Confirming submission to Surfaces and Interfaces

From: Surfaces and Interfaces (em@editorialmanager.com)

To: uyi_sulaeman@yahoo.com

Date: Tuesday, October 19, 2021, 04:30 PM GMT+7

This is an automated message.

Surface modification of Ag3PO4 using the alginate for highly active photocatalyst under visible light irradiation

Dear Dr. Sulaeman,

We have received the above referenced manuscript you submitted to Surfaces and Interfaces.

To track the status of your manuscript, please log in as an author at https://www.editorialmanager.com/surfin/, and navigate to the "Submissions Being Processed" folder.

Thank you for submitting your work to this journal.

Kind regards,
Surfaces and Interfaces

More information and support

You will find information relevant for you as an author on Elsevier's Author Hub: https://www.elsevier.com/authors

FAQ: How can I reset a forgotten password?
https://service.elsevier.com/app/answers/detail/a_id/28452/supporthub/publishing/
For further assistance, please visit our customer service site:
https://service.elsevier.com/app/home/supporthub/publishing/
Here you can search for solutions on a range of topics, find answers to frequently asked questions, and learn more about Editorial Manager via interactive tutorials. You can also talk 24/7 to our customer support team by phone and 24/7 by live chat and email

#AU_SURFIN#

To ensure this email reaches the intended recipient, please do not delete the above code

Decision on submission to Surfaces and Interfaces

From: Surfaces and Interfaces (em@editorialmanager.com)

To: uyi_sulaeman@yahoo.com

Date: Sunday, November 7, 2021, 08:33 AM GMT+7

Manuscript Number: SURFIN-D-21-02538

Surface modification of Ag3PO4 using the alginate for highly active photocatalyst under visible light irradiation

Dear Dr. Sulaeman,

Thank you for submitting your manuscript to Surfaces and Interfaces.

I have completed my evaluation of your manuscript. The reviewers recommend reconsideration of your manuscript following major revision. I invite you to resubmit your manuscript after addressing the comments below. Please resubmit your revised manuscript by Nov 27, 2021.

When revising your manuscript, please consider all issues mentioned in the reviewers' comments carefully: please outline every change made in response to their comments and provide suitable rebuttals for any comments not addressed. Please note that your revised submission may need to be re-reviewed.

To submit your revised manuscript, please log in as an author at https://www.editorialmanager.com/surfin/, and navigate to the "Submissions Needing Revision" folder.

Surfaces and Interfaces values your contribution and I look forward to receiving your revised manuscript.

Kind regards,
Hong Deng
Editor

Surfaces and Interfaces

Editor and Reviewer comments:

Reviewer #1: Manuscript ID: SURFIN-D-21-02538
Title: Surface modification of Ag3PO4 using the alginate for highly active photocatalyst under visible light irradiation
The manuscript reported a feasible surface modification strategy for enhancement of the photocatalytic activity of Ag3PO4, in which the alginate was incorporated on the surface of Ag3PO4 under the chemisorption method. The physical and photochemical properties of the as-prepared photocatalysts were detailed characterizations. It was found that the alginate can act as a donor electron, thus the as-fabricated product showed the improving photocatalytic degradation of RhB under visible light irradiation. This manuscript is well written and interpreted. Moreover, the possible photocatalytic mechanism was studied. Now the manuscript is recommendation with Minor revisions for publication in the journal of Surfaces and Interfaces. There are three concerns founded in the manuscript are as follows:
1. Generally, the BET surface area is an important factor for enhancing the photocatalytic performance, thus the related data of as-prepared products should be added in the revised manuscript.
2. The photocatalytic mechanism is not carefully discussed.
3. In the field of photocatalysis, some recent articles (Journal of Alloys and Compounds 881 (2021) 160437; Renewable Energy 178 (2021) 757-765; Journal of Physics and Chemistry of Solids 159 (2021) 110283; International Journal of Hydrogen Energy 45 (2020) 6425-6436) should be referred.

Reviewer #2: In this work, the authors modified the Ag3PO4 with the alginate for enhanced photocatalytic dye degradation. The author confirmed that alginate was successful chemically bonded on the surface of Ag3PO4 by XPS and other technical characterizations. They believed that the high activity of modified Ag3PO4 was due to conjugate molecules formation which can act as a donor electron under visible light irradiation. This work seems interesting. I think this manuscript can be accepted for publication in Surfaces and Interfaces after major revision. However, there are some points should be revised and improved.

1. In order to give the structure information more clearly, it is suggested that the authors provide the HRTEM images of samples.
2. Can the author give the specific structure of the surface alginate on Ag3PO4?
3. Are there any Ca species such as Ca3(PO4)2 on the material surface (although XRD can not be detected due to low content or low crystallinity)?
4. In FTIR analysis, why spectra for all samples (pristine and modified Ag3PO4) are almost the same regardless of the modification?
5. "The incorporation of alginate on the surface of Ag3PO4 created a new small edge absorption at 729 nm that can be converted to 1.70 eV of bandgap energy (insert Fig.2). This new phenomenon in absorption might be generated by the interaction of alginate and AP-H". How to determine this conclusion? The UV-vis DRS of alginate should be provided for the comparision.
6. For the mechanism in Fig. 13, where do photogenerated holes of alginate migrate? What substance captures photogenerated holes? Are photogenerated holes of Ag3PO4 migrating to HOMO of migrate?
7. In order to prove the photocatalysis mechanism and clarify the promotion of charge transfer, the author needs to supplement the PL and photoelectrochemistry of materials.
8. The material after the cyclic test should be characterized.
9. Some typos are found in this manuscript. such as "Fig. 4c dan 4d" should be "Fig. 4c and 4d". The authors should carefully check this manuscript and revise all the typos. Some descriptions are inaccurate. Such as "Sharp absorption at around 3130 cm-1", this is a broad band, not a sharp band.

An Itemized List of the Changes in the Revised Manuscript

Manuscript Reference: SURFIN-D-21-02538

Title : Surface modification of Ag_3PO_4 using the alginate for highly active photocatalyst under visible light irradiation

Authors : Uyi Sulaeman, Yusvirza Khairullah Gandasasmita, Hartiwi Diastuti, Ponco Iswanto, Isnaeni, Ardiansyah Taufik, Shu Yin.

The authors greatly appreciate the reviewer's favourable comments. Here are the replies to each point. The response is in **bold 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!

Reviewer #1:

The manuscript reported a feasible surface modification strategy for enhancement of the photocatalytic activity of Ag3PO4, in which the alginate was incorporated on the surface of Ag3PO4 under the chemisorption method. The physical and photochemical properties of the as-prepared photocatalysts were detailed characterizations. It was found that the alginate can act as a donor electron, thus the as-fabricated product showed the improving photocatalytic degradation of RhB under visible light irradiation. This manuscript is well written and interpreted. Moreover, the possible photocatalytic mechanism was studied. Now the manuscript is a recommendation with Minor revisions for publication in the journal of Surfaces and Interfaces. There are three concerns found in the manuscript are as follows:

1. Generally, the BET surface area is an important factor for enhancing the photocatalytic performance, thus the related data of as-prepared products should be added in the revised manuscript.

According to the comment, I have added the Table of BET analysis.

Table 1 BET surface area, pore-volume, and pore diameter of AP, AP-H and AP-HG15

Samples	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
AP	0.776	0.0036	18.73
AP-H	0.673	0.0022	13.17
AP-HG15	0.901	0.0035	15.41

The BET surface area, pore-volume, and pore diameter of AP, AP-H and AP-HG15 were measured, and the results can be seen in Table 1. There are no significant changes in specific surface area, pore-volume, and pore diameter implying that the enhanced photocatalytic activity might not be influenced by these characteristics.

2. The photocatalytic mechanism is not carefully discussed.

According to the comment, I have revised the mechanism and the explanation.

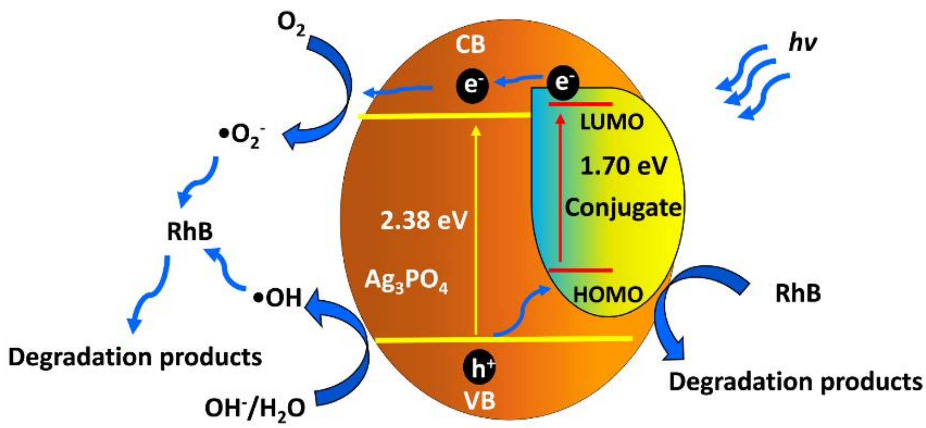

Fig. 14. Mechanism of a photocatalytic reaction on the surface of Ag_3PO_4 photocatalyst modified using alginate.

The proposed mechanism of photocatalytic reaction in the surface of AP-HG15 can be seen in Fig. 14. Upon blue light irradiation, the electron in VB can be exited into CB, producing a hole in VB which oxidizes the hydroxyl ion or water into hydroxyl radical. The conjugate molecule generated on the surface might act as a sensitizer that contributes to producing the photogenerated electron. The electron of HOMO can be exited into the LUMO of the sensitizer that directly transfers to the CB of Ag_3PO_4. The sensitizer can act as an electron donor. This phenomenon enhances the reduction of oxygen to produce more superoxide radicals. Meanwhile, the hole formed in VB of Ag_3PO_4 might have migrated to the HOMO of conjugate increasing the separation of photogenerated electrons and holes. The HOMO directly reacts with RhB to produce the degradation products.

3. In the field of photocatalysis, some recent articles (Journal of Alloys and Compounds 881 (2021) 160437; Renewable Energy 178 (2021) 757-765; Journal of Physics and Chemistry of Solids 159 (2021) 110283; International Journal of Hydrogen Energy 45 (2020) 6425-6436) should be referred.

Thank you very much I have obtained a lot of knowledge from these papers that was inspiring me to develop the research in the future. I have added two references from the list.

Reviewer #2:

In this work, the authors modified the Ag3PO4 with the alginate for enhanced photocatalytic dye degradation. The author confirmed that alginate was successful chemically bonded on the surface of Ag3PO4 by XPS and other technical characterizations. They believed that the high activity of modified Ag3PO4 was due to conjugate molecules formation which can act as a donor electron under visible light irradiation. This work seems interesting. I think this manuscript can be accepted for publication in Surfaces and Interfaces after major revision. However, some points should be revised and improved.

1. In order to give the structure information more clearly, it is suggested that the authors provide the HRTEM images of samples.

Thank you for the suggestion. The HRTEM is very useful to visualize the images of the structure. However, this instrument is not available in my laboratory, I could not evaluate the sample with HRTEM.

2. Can the author give the specific structure of the surface alginate on Ag_3PO_4?

The structure of synthesized material is a composite, the alginate incorporated on the surface of Ag_3PO_4. This structure is based on the XPS analysis. The XPS analysis showed significant evidence of alginate chemically bonded on the Ag_3PO_4 surface.

3. Are there any Ca species such as $Ca_3(PO_4)_2$ on the material surface (although XRD cannot be detected due to low content or low crystallinity)?

According to the comment, I have analyzed the Ca content of AP-H and AP-HG15 using the high resolution of XPS. The results were added as Supplementary material. There is no Ca significantly bound to the surface of Ag_3PO_4.

To make sure there is no $CaHPO_4$/hydroxyapatite, the Ca atom on the surface of Ag_3PO_4 was analyzed using high resolution of XPS (Fig.S3 in the Supplementary Material). The atomic percentage of 0.24% and 0.11% were found in the sample of AP-H and AP-HG15, respectively. After Ar^+ sputtering, the Ca content decreased to 0.14% and 0.00% for the sample of AP-H and AP-HG15 respectively. All the Ca atomic percentages are very small suggesting that the Ca-based compounds do not significantly exist.

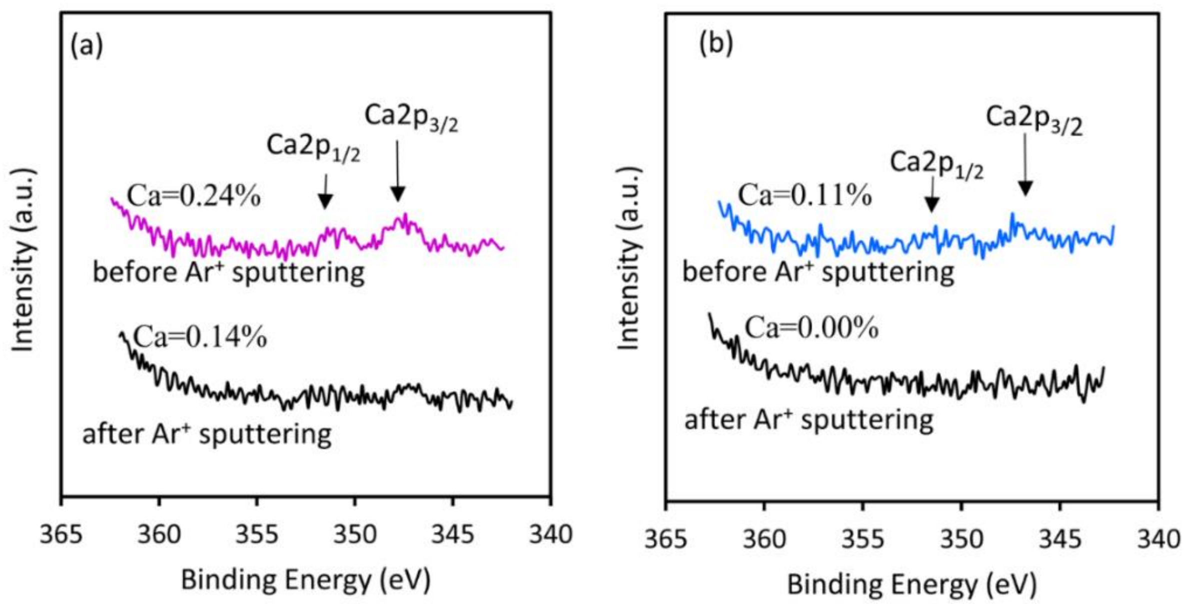

Fig. S3. The high resolution of XPS for detecting the Ca in AP-H (a) and AP-HG15 (b).

4. In FTIR analysis, why spectra for all samples (pristine and modified Ag_3PO_4) are almost the same regardless of the modification?

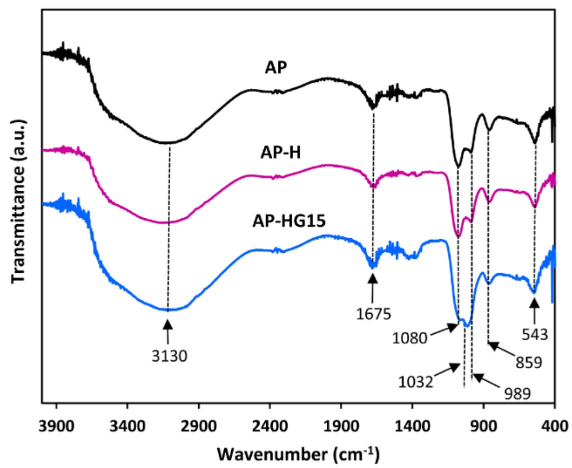

Fig. 4. FTIR spectra of AP, AP-H, and AP-HG15

The AP and AP-H are almost the same because the synthesis was not utilized alginate. It only used different phosphate sources. In contrast, the sample of AP-HG15 showed a significant difference in vibration at 1032 cm^{-1}. It is a spectrum of alginate that is attributed to its saccharide structure (C-O-C stretching) based on reference.

Specific vibration among the samples was found at 1032 cm^{-1} assigned to saccharide structure (C-O-C stretching) of AP-HG15 [35].

5. "The incorporation of alginate on the surface of Ag_3PO_4 created a new small edge absorption at 729 nm that can be converted to 1.70 eV of bandgap energy (insert Fig.2). This new phenomenon in absorption might be generated by the interaction of alginate and AP-H". How to determine this conclusion? The UV-vis DRS of alginate should be provided for the comparison.

According to the comment,
based on the data of UV-Vis DRS, a small band-edge absorption in AP-HG15 samples was created. The UV-DRS of sodium alginate was also provided and showed a small absorption in 671 nm. I have argued that this absorption can be responsible for a new edge absorption formation. Moreover, the high interaction of alginate and Ag_3PO_4 might induce electron delocalization on the surface.

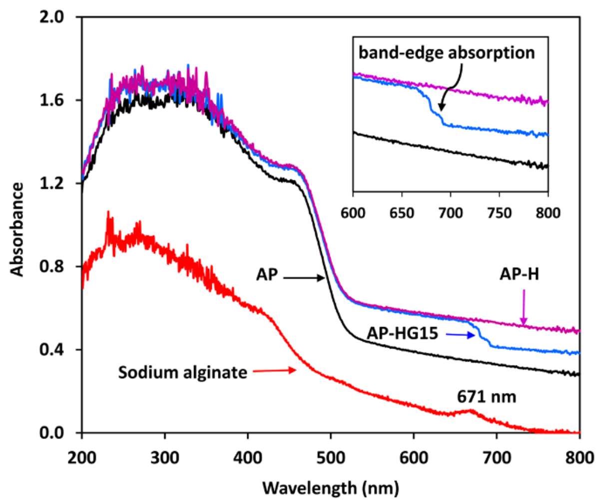

Fig. 2. Absorption spectra of AP, AP-H, AP-HG15, and sodium alginate

6. For the mechanism in Fig. 13, where do photogenerated holes of alginate migrate? What substance captures photogenerated holes? Are photogenerated holes of Ag3PO4 migrating to HOMO of migrate?

According to the comment, I revised the explanation of the mechanism based on the data.

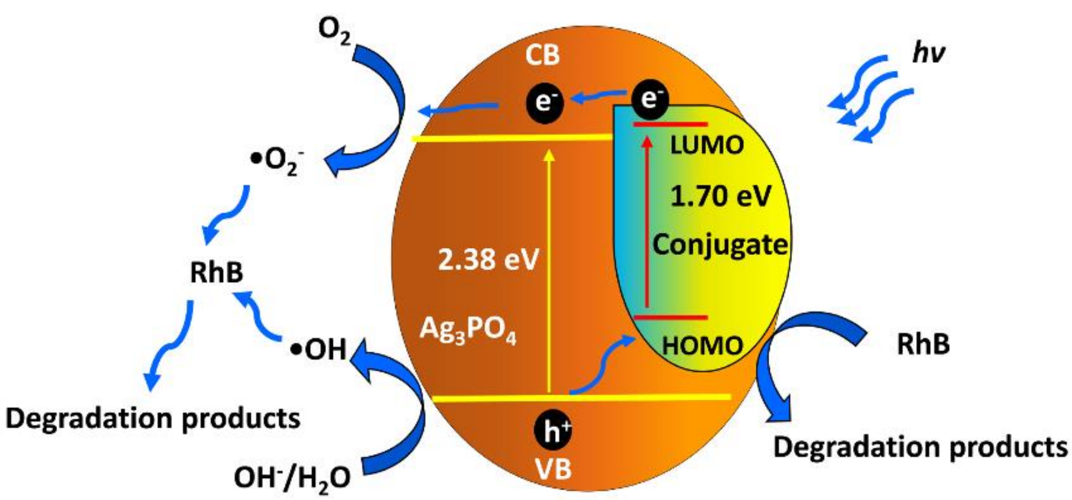

Fig. 14. Mechanism of a photocatalytic reaction on the surface of Ag_3PO_4 photocatalyst modified using alginate.

The proposed mechanism of photocatalytic reaction in the surface of AP-HG15 can be seen in Fig. 14. Upon blue light irradiation, the electron in VB can be exited into CB, producing a hole in VB which oxidizes the hydroxyl ion or water into hydroxyl radical. The conjugate molecule generated on the surface might act as a sensitizer that contributes to producing the photogenerated electron. The electron of HOMO can be exited into the LUMO of the sensitizer that directly transfers to the CB of Ag_3PO_4. The sensitizer can act as an electron donor. This phenomenon enhances the reduction of oxygen to produce more superoxide radicals. Meanwhile, the hole formed in VB of Ag_3PO_4 might have migrated to the HOMO of conjugate increasing the separation of photogenerated electrons and holes. The HOMO directly reacts with RhB to produce the degradation products.

7. In order to prove the photocatalysis mechanism and clarify the promotion of charge transfer, the author needs to supplement the PL and photoelectrochemistry of materials.

According to the comment, I have evaluated the sample using PL spectra, whereas the photoelectrochemistry of materials could not be done due to not being available in my lab.

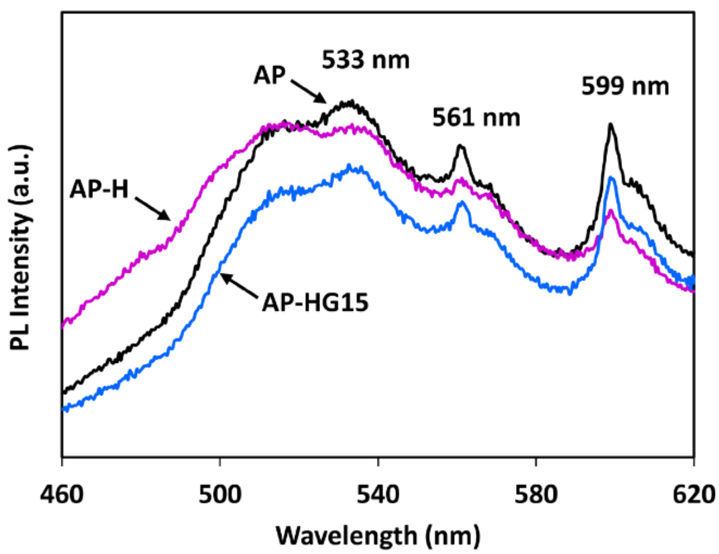

Fig. 3. PL spectra of AP, AP-H, and AP-HG15 at the excitation wavelength of 405 nm

The PL spectra are very useful to assess the photogenerated charge separation of photocatalysts [30]. Figure 3 displayed the PL spectra of AP, AP-H and AP-HG15 under the excitation wavelength of 405 nm. The PL spectra of AP exhibited high three strong emission peaks at 533, 561 and 599 nm, which were related to the recombination of photogenerated electron and hole pairs of Ag_3PO_4. The decreased emission of AP-H, mainly in a lower wavelength of 599 nm, implies that the synthesis of Ag_3PO_4 using the composite of $CaHPO_4$/hydroxyapatite as a source of phosphate ion prevents the recombination rate. It might be the defect formation in Ag_3PO_4 effectively trapping the photogenerated electron. The lowest PL spectra at 533 nm and 561 nm peak emissions were found in AP-HG15 indicating that the alginate effectively improves the separation of photogenerated electrons and holes.

8. The material after the cyclic test should be characterized.

According to the comment, I have analyzed the sample after recycle test using XRD and added as a Supplementary Materials.

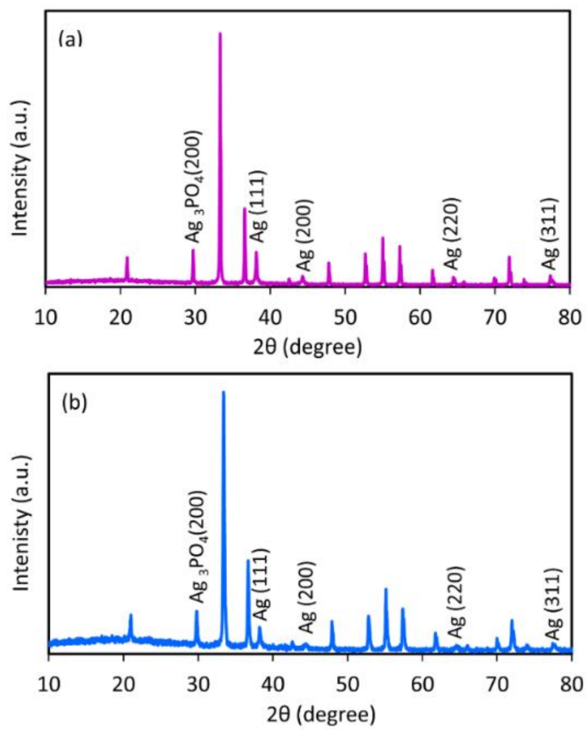

Fig. S5. The XRD analysis after cyclic test of photocatalytic reaction for AP-H (a) and AP-HG15 (b).

Both AP-H and AP-HG15 exhibited a metallic Ag (Ag^0), indicating that the photoreduction occurred on the surface. The content of Ag^0 in AP-HG15 is lower than that of AP-H, suggesting that the alginate can suppress the photoreduction of Ag^+ as shown in Fig. S5 in the Supplementary Material.

I have added the notes in the Supplementary material:

The XRD peak at 2θ of 38.13 °, 44.32 °, 64.48 ° and 77.43 ° could be assigned to the 111, 200, 220 and 311 crystal planes of the face-centred cubic (fcc) Ag^0 in the AP-H sample [3], whereas the peak 2θ of 38.20°, 44.43°, 64.63 and 77.5° crystal planes were found in AP-HG15. The Ag(111)/Ag3PO4(200) ratio of 0.92 and 0.56 was calculated from the samples AP-H and AP-HG15, respectively. It indicates that the concentration of metallic Ag in APHG-15 is lower than the AP-H suggesting that the modification of Ag3PO4 using the alginate can suppress the photoreduction.

9. Some typos are found in this manuscript. such as "Fig. 4c dan 4d" should be "Fig. 4c and 4d". The authors should carefully check this manuscript and revise all the typos. Some descriptions are inaccurate. Such as "Sharp absorption at around 3130 cm^{-1}", this is a broad band, not a sharp band. **Thank you very much, I have already checked and revised the manuscript carefully.**

Confirming submission to Surfaces and Interfaces

From: Surfaces and Interfaces (em@editorialmanager.com)

To: uyi_sulaeman@yahoo.com

Date: Saturday, November 27, 2021, 09:46 AM GMT+7

This is an automated message.

Manuscript Number: SURFIN-D-21-02538R1

Surface modification of Ag3PO4 using the alginate for highly active photocatalyst under visible light irradiation

Dear Dr. Sulaeman,

We have received the above referenced manuscript you submitted to Surfaces and Interfaces.

To track the status of your manuscript, please log in as an author at https://www.editorialmanager.com/surfin/, and navigate to the "Revisions Being Processed" folder.

Thank you for submitting your revision to this journal.

Kind regards,
Surfaces and Interfaces

More information and support

You will find information relevant for you as an author on Elsevier's Author Hub: https://www.elsevier.com/authors

FAQ: How can I reset a forgotten password?
https://service.elsevier.com/app/answers/detail/a_id/28452/supporthub/publishing/
For further assistance, please visit our customer service site:
https://service.elsevier.com/app/home/supporthub/publishing/
Here you can search for solutions on a range of topics, find answers to frequently asked questions, and learn more about Editorial Manager via interactive tutorials. You can also talk 24/7 to our customer support team by phone and 24/7 by live chat and email

#AU_SURFIN#

To ensure this email reaches the intended recipient, please do not delete the above code

Decision on submission to Surfaces and Interfaces

From: Surfaces and Interfaces (em@editorialmanager.com)

To: uyi_sulaeman@yahoo.com

Date: Tuesday, December 7, 2021, 09:11 PM GMT+7

Manuscript Number: SURFIN-D-21-02538R1

Surface modification of Ag3PO4 using the alginate for highly active photocatalyst under visible light irradiation

Dear Dr. Sulaeman,

Thank you for submitting your manuscript to Surfaces and Interfaces.

I am pleased to inform you that your manuscript has been accepted for publication.

My comments, and any reviewer comments, are below.
Your accepted manuscript will now be transferred to our production department. We will create a proof which you will be asked to check, and you will also be asked to complete a number of online forms required for publication. If we need additional information from you during the production process, we will contact you directly.

We appreciate you submitting your manuscript to Surfaces and Interfaces and hope you will consider us again for future submissions.

Kind regards,
Hong Deng
Editor

Surfaces and Interfaces

Editor and Reviewer comments:

Reviewer #1: I reviewed the revised manuscript very carefully and all of my comments are implemented. Thus, the revised manuscript can be accepted now.

More information and support

FAQ: When and how will I receive the proofs of my article?
https://service.elsevier.com/app/answers/detail/a_id/6007/p/10592/supporthub/publishing/related/

You will find information relevant for you as an author on Elsevier's Author Hub: https://www.elsevier.com/authors

FAQ: How can I reset a forgotten password?
https://service.elsevier.com/app/answers/detail/a_id/28452/supporthub/publishing/
For further assistance, please visit our customer service site:
https://service.elsevier.com/app/home/supporthub/publishing/
Here you can search for solutions on a range of topics, find answers to frequently asked questions, and learn more about Editorial Manager via interactive tutorials. You can also talk 24/7 to our customer support team by phone and 24/7 by live chat and email

#AU_SURFIN#

To ensure this email reaches the intended recipient, please do not delete the above code