect of silver vacancy might be generated in E-APO that is consistent with the previous result [22]. The incorporating Au in both APO/Au and E-APO/Au generated a broad absorption peak at 520 to 640 nm (insert picture of Figure 3). These absorptions might originate from the surface plasmon resonance of Au metallic nanocluster in Ag₃PO₄ [25]. Due to the small amount of metallic Au on the surface of Ag₃PO₄, these plasmon absorptions are not so strong.

The optical bandgap of the samples can be estimated using Tauc’s relation [26] using the following Equation (1):

$$\alpha h\nu = A\left(h\nu - E_g\right)^n$$

(1)

where, $\alpha$ is the absorption coefficient, $h$ is Planck’s constant, $\nu$ is the transition frequency, $A$ is a constant, $E_g$ is the bandgap energy, and the exponent $n$ represents the nature of transitions. The bandgap energy is determined from the linear extrapolation of $(\alpha h\nu)^2$ versus $h\nu$ (n=1/2 for direct allowed transition). The results showed that the optical bandgap energies of APO, E-APO, APO/Au, and E-APO/Au are 2.40 eV, 2.37 eV, 2.42 eV, 2.42 eV respectively (Table 1). The decrease of bandgap in the E-APO sample might be caused by the defect of silver vacancy [22], whereas the increase of bandgap in APO/Au and E-APO/Au might be caused by Au incorporation on the surface.

The XPS profile of the Ag₃PO₄ (E-APO/Au) was displayed in Figure 4. The peak of 373.9 and 367.9 eV originates from the Ag3d³/₂ and Ag3d₅/₂ respectively, indicating that the state of silver is Ag⁺ (Figure 4a) and no Ag metallic was formed [27]. The P2p₁/₂ and P2p₃/₂ were also observed at 133.4 eV and 132.4 eV, indicating that the P⁵⁺ existed in the surface of Ag₃PO₄ (Figure 4b) [28]. There are two types of oxygen at 532.2 eV and 530.5 eV which are assigned to the oxygen of hydroxyl in the surface and oxygen in the lattice, respectively (Figure 4c) [29]. The Au incorporation was observed in XPS spectra with an atomic percent of 3.34% (2.12% metal Au⁰ and 1.22% ion Au³⁺). There are two states of Au in the samples suggesting that both metallic and ionic were formed in the surface as shown in Figure 4d. The 88.4 eV and 84.7 eV originate from the Au4f₅/₂ and Au4f₇/₂ respectively with a spin–orbital doublet split-
Figure 4. The XPS profile of E-APO/Au photocatalyst: Ag3d (a), P2p (b), O1s (c), and Au4f (d).

Figure 5. (A) Photocatalytic activity of APO (a), E-APO (b), APO/Au (c), and E-APO/Au (d) with (B) their rate constants and (C) the investigation of reaction mechanism on E-APO/Au using the ammonium oxalate (AO), benzoquinone (BQ), and isopropyl alcohol (IPA) as a scavenger with (D) their rate constants.
A major result was found in the calculation of the Ag/P atomic ratio from the XPS data. The Ag/P atomic ratio of 3.76 was observed in E-APO/Au. This value was higher compared to the Ag₃PO₄ (2.80) and defect-Ag₃PO₄ (2.49) that were previously reported [23]. The high ratio of Ag/P suggesting that the phosphate was substituted by Au and AuCl⁻. Interestingly, the atomic ratio of Ag/P in E-APO/Au was higher than the incorporating platinum complexes on the defect-Ag₃PO₄ (2.97) [23]. This higher ratio of Ag/P in E-APO/Au might be induced by metallic Au formation on the lattice of Ag₃PO₄ which replaced much higher phosphate ion. Therefore, phosphate deficiency in E-APO/Au was created.

Based on XPS analysis, the formation of AuCl⁻ and Au⁰ can be explained. The compound of HAuCl₄·4H₂O can be ionized into AuCl⁻ ions in water. AuCl⁻ ions can substitute PO₄³⁻ ions of Ag₃PO₄ on the surface. This unbalanced charge species substitution might easily induce electron transfers. During this process, the photoreduction of AuCl⁻ in low intensity of lightroom might occur, resulting in Au⁰. Therefore, both AuCl⁻ and Au⁰ existed on the surface of Ag₃PO₄ as observed in XPS.

3.2 Photocatalytic Evaluation

Figure 5A showed the photocatalytic activity of APO, E-APO, APO/Au, and E-APO/Au. The photocatalytic activity rates are studied using the pseudo-first-order kinetics, \( \ln(C_0/C_t) = kt \), where \( C_0 \) and \( C_t \) are the RhB concentration at times 0 and \( t \), respectively, and \( k \) is the rate constant [22]. After plotting \( \ln(C_0/C_t) \) versus \( t \), all reactions followed the pseudo-first-order kinetics with the rate constant of 0.126 min⁻¹, 0.223 min⁻¹, 0.162 min⁻¹, and 0.391 min⁻¹ for the samples of APO, E-APO, APO/Au, and E-APO/Au, respectively (Figure 5B). The ethanol treatment in the preparation of samples enhances catalytic activities. The incorporation of Au on APO increases the catalytic activity as found in the APO/Au sample however it is lower than the E-APO sample. The lower activity might be caused by the lower absorption of APO/Au in the visible region due to decreased amount of electron excitation on the surface. The treatment of Au on E-APO significantly improves the photocatalytic activity as found in E-APO/Au. It was increased 3 times higher compared to the APO. The highest activity of E-APO/Au might be caused by the dual effect of Au⁰ and AuCl⁻ that acted as effective electron acceptors on the surface of Ag₃PO₄.

The photocatalytic reaction mechanism in E-APO/Au surface was studied using ammonium oxalate (AO), benzoquinone (BQ), and isopropyl alcohol (IPA) as a scavenger for the hole (h⁺), superoxide radicals (O₂⁻•), and hydroxyl radical (•OH), respectively [31]. The mechanism of these scavengers can be summarized by reaction (2–4) based on literature reports [32–34].

\[
\begin{align*}
\text{C}_6\text{H}_5\text{H}_2\text{O}_2 + \text{O}_2 \rightarrow & \text{C}_6\text{H}_5\text{H}_2\text{O}_2^- + \text{O}_2 \quad (\text{BQ}) \\
\text{C}_6\text{H}_5\text{O}_4^- + \text{h}^+ \rightarrow & \text{CO}_2 + \text{CO}_2^0 \quad (\text{AO}) \\
\text{CH}_3\text{CHOHCH}_2^- + \cdot\text{OH} \rightarrow & \text{CH}_3\cdot\text{COHCH}_3 + \text{H}_2\text{O} \quad (\text{IPA}) \\
\end{align*}
\]

The results of the reaction mechanism study were shown in Figures 5C and 5D. The reactions in the surface were suppressed under the addition of AO and BQ, indicating that the role of hole and superoxide radicals were more prominent in the reaction. Based on this investigation, the reaction mechanism can be summarized in reactions (5–13).

\[
\begin{align*}
\text{Ag}_3\text{PO}_4 + \text{hv} & \rightarrow \text{h}^+ + \text{e}^- + \text{h}^+ + \text{e}^- + >\text{Au} \quad (5) \\
\text{e}^- + >\text{Au} & \rightarrow >\text{Au} \quad (6) \\
>\text{Au} + \text{O}_2^- & \rightarrow >\text{Au} + \text{O}_2^- + \text{O}_2 \quad (7) \\
>\text{Au} + \text{O}_2^- & \rightarrow >\text{Au} + \text{O}_2^- + \text{O}_2 \quad (8) \\
\text{O}_2^- + \text{e}^- + >\text{Au} & \rightarrow \text{O}_2^- \quad (9) \\
\text{O}_2^- + \text{h}^+ & \rightarrow >\text{Au} + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \quad (10) \\
\text{O}_2^- + \text{H}_2\text{O}_2 & \rightarrow \text{OH} + \text{OH}^- + \text{O}_2 \quad (11) \\
\text{h}^+ + \text{H}_2\text{O} & \rightarrow \cdot\text{OH} + \text{H}^+ \quad (12) \\
\cdot\text{OH} + \text{RhB} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{NO}_3^- + \text{NH}_4^+ \quad (13)
\end{align*}
\]

The proposed mechanism in the surface of E-APO/Au can be illustrated and shown in Figure 6. Under visible light irradiation, the photo-excited electrons are injected into the conduction band of Ag₃PO₄. At the same time, the Au(III) ion acts as an electron acceptor and carries out the redox reaction on the surface of the photocatalyst, producing superoxide radicals.

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**Figure 6. Proposed mechanism of photocatalytic reaction on the surface of E-APO/Au.**
Meanwhile, the metallic Au incorporated on the surface of Ag₃PO₄ generated the highest Schottky barrier that also facilitated the electron transfer [10]. The trapped electron is transferred to the adsorbed oxygen, producing superoxide radicals. These phenomena promote charge separation leading to high photocatalytic activity. The excellent photocatalytic activity is ascribed to efficient electron transfer from the conduction band of Ag₃PO₄ to Au(III) complexes chemically bonded surface and metallic Au, which brings to high charge separation, resulting in higher quantities of O₂•− radical anions [35]. The O₂•− radical anions under excess electron can produce H₂O₂, resulting in much higher •OH radicals. These species have very important roles in the oxidation of RhB into CO₂, H₂O, NO₃−, and NH₄⁺ [36].

4. Conclusions

The metallic Au nanoparticles and AuCl₄⁻ complexes ions were successfully incorporated on the surface of Ag₃PO₄. The ion of AuCl₄⁻ complex substituted the PO₄³⁻ of Ag₃PO₄ surface. The substitution was effectively on Ag₃PO₄ that synthesized under ethanol-water solution. The high photocatalytic activity of Au/AuCl₄⁻/Ag₃PO₄ was mainly caused by metallic Au and Au(III) complex as electron acceptors.

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