Manuscript Details

Manuscript number	SSSCIE_2018_693
Title	Design of Ag3PO4 for highly enhanced photocatalyst using hydroxyapatite as a source of phosphate ion
Article type	Full Length Article

Abstract

The effect of hydroxyapatite on structure, morphology, and band gap energy of silver orthophosphate (Ag3PO4) has been investigated. The hydroxyapatite as a source of phosphate ion was prepared using the coprecipitation of CaCl2 and KH2PO4. To produce the product of Ag3PO4, the as-synthesized hydroxyapatite was suspended in water and quickly added to a silver nitrate solution. The photocatalysts were characterized using XRD, SEM, DRS, and XPS. The high crystallinity of single phase Ag3PO4 was easily produced using the hydroxyapatite. Photocatalytic activities of the product were evaluated using RhB decomposition under blue light irradiation. The hydroxyapatite as a source of phosphate ion dramatically decreases the particle size and improves the photocatalytic activity of silver orthophosphate. The mechanism of this reaction works in the following order: holes > superoxide radical > hydroxyl radical.

Keywords	hydroxyapatite; silver orthophosphate; defect sites; phosphate Ion; photocatalyst.

Corresponding Author	Uyi Sulaeman
Order of Authors	Uyi Sulaeman, Suhendar Suhendar, Hartiwi Diastuti, Anung Riapanitra, Yin Shu

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Fig 1.tif [Figure]

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Fig 4.tif [Figure]

Fig 5.tif [Figure]

Fig 6.tif [Figure]

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July 6th, 2018

Dear Editor,

I would like to submit a paper entitled "***Design of Ag_3PO_4 for highly enhanced photocatalyst using hydroxyapatite as a source of phosphate ion***" to **Solid State Sciences.** Attached please find the files of the written manuscript.

In the present research, the Ag_3PO_4 solid was successfully synthesized by co-precipitation method using hydroxyapatite as a source of phosphate ion. The results showed that this method of synthesis dramatically decreases the particle size and improves the photocatalytic activity of silver orthophosphate. The mechanism of this reaction was also studied, showing that the mechanism works in the following order: holes > superoxide radical > hydroxyl radical. This is a new method of Ag_3PO_4 preparation to improve the properties of Ag_3PO_4. This investigation could be very useful for other researchers to develop the silver phosphate based photocatalyst in the future.

Based on above reason, I would be grateful if you examine its acceptance to **Solid State Sciences.**

Sincerely yours,

Dr. Uyi Sulaeman

Associate Professor,
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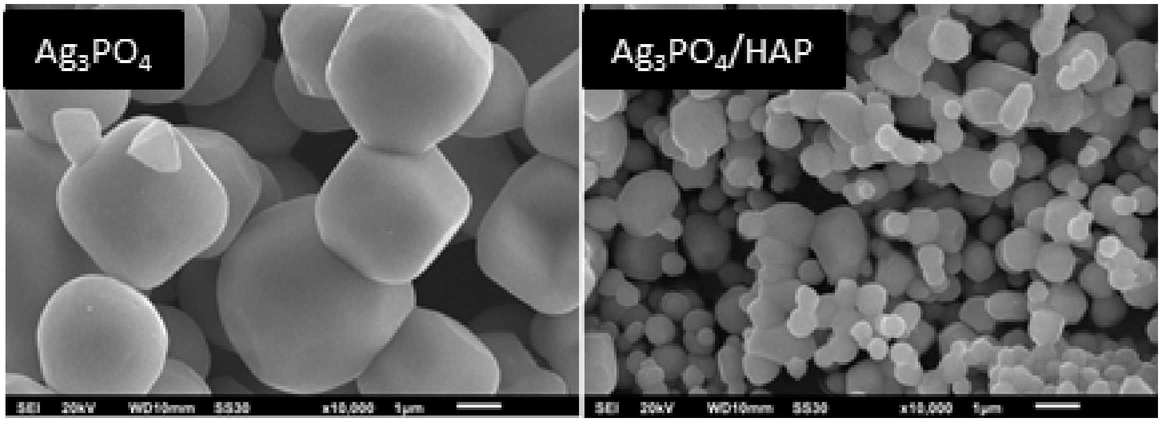
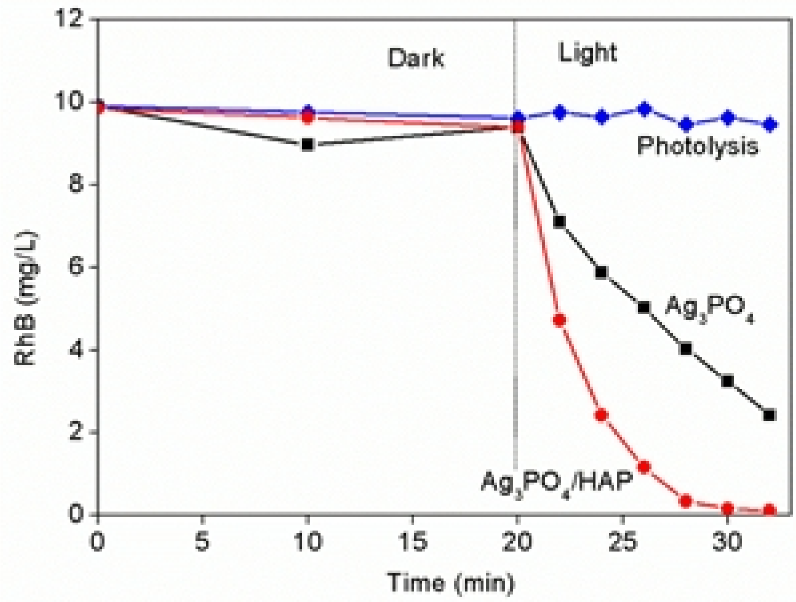

Ag3PO4
Ag3PO4/HAP
SEI 20kV WD10mm SS30 x10,000 1μm
SEI 20kV WD10mm SS30 x10,000 1μm


Dark
Light
Photolysis
Ag3PO4
Ag3PO4/HAP
RhB (mg/L)
Time (min)
0
2
4
6
8
10
12
0
5
10
15
20
25
30

Manuscript Details

Manuscript number	SSSCIE_2018_693_R1
Title	Design of Ag3PO4 for highly enhanced photocatalyst using hydroxyapatite as a source of phosphate ion
Article type	Full Length Article

Abstract

The effect of hydroxyapatite on structure, particle size, and band gap energy of silver orthophosphate (Ag3PO4) have been investigated. The hydroxyapatite as a source of phosphate ion was prepared using the coprecipitation of CaCl2 and KH2PO4. To produce the product of Ag3PO4, the as-synthesized hydroxyapatite was suspended in water and quickly added to a silver nitrate solution. The obtained photocatalysts were characterized using XRD, SEM, DRS, and XPS. The high crystallinity of single phase Ag3PO4 was easily produced using the hydroxyapatite. Photocatalytic activities of the product were evaluated using RhB decomposition under blue light irradiation. The hydroxyapatite as a source of phosphate ion dramatically decreases the particle size and increases the absorption in the visible region. This obtained photocatalyst significantly improves the photocatalytic activity. The mechanism of reaction works in the following order: holes > superoxide radical > hydroxyl radical.

Keywords	defect sites; hydroxyapatite; phosphate Ion; photocatalyst; silver orthophosphate.

Corresponding Author	Uyi Sulaeman
Order of Authors	Uyi Sulaeman, Suhendar Suhendar, Hartiwi Diastuti, Anung Riapanitra, Yin Shu

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September 15th, 2018

Dear Editor,

I would like to submit a revised manuscript entitled "***Design of Ag_3PO_4 for highly enhanced photocatalyst using hydroxyapatite as a source of phosphate ion***" to **Solid State Sciences.** Attached please find the files of the written manuscript.

This manuscript has been revised based on the Reviewer comments. I would like to appreciate to all Reviewers for comments in this manuscript. It is very valuable. I have found the clear data and good explanation after following the comments, especially the XPS analysis after photocatalytic reaction. This investigation could be very useful for other researchers to develop the silver phosphate based photocatalyst.

Based on above reason, I would be grateful if you examine its acceptance to **Solid State Sciences.**

Sincerely yours,

Dr. Uyi Sulaeman

Associate Professor,
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An Itemized List of the Changes in the Revised Manuscript

Journal : Solid State Sciences

Ms. Ref. No. : SSSCIE-2018-693

Title : Design of Ag_3PO_4 for highly enhanced photocatalyst using hydroxyapatite as a source of phosphate ion

Authors : Uyi Sulaeman, Suhendar Suhendar, Hartiwi Diastuti, Anung Riapanitra, Shu Yin

The authors greatly appreciate the reviewer's favorable comments. Here are the replies to each point. The response is in brown font, and the changes in the manuscript are in blue font. Please take some time to review this revised manuscript again, thank you very much!

Reviewers' comments:

Reviewer #1: In general, this paper reports an interesting experimental result. Using hydroxyapatite as a source of phosphate ion to synthesize Ag3PO4. The obtained products were characterized by XRD, SEM, XPS and UV-Vis analysis. The photocatalytic properties were investigated by degradation of Rhodamine B (RhB). However, in order to further improve the quality of this paper, several comments listed below should be fully addressed.

1. The photo-corrosion often takes place in the Ag based photocatalysts. The revised manuscript should present XPS results of sample after used.

According to the comment, I did the XPS analysis for the sample after used. The results are shown in Fig.7 and Table 1. The explanations are in page 8-9.

…To investigate the effect of photocatalytic reaction, the photocatalyst of Ag_3PO_4/HAP after 4 cycles test was analyzed using the XPS. The results were shown in Fig.7. The deconvolution of Ag3d showed that the BE of 374.2 eV and 368.5 were observed (Fig.7(a)), indicating that the Ag^0 was formed on the surface [27]. This formation was generated by the photoreduction of Ag^+ to Ag^0 during the photocatalytic reaction. The decreased BE of P2p (132.1 eV) was also observed after photocatalytic reaction suggesting that the chemical environment of P2p has changed (Fig.7(b)). The peak of O1s was deconvoluted into three peaks of 529.5 eV, 531.2 eV, and 533.1 eV (Fig.7(c)). The BE of 529.5 eV was assigned to the lattice oxygen atom of Ag_3PO_4 [28], whereas the BE of 531.2 eV and 533.1 eV were assigned to the O=C−OH and C−O, respectively [29]. The high intensity of 531.2 eV might also be coincident with the chemisorbed water or surface hydroxyl group [30,31]. These suggested that the catalyst after cyclic test might adsorb the product of RhB degradation. The BE of 284.4 eV, 285.6 eV, 286.9 eV, and 288.2 eV at C1s assigned to sp^2, sp^3 hybridized C atom, C−O, and COOH respectively (Fig.7(d)) [19]. The concentration of C1s after the cyclic test was higher compared to before cyclic test, suggesting that the carbon compounds from the RhB degradation highly adsorbed on the surface of Ag_3PO_4/HAP (Table 1). The N1s and Cl2p were also identified in the sample (Fig.7(e,f)), indicating that the products of RhB degradation contain nitrogen and chlorine adsorbed on to the surface of Ag_3PO_4. The peak with the BE of 399.7 eV at N1s was assigned to C-N configuration [32,33]. The BE of 197.5 eV and 199.5 eV were assigned to Cl $2p_{3/2}$ and $2p_{1/2}$ spin-orbit doublet [34], respectively.

2. Before using abbreviation e.g. BE in paragraph 4, page 6, full name should be added.
According to the comment, I have changed it, could be seen in page 7, paragraph 2.
The binding energy (BE) of 373.8 eV and 367.8 eV were assigned to the $Ag3d_{3/2}$ and $Ag3d_{5/2}$, respectively (Fig.4(b)).

3. Photocatalytical mechanism about the role of Ag is not clear. The authors should be discussed carefully.
According to the comment, I have changed it, the explanation based on the data and references The explanation could be seen in page 8 paragraph 1, and in page 9 paragraph 2.

4. In Figure 5, the authors think the high photocatalytic activity might be caused by small particle size and defect sites. However, they didn't provide detailed illustration or cite reference's results.
According to the comment, I have changed it, the explanation based on the data and references, see page 8, paragraph 1.
The high photocatalytic activity might be caused by smaller particle size that has a relatively higher specific surface area [25]. The higher the photocatalyst surface area, the higher the absorption that contributes to the photocatalytic reaction [26]. It is also possible that the Ag_3PO_4/HAP has a defect site due to having a high absorption above 500 nm as shown in Fig.2. The previous results showed that the native defect of silver vacancy was observed in the sample that has high absorption in the visible region [3]. The defect sites might act as capture centers for the photoexcited electron that effectively suppress the recombination of electron and holes.

5. In the section of the introduction, it is incomplete to summarize the development of Ag-based heterojunction photocatalyst, some recent papers about Ag-based photocatalyst should be discussed in the introduction, e.g. SOLID STATE SCIENCES, 2016, 56: 10-15, SOLID STATE SCIENCES, 2018, 80: 1-5, Chinese J. Catal. 2017, 38, 337-347, Applied Catalysis B: Environmental, 2018, 234: 90-99, Appl. Catal. B, 2016, 187, 163-170..

According to the comment, I have added the introduction based on these references, see page 2, paragraph 1.

…Many researchers have mainly focused on Ag-based heterojunction in Ag_3PO_4 photocatalyst improvement. For example, the incorporation of reduced graphene oxide (RGO) into the $BiPO_4/Ag/Ag_3PO_4$ heterojunction improved the charge transfer and suppressed the recombination of electron/hole pairs [4]. The Z-scheme heterojunction and surface plasmon resonance effect could also be generated by the design of $Ag_3PO_4/Ag/Ag_2MoO_4$ [5]. This impressive design enhanced the photocatalytic activity and stability. Another photocatalyst, TiO_2, could also be improved by forming the Ag quantum dots on TiO_2. This modification could generate the surface plasmon resonance effect that improves the visible light photocatalytic activity [6]. However, the formation of metallic Ag could decrease the stability, for instance, the addition of Ti(IV) co-catalyst on AgBr decreases the stability because the accumulated electron in CB promotes the reduction of Ag^+ ions into metallic Ag [7]. This problem could be improved by surface modification using Fe(III) as an electron co-catalyst. The photocatalytic activity was not only affected by the Ag nanoparticle but also affected by phosphate ion. The grafting of phosphate on the surface-phase junction structure of twinned $BiPO_4$ affected the position of energy band and improve the redox ability [8].

Reviewer #2:

In this manuscript, the authors primarily introduced a method of investigation of the effect of hydroxyapatite on structure, morphology, and band gap energy of silver orthophosphate (Ag_3PO_4). The authors provide relevant analysis results to explain the advantages of this method, but I think it can be published after major revise.

1. Please give the annotation under every figure.

According to the comment, I have added the annotation under every Figures. The changes could be seen in Figure caption.

2. In Fig. 3b, the agglomeration of Ag_3PO_4/HAP is obvious, but the photocatalytic activities of are very preeminent. I think the author should give explanation.

Yes, the agglomeration of Ag_3PO_4/HAP is obvious. However, the different particle size could be seen clearly. Beside particle size, the high absorption of Ag_3PO_4/HAP has been observed. Previous results showed that this phenomenon is caused by defect in the surface of Ag_3PO_4 that improve the catalytic activity. I have changed the explanation based on the data and references in page 8, paragraph 1.

The high photocatalytic activity might be caused by smaller particle size that has a relatively higher specific surface area [25]. The higher the photocatalyst surface area, the higher the absorption that contributes to the photocatalytic reaction [26]. It is also possible that the Ag_3PO_4/HAP has a defect site due to having a high absorption above 500 nm as shown in Fig.2. The previous results showed that the native defect of silver vacancy was observed in the sample that has high absorption in the visible region [3]. The defect sites might act as capture centers for the photoexcited electron that effectively suppress the recombination of electron and holes.

3. In the manuscript, the authors mention that the effect of hydroxyapatite on structure, morphology, and band gap energy of silver orthophosphate (Ag3PO4) has been investigated. However, in this manuscript, I don't find the analysis of effect of morphology to the photocatalytic activities.

According to the comment, I have changed it as shown in the Abstract.

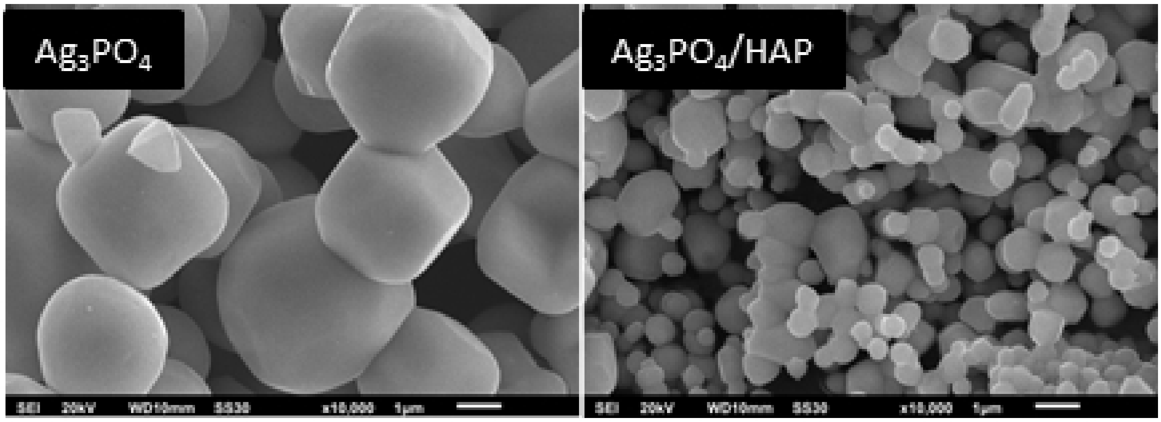
The effect of hydroxyapatite on structure, particle size, and band gap energy of silver orthophosphate (Ag_3PO_4) have been investigated.

4. In the manuscript, the authors mention that when the HAP adding, the size of Ag_3PO_4 significantly decreases and the photocatalytic activities significantly increases. I think the authors should give some explanation.

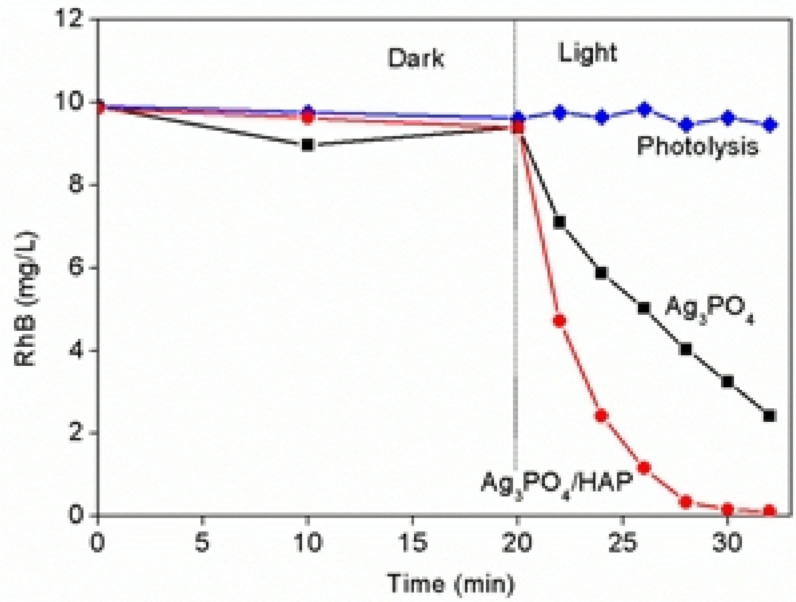
According to the comment, I have changed the explanation, see page 8, paragraph 1

The high photocatalytic activity might be caused by smaller particle size that has a relatively higher specific surface area [25]. The higher the photocatalyst surface area, the higher the absorption that contributes to the photocatalytic reaction [26]. It is also possible that the Ag_3PO_4/HAP has a defect site due to having a high absorption above 500 nm as shown in Fig.2. The previous results showed that the native defect of silver vacancy was observed in the sample that has high absorption in the visible region [3]. The defect sites might act as capture centers for the photoexcited electron that effectively suppress the recombination of electron and holes.

- The Ag_3PO_4 was successfully synthesized using hydroxyapatite
- Hydroxyapatite could be used as a source of phosphate ion
- Hydroxyapatite dramatically decreases the particle size of Ag_3PO_4
- The highly enhanced Ag_3PO_4 could be easily produced.



Ag_3PO_4
Ag_3PO_4/HAP
SEI 20kV WD10mm SS30 x10,000 1μm
SEI 20kV WD10mm SS30 x10,000 1μm



Dark
Light
Photolysis
Ag_3PO_4
Ag_3PO_4/HAP
RhB (mg/L)
Time (min)
0
2
4
6
8
10
12
0
5
10
15
20
25
30

From: Sang Woo Han (Solid State Sciences) <EviseSupport@elsevier.com>
Sent: Sunday 30th September 2018 14:41
To: Uyi Sulaeman <sulaeman@unsoed.ac.id>
Subject: Your manuscript SSSCIE_2018_693_R1 has been accepted

Ref: SSSCIE_2018_693_R1
Title: Design of Ag3PO4 for highly enhanced photocatalyst using hydroxyapatite as a source of phosphate ion
Journal: Solid State Sciences

Dear Dr. Sulaeman,

I am pleased to inform you that your paper has been accepted for publication. My own comments as well as any reviewer comments are appended to the end of this letter. Now that your manuscript has been accepted for publication it will proceed to copy-editing and production.

Thank you for submitting your work to Solid State Sciences. We hope you consider us again for future submissions.

Kind regards,

Sang Woo Han
Regional Editor
Solid State Sciences

Comments from the editors and reviewers:
- **Reviewer 2**

-

The author has been modified the manuscript as the comments and the subject addressed in this article is worthy of investigation. So, in my opinion, this manuscript could be published in present form.

Corrections received

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Article title: Design of Ag3PO4 for highly enhanced photocatalyst using hydroxyapatite as a source of phosphate ion
Article reference: SSSCIE5764
Journal title: Solid State Sciences
Corresponding author: Dr Uyi Sulaeman
First author: Dr Uyi Sulaeman
Accepted manuscript available online: 4-OCT-2018
DOI information: 10.1016/j.solidstatesciences.2018.09.015

Dear Dr Sulaeman,

We are pleased to inform you that your accepted manuscript (unformatted and unedited PDF) is now available online at:

https://doi.org/10.1016/j.solidstatesciences.2018.09.015

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