nature portfolio

Peer Review File

The collective photothermal effect of silver nanoparticles probed by a microbolometer

Web links to the author's journal account have been redacted from the decision letters as indicated to maintain confidentiality.

Decision letter and referee reports: first round

4th Jan 24

Dear Professor Neuzil,

Thank you for submitting your manuscript, "Shedding Light on Plasmon Effect from a Single Nanoparticle", to Communications Materials, and please accept our sincere apologies for the unusual time required to review your study, due to end-of-year commitments of our reviewers.

Your manuscript has now been seen by 3 referees, whose comments are appended below. You will see that the referees are giving mixed recommendations regarding the significance of your study and have raised important concerns that must be addressed. In light of these comments, we cannot accept the manuscript for publication, but are interested in considering a revised version that addresses these serious concerns.

We hope you will find the referees' comments useful as you decide how to proceed. Should further experimental data and discussion allow you to address these criticisms, we would be happy to look at a substantially revised manuscript. However, please bear in mind that we will be reluctant to approach the referees again in the absence of major revisions. If the revision process takes significantly longer than three months, we will be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

-A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.

-A marked-up version of the manuscript with all changes to the text in a different colored font. Please do not include tracked changes or comments. Please select the file type ‘Revised Manuscript - Marked Up’ when uploading the manuscript file to our online system.

-A clean version of the manuscript. Please select the file type ‘Article File’.

-An updated Editorial Policy checklist, uploaded as a ‘Related Manuscript File’ type. This checklist is to ensure your paper complies with all relevant editorial policies. If needed, please revise your manuscript in response to these points. Please note that this form is a dynamic ‘smart pdf’ and must therefore be downloaded and completed in Adobe Reader. Clicking this link will download a zip file containing the pdf.

Please use the following link to submit your revised manuscript files:

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** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

Please do not hesitate to contact me if you have any questions or would like to discuss the required revisions further. Thank you for the opportunity to review your work.

Best regards,

Aldo

Dr Aldo Isidori

Senior Editor

Communications Materials

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

This article presents a novel method for detecting the nanoscale heat generation of silver nanoparticles. The experimental work is well done and the results are explained in a very detailed manner. The results are very impactful for the community of plasmonic heating, and I recommend publication of this article in Nat Comm Mat after fully addressing all my comments and suggestions below.

Title: The title is slightly misleading, as the results only indirectly indicate the heat generation from single nanoparticles. The experimental results actually measure the collective effect of ~7000 nanoparticles. I recommend changing the title to reflect this. I would also include specific terms to specify that you are interested in plasmonic heating at the nanoscale dimensions.

Page 1 – “Oxonic cations”: Please refer to H_3O^+ ions as hydroxonium ions.

Page 2: Part of the text has a different font size.

Figure 1: The legend spells “AuNP” instead of AgNPs.

Page 3: “… using the method mentioned in the previous section”: This is likely a reference to the experimental section. Please clarify. Also in this section there are a number of variables mentioned that are not specified. In fact, I would recommend to include the methods section “characterization of the bolometer" in this paragraph, which would clarify the text.

Page 3: “We adopted a linear curve fitting according to Eq. (1)”: It would be helpful if these equations are shown at this location as well.

Page 3: “Measurements from three bolometer sets…”: The authors mention a time constant (tau), which hasn’t been introduced yet. Please clarify its meaning.

Page 3: “One of our test experiments was 10 min less affected by the temperature fluctuation.”: I don’t understand what is meant with this sentence, please explain further.

Page 3: To avoid confusion and improve readability, it would be helpful to refer to the different experimental variables by their actual meaning. For instance, please refer to the “thermal conductance” instead of “G value”. The same holds for variables Vb, S, and B, and others.

Page 4: “addition of an acid”: Please change to “Addition of diluted hydrochloric acid”.

Page 4: “The surface charge of any material significantly depends on its surroundings.” I recommend phrasing this more precisely, such as: “The surface charge of the Ti and Si materials, and their electrostatic interaction with the negatively charged Ag nanoparticles (citrate-stabilized), significantly depends on the isoelectric points of the natively-oxidized surfaces (TiO_2 and SiO_2, respectively) and the

pH of the AgNP dispersion. Therefore we expect a strong surface interaction in the pH range where citrate remains deprotonated (pKa > 3.1) and where the surface develops a positive charge by protonation." The aggregation below pH 3.5 is likely to be connected to the loss of citrate around the Ag NPs, due to full protonation of the citrate.

Page 4: "each AgNP measured 2 pixels in both length and width" – How can the particles be distinguished from noise if they only measure 2 pixels? This aspect does not seem convincing. How did the authors confirm that the analysis yielded accurate results? Could the authors not better stitch multiple higher resolution SEM images together and analyze the composite image?

Page 5: "This effect is caused by the rough Si surface underneath the membrane after XeF2 etching". Can the authors present a spectrum in absence of AgNPs? Further, can the authors explain in more detail what causes this loss of absorbance?

Figure 3A: a large portion of these data is not discussed in text. I would recommend moving SEM images for pH 4, 5, 5.5, 6, and 6.9 to the supporting information to increase the clarity of your figure.

Figure 3C and D: The y-axis scales are confusing and do not seem to match between panels. Can the authors present an explanation? Why would one panel have maximum values and the other positive values? Finally, please include an explanation why there are three lines (I'm assuming three different devices?).

Page 6: You mention a heat generation per single AgNP with a unit of fW, but such a magnitude is meaningless because it is very specific to the experimental conditions. I would recommend transforming these figures into more meaningful quantities by dividing it by the incoming light intensity (W/m2). This would essentially then represent an absorption cross section value in m2, and should for 100 nm Ag nanoparticles be in the order of 1×10-13 m2. If you would approach such values, what you've basically created is an electrical sensor for measuring spectral absorption cross sections, which would be very exciting, and this would certainly enhance the impact of this article!

Page 7: The heat generation spectra do not correspond very well with the data presented in Figure 3: the heat spectra are much broader than the AgNP plasmon peak at 380 nm. A clear explanation for this discrepancy is still missing. I am interpreting this as a broadening due to cluster formation or because the AgNPs experience a different dielectric environment; am I correct? Perhaps the Si surface effect is masking absorption features from the AgNPs in that spectral range, for instance those induced by clustering. It is quite essential to understand this part of the data and it would be good to explicitly state the reasons, or at the very least present an argumentative speculation.

Page 7: “While the resonance frequency is at a wavelength of 480 nm”: you mentioned before that it was 380 nm in Figure 3? Please explain the spectral discrepancy between 460 nm and 380 nm (see comment above).

Page 7: Please include a few sentences on how the bolometer could be improved in the future. Can the device be fabricated in absence of Si and Ti, to produce cleaner results? How could you further reduce the clustering of Ag NPs on the surface?

Page 8: There are not enough details given to be able to reproduce the fabrication described in this work. For example, the HMDS vapor treatment is ambiguously described, the spin coating thickness is not mentioned, the Si etching procedure is not described in detail, the reaction ion etching of Ti is not described sufficiently, etc.

Reviewer #2 (Remarks to the Author):

This manuscript reported the improved bolometer properties based on the photothermal effect of Ag NPs. The power dissipated by a single Ag NP are calculated according to the thermal and spectral behaviors of bolometer. This manuscript is well-written, however, I believe further work should be done to improve the quality of this manuscript before publishing.

1) The Ag NPs are obtained by immersing into Ag NPs solution. Did the author put the sample r1 and r3 into the same solution without Ag NPs? As a reference sample, I think it should be handled using the same process.

2) What’s the different curves in figure 3c and 3d? Why there are differences? What’s the absorption results of samples at the other pH? Could the author measure the sample without Ag NPs to prove that the decrease of absorption is caused by the rough Si surface?

3) In Figure 5c, why the values of power of single Ag NPs are different for bolometer d?

4) In Table 1, why the number of bolometers start from c rather than a? And why r2 is skipped?

5) In my opinion, it will be more interesting if it can be used as a calculator of the amount of Ag NPs. Could the author add some experiments based on this?

Reviewer #3 (Remarks to the Author):

This work deposits Ag NPs on the surface of bolometer to estimate its power dissipation. However, this is essentially a measurement of plasmonic thermal effect by bolometer. No new science or new understanding were really revealed in this work. All the observation seems to suggest the well-known effect of plasmonic heating, which is sensitive to the illumination wavelength. Following are the detailed comments on this manuscript:

-People is more interested to know the exact surface temperature of the Ag NP at illumination, can this value measured with bolometer?

-also can the heating and cooling dynamics based on single Ag NP be measured by the bolometer?

-in Fig. 1b, the red labels should be AgNPs.

-why the absorbance in Fig 3c,d are negative? what is the difference among the colored lines in Fig 3c,d.

-why is it different for Fig 4c and d?

-why the peak of power dissipation is at ~460 nm?

-many of the statements in the manuscript is very vague, for instance, the authors state in conclusion that these observations lay a solid foundation for deeper investigations into nanoparticle plasmon physics. but no idea of what is the deeper investigation? what is the potential for harnessing the power dissipated by individual nanoparticles and why it is related to this work?

-the title is very vague too, just state exactly what is the effect/results this work reveals. cgi-bin/main.plex

author responses: first round

Reviewer #1 (Remarks to the Author):

This article presents a novel method for detecting the nanoscale heat generation of silver nanoparticles. The experimental work is well done and the results are explained in a very detailed manner. The results are very impactful for the community of plasmonic heating, and I recommend the publication of this article in Nat Comm Mat after fully addressing all my comments and suggestions below.

Title: The title is slightly misleading, as the results only indirectly indicate the heat generation from single nanoparticles. The experimental results measure the collective effect of ~7000 nanoparticles. I recommend changing the title to reflect this. I would also include specific terms to specify that you are interested in plasmonic heating at the nanoscale dimensions.

Thank you for the suggestion of title improvement. Here the new title is *Efficient Heat Detection via Localized Surface Plasmon Resonance with Silver Nanoparticles by a Microbolometer.*

Page 1 – "Oxonic cations": Please refer to H_3O^+ ions as hydroxonium ions.

We modified the text according to your suggestion. We also change the term *concentration* into an *activity*.

Page 2: Part of the text has a different font size.

Thank you for noticing that mistake, we fixed the font size.

Figure 1: The legend spells "AuNP" instead of AgNPs.

AuNPs is a typo that we overlooked, thank you. The picture legend is fixed in the revised version of the manuscript.

Page 3: "… using the method mentioned in the previous section": This is likely a reference to the experimental section. Please clarify. Also in this section, there are several variables mentioned that are not specified. I would recommend including the methods section "characterization of the bolometer" in this paragraph, which would clarify the text.

The method section is at the end of the manuscript with described bolometer characterization as well as having explained all variables. The variables were also explained in the text.

Page 3: "We adopted a linear curve fitting according to Eq. (1)": It would be helpful if these equations were shown at this location as well.

Thank you for pointing this out. The equation was originally only in the method section at the end of the manuscript and in Supplementary section I. We added the equation to the main text as suggested.

Page 3: "Measurements from three bolometer sets…": The authors mention a time constant

(tau), which hasn't been introduced yet. Please clarify its meaning.

Thank you for the suggestion, we updated part of the paragraph where H, G, and "tau" are introduced.

Page 3: "One of our test experiments was 10 min less affected by the temperature fluctuation.": I don't understand what is meant by this sentence, please explain further.

The confusing sentence has been removed. It was probably a residuum from the previous version of the manuscript.

Page 3: To avoid confusion and improve readability, it would be helpful to refer to the different experimental variables by their actual meaning. For instance, please refer to the "thermal conductance" instead of "G value". The same holds for variables Vb, S, and B, and others.

We can do as requested but with all respect to the reviewer, we would prefer to keep it current way as per our opinion, the reason why the variables are introduced is using them. If we do keep using e.g. "thermal conductance" instead of "G value", we feel there is no reason to define it. On the other hand, if the reviewer does insist we should have it as described in his/her comment, we will change it.

Page 4: "addition of an acid": Please change to "Addition of diluted hydrochloric acid".

Thank you for the suggestion. We changed it accordingly.

Page 4: "The surface charge of any material significantly depends on its surroundings." I recommend phrasing this more precisely, such as: "The surface charge of the Ti and Si materials, and their electrostatic interaction with the negatively charged Ag nanoparticles (citrate-stabilized), significantly depends on the isoelectric points of the natively-oxidized surfaces (TiO2 and SiO2, respectively) and the pH of the AgNP dispersion. Therefore, we expect a strong surface interaction in the pH range where citrate remains deprotonated (pKa > 3.1) and where the surface develops a positive charge by protonation." The aggregation below pH 3.5 is likely to be connected to the loss of citrate around the Ag NPs, due to full protonation of the citrate.

We have modified the paragraph as suggested.

Page 4: "each AgNP measured 2 pixels in both length and width" – How can the particles be distinguished from noise if they only measure 2 pixels? This aspect does not seem convincing. How did the authors confirm that the analysis yielded accurate results? Could the authors not better stitch multiple higher-resolution SEM images together and analyze the composite image?

The reviewer is correct, it is not possible to use directly only 2 pixels per particle to get such a high resolution. We therefore use the diameter of 100 nm provided in the AgNPs manufacturer's datasheet.the text using 100 nm size as the manufacturer declared and added the reference to the datasheet online.

Page 5: "This effect is caused by the rough Si surface underneath the membrane after XeF_2 etching". Can the authors present a spectrum in absence of AgNPs? Further, can the authors explain in more detail what causes this loss of absorbance?

The surface underneath the membrane is relatively near to the membrane and scattered light

from the surface does affect the optical measurement. The way how to improve it would be using either longer etching of the Si to push the substrate surface underneath the membrane further from it, Opening the substrate from the back side to eliminate scattered light, or using silicon-on-insulator wafer to also eliminate scattered light getting back to the detector. The text has been modified.

Figure 3A: a large portion of these data is not discussed in text. I would recommend moving SEM images for pH 4, 5, 5.5, 6, and 6.9 to the supporting information to increase the clarity of your figure.

We have removed the SEM images to the newly created Supplementary section IV and the original Supplementary section IV has been renamed as Supplementary section V.

Figure 3C and D: The y-axis scales are confusing and do not seem to match between panels. Can the authors present an explanation? Why would one panel have maximum values and the other positive values? Finally, please include an explanation why there are three lines (I'm assuming three different devices?).

The Y scale is in arbitrary units and matching between panels is unlikely. We moved the second measurement to Supplementary section IV. Also we would like to mention that the Figures 3C and D differ probably due light scattered from different backgrounds.

The three lines in each figure are due to conducting the measurement at three different spots. Each image was created by subtraction data from the bolometer without AgNPs from the date with AgNPS.

Page 6: You mention a heat generation per single AgNP with a unit of fW, but such a magnitude is meaningless because it is very specific to the experimental conditions. I would recommend transforming these figures into more meaningful quantities by dividing it by the incoming light intensity (W/m2). This would essentially then represent an absorption cross section value in m^2, and should for 100 nm Ag nanoparticles be in the order of 1×10^{-13} m^2. If you would approach such values, what you've basically created is an electrical sensor for measuring spectral absorption cross sections, which would be very exciting, and this would certainly enhance the impact of this article!

This is a good suggestion thus we calculated the power efficiency per unit of the area getting ≈22.9 $W\cdot m^{-2}$ at the incident light power we used. The text has been modified accordingly.

Page 7: The heat generation spectra do not correspond very well with the data presented in Figure 3: the heat spectra are much broader than the AgNP plasmon peak at 380 nm. A clear explanation for this discrepancy is still missing. I am interpreting this as a broadening due to cluster formation or because the AgNPs experience a different dielectric environment; am I correct? Perhaps the Si surface effect is masking absorption features from the AgNPs in that spectral range, for instance those induced by clustering. It is quite essential to understand this part of the data and it would be good to explicitly state the reasons, or at the very least present an argumentative speculation.

We would like to thank the reviewer for this note. We think that there is a strong effect of the substrate influence which can be seen at the different data values at ≈470 nm. Apart from the different substrates, the measured surfaces are very similar to each other, yet. The results at

≈470 nm are quite different. We can speculate, that it is caused by the substrate light scattering. We think that the actual spectrum absorbance maximum is at a higher wavelength than 380 nm. Per the particle data sheet (reference is attached) the maxima should be between 490 and 515 nm. We assume that the rough surface under the bolometer membrane light scattering effect prevails in the range from 380 to 500 nm. We modified the text to take this into account.

Page 7: "While the resonance frequency is at a wavelength of 480 nm": you mentioned before that it was 380 nm in Figure 3? Please explain the spectral discrepancy between 460 nm and 380 nm (see comment above).

This should be linked to the manufacturer's datasheet stating that the resonance frequency (absorption peak) is from 490 to 515 nm. If the particles are smaller as the SEM results suggest, the resonance frequency should be also lower. We think that the term *resonance frequency* is incorrect thus we changed it everywhere into *SPR absorption maximum*. We also stated above that the SPR absorption maximum is not at 380 nm since there is a strong substrate scattering effect. We modified the manuscript accordingly.

Page 7: Please include a few sentences on how the bolometer could be improved in the future. Can the device be fabricated in absence of Si and Ti, to produce cleaner results? How could you further reduce the clustering of Ag NPs on the surface?

We think that the absence of the rough Si substrate would improve the results. We added a few suggestions on how to achieve it. The text is here: The problem of scattered light from the rough surface of the Si substrate underneath the membrane can be suppressed by using longer etching of the Si to push the substrate surface underneath the membrane further from it. Alternatively, opening the substrate from the back side would eliminate scattered light, as well as using a silicon-on-insulator wafer as a substrate for bolometer fabrication.

Page 8: There are not enough details given to be able to reproduce the fabrication described in this work. For example, the HMDS vapor treatment is ambiguously described, the spin coating thickness is not mentioned, the Si etching procedure is not described in detail, the reaction ion etching of Ti is not described sufficiently, etc.

We added details about the device fabrication but we have to state, that particular times/conditions for these processes are not very relevant for readers as they would have to use identical equipment to take advantage of those details. We can certainly add more details if the reviewer thinks it is essential. The particular fabrication of bolometers has been described in our previous work.[1-3]

Reviewer #2 (Remarks to the Author):

This manuscript reported the improved bolometer properties based on the photothermal effect of Ag NPs. The power dissipated by a single Ag NP are calculated according to the thermal and spectral behaviors of bolometer. This manuscript is well-written, however, I believe further work should be done to improve the quality of this manuscript before publishing.

1) The Ag NPs are obtained by immersing into Ag NPs solution. Did the author put the sample r1 and r3 into the same solution without Ag NPs? As a reference sample, I think it should be handled using the same process.

Both types of samples, with and without AgNPs, were rinsed with DI water and dried with compressed nitrogen in the last step since it was necessary to remove any unwanted residues before subjecting them to XeF_2 vapors. We extended sentences in the paper to make it clearer.

2) What's the different curves in figure 3c and 3d? Why there are differences? What's the absorption results of samples at the other pH? Could the author measure the sample without Ag NPs to prove that the decrease of absorption is caused by the rough Si surface?

We answered this point when we responded to the reviewer 1, which follows:

The Y scale is in arbitrary units and matching between panels is unlikely. We moved the second measurement to Supplementary section IV. Also, we would like to mention that the Figures 3C and D differ probably due light scattered from different backgrounds.

The three lines in each figure are due to conducting the measurement at three different spots. Each image was created by subtraction data from the bolometer without AgNPs from the date with AgNPS.

3) In Figure 5c, why the values of power of single Ag NPs are different for bolometer d?

After renaming the bolometers, it is concerning the bolometer labeled "b". The problem could be different incident power for each bolometer due to difficulties with precise device positioning under the light source as well as possibly different light scattering from the surface underneath the bolometer membrane. Regardless, the results from devices "a", "c" and "d" are very consistent. We also calculated the mean value and standard deviation from all four devices and we modified the sentence accordingly.

4) In Table 1, why the number of bolometers start from c rather than a? And why r2 is skipped?

We originally labeled the bolometers based on their position on the chip. However, based on your comment, we changed the labeling as suggested to enhance clarity.

5) In my opinion, it will be more interesting if it can be used as a calculator of the amount of Ag NPs. Could the author add some experiments based on this?

Certainly, the number of adsorbed particles can be calculated from total dissipated power eliminating the need to use SEM imaging. We added a sentence to reflect this.

Reviewer #3 (Remarks to the Author):

This work deposits Ag NPs on the surface of bolometer to estimate its power dissipation. However, this is essentially a measurement of plasmonic thermal effect by bolometer. No new science or new understanding were really revealed in this work. All the observation seems to suggest the well-known effect of plasmonic heating, which is sensitive to the illumination wavelength. Following are the detailed comments on this manuscript:

-People is more interested to know the exact surface temperature of the Ag NP at illumination, can this value measured with bolometer?

We are not sure if we understand the comment. We assume that the reviewer meant the local temperature at the AgNPs. If yes, this is difficult to measure since the bolometer in a vacuum heat up due to total power dissipated at its membrane. Thus, measurement of a temperature at a single particle by a bolometer is not possible. Yes, we can calculate dissipated power at the particle, but we do not know the rate of energy transfer into the membrane. We have modified the manuscript introduction to reflect this.

-also can the heating and cooling dynamics based on single Ag NP be measured by the bolometer?

This is not possible with a bolometer since the bolometer's membrane temperature responds to total dissipated power at it. We added a comment to the introduction of the manuscript.

-in Fig. 1b, the red labels should be AgNPs.

Thank you for noticing that typo, which we overlooked. The picture legend was fixed in the revised version of the manuscript.

-why the absorbance in Fig 3c,d are negative? what is the difference among the colored lines in Fig 3c,d.

The negative part of the absorption spectra, in our opinion, is caused by light scattering from the rough Si surface underneath the bolometer membrane. The Si substrate membrane distance is always different at each location. Unfortunately, it is a well-known phenomenon that XeF_2 etching is not homogeneous for each cell; hence, the trench under the bolometer possesses a different geometry for each cell, which generates different background values.

The absorbance was always measured on three spots of one bolometer membrane because we wanted to prove the similarity of the measured spectra. We added a description to the main text and figure caption.

-why is it different for Fig 4c and d?

The graph is a bit confusing; its X-axis is the time since we set the monochromator to set a new wavelength every 10 s. Thus graphs 4c and 4d are enhancements of the orange and blue areas from Figure 4b, respectively. Graph 4c corresponds to the bolometer power response while illuminating at a wavelength from 300 to 400 nm, showing the response of the bolometer with AgNPs was different when achieving 360 nm. Graph 4d shows the bolometer power response while illuminating at a wavelength from 620 to 750 nm, showing the identical response to light of both bolometers after 680 nm.

-why the peak of power dissipation is at ~460 nm?

The particle datasheet states that their SPR power absorption maxima is from 490-515 nm. This maximum is influenced by exact particle sizes and the substrate. 460 nm is not very far from the manufacturer's declared value. We modified the text accordingly.

-many of the statements in the manuscript is very vague, for instance, the authors state in conclusion that these observations lay a solid foundation for deeper investigations into nanoparticle plasmon physics. but no idea of what is the deeper investigation, what is the potential for harnessing the power dissipated by individual nanoparticles and why it is related to this work?

The manuscript was checked for vague statements and a few were removed. We added a comment on why the single particle power dissipation is important.

-the title is very vague too, just state exactly what is the effect/results this work reveals. Thank you for the suggestion. We changed the title of the manuscript to *Efficient Heat Detection via Localized Surface Plasmon Resonance with Silver Nanoparticles by a Microbolometer*. We hope it is now more suitable for the content of the paper.

References:

1 Svatos, V., Gablech, I., Pekarek, J., Klempa, J. & Neuzil, P. Precise determination of thermal parameters of a microbolometer. *Infrared Phys Techn* **93**, 286-290, doi:10.1016/j.infrared.2018.07.037 (2018).

2 Svatos, V., Gablech, I., Ilic, B. R., Pekarek, J. & Neuzil, P. In situ observation of carbon nanotube layer growth on microbolometers with substrates at ambient temperature. *J Appl Phys* **123**, doi:Artn 114503 10.1063/1.5016465 (2018).

3 Pekárek, J. *et al.* Self-compensating method for bolometer–based IR focal plane arrays. *Sensors and Actuators A: Physical* **265**, 40-46 (2017).

Decision letter and referee reports: second round

12th Feb 24

Dear Professor Neuzil,

Thank you for submitting your revised manuscript, "Efficient Heat Detection via Localized Surface Plasmon Resonance with Silver Nanoparticles by a Microbolometer", to Communications Materials. It has now been seen again by our 3 referees, whose comments are appended below. As you will see, Reviewer #2 is still concerned by the absence of additional work (in terms of data and analysis) that was requested at the previous round, mentioning that it is not sufficient to simply provide explanations. The additional work is necessary to fully demonstrate the importance and advance provided by this study, and therefore to meet our editorial criteria.

In light of these comments, we cannot accept the manuscript for publication, but are interested in considering a revised version that addresses these serious concerns.

We hope you will find the referees' comments useful as you decide how to proceed. Should further experimental work and analysis allow you to address these criticisms, we would be happy to look at a substantially revised manuscript. However, please bear in mind that we will be reluctant to approach the referees again in the absence of major revisions. If the revision process takes significantly longer than three months, we will be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

-A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.

-A marked-up version of the manuscript with all changes to the text in a different colored font. Please do not include tracked changes or comments. Please select the file type ‘Revised Manuscript - Marked Up’ when uploading the manuscript file to our online system.

-A clean version of the manuscript. Please select the file type ‘Article File’.

-An updated Editorial Policy checklist, uploaded as a ‘Related Manuscript File’ type. This checklist is to ensure your paper complies with all relevant editorial policies. If needed, please revise your manuscript in response to these points. Please note that this form is a dynamic ‘smart pdf’ and must therefore be downloaded and completed in Adobe Reader. Clicking this link will download a zip file containing the pdf.

Please use the following link to submit your revised manuscript files:

Link redacted

** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

Please do not hesitate to contact me if you have any questions or would like to discuss the required revisions further. Thank you for the opportunity to review your work.

Best regards,

Aldo

Dr Aldo Isidori

Senior Editor

Communications Materials

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

I feel that most of the points raised in the previous round of review have been satisfactorily addressed and I recommend the manuscript for publication.

Reviewer #2 (Remarks to the Author):

The authors have answered some of my questions. However, I believe this work still need to be improved before publishing.

1) The authors explained that the lines in figure 3 are obtained from the same bolometer membrane using three different spots. However, legend is lost and it is not clear why three spots should be measured or what's difference of the three spots. The authors explain that each image was created by subtraction data from the bolometer without AgNPs from the data with AgNPs. However, they don't add the measurement results of the background as suggested.

2) The authors provide the deviation (165fW with error of 45fW) from four devices. However, the error is close to 30%. I think the experimental condition should be optimized.

3) The number of bolometers were labeled based on the position on chip. So, why the others are skipped?

4) As I understand, the difference between different bolometers is the amount of Ag NPs on them. It is meaningful to measure the relationship between NP amount and properties of bolometer, i.e., change the NP amount and add more data. If the final aim is not to use it as calculator but only to improve the bolometer property, why four devices are shown here?

I think more work should be done before publishing rather than simply explain. Otherwise, innovation is lacking in this manuscript. In addition, the author should revise the work with a more serious attitude. For example, the font size of sentence near equation 1 is different from others. And there are some spelling mistake in the response letter. The Supplementary file is also missing.

Reviewer #3 (Remarks to the Author):

The authors have addressed most of my comments however the title is still a bit lengthy. It is suggested to use the title like "Collective photothermal effect of silver nanoparticles probed by a microbolometer".

Response Letter

We thank the reviewers for taking the time to review our manuscript and providing insightful comments. To facilitate reading of this response letter, we have used blue for the reviewer comments while our response is written in black.

Reviewers' comments:

Reviewer #1:

I feel that most of the points raised in the previous round of review have been satisfactorily addressed and I recommend the manuscript for publication.

Thank you for the previous comments of the reviewer to improve the quality of the manuscript.

Reviewer #2 (Remarks to the Author):

The authors have answered some of my questions. However, I believe this work still needs to be improved before publishing.

1) The authors explained that the lines in Figure 3 are obtained from the same bolometer membrane using three different spots. However, the legend is lost and it is not clear why three spots should be measured or what's difference between the three spots. The authors explain that each image was created by subtraction data from the bolometer without AgNPs from the data with AgNPs. However, they don't add the measurement results of the background as suggested.

We would like to thank the reviewer for this comment as it was our fault for misinterpreting the original message. Each Si chip consisted of 48 bolometers and the bolometers at the same chip were subject to the same pH solution during the AgNPs adsorption. The best adsorption was found to be at pH ≈ 3.5 and we measured light reflection using the scanning near field optical microscopy (SNOM) technique in dark field mode using a 100× objective lens. All SNOM data from 23 devices with AgNPs adsorbed using a solution with a pH value of 3.5 are shown in the newly added **Supplementary Section IV**. SNOM results from 4 different bolometers (three spots each) with the added background are in **Fig.3b**. Then we selected bolometer G3 to display its data of three different spots in **Fig.3c** showing AgNPs' uniformity on the bolometer surface, as the G3 was the one we have an SEM image from and the SNOM data are shown in **Fig.3a** with pH of ≈ 3.5. We also fixed the legends, which indeed were missing and it is our fault.

2) The authors provide the deviation (165 fW with an error of 45 fW) from four devices. However, the error is close to 30%. I think the experimental condition should be optimized.

The reviewer is correct. The enhanced photothermal effect of AgNPs on the surface of a bolometer is based on the unique LSPR properties of AgNPs. In addition to being influenced by the light source, it also significantly relates to the uniformity, density, and inter-particle spacing of the particles on the bolometer surface. Our process achieves the distribution of AgNPs on the bolometer surface by adjusting the pH value of AgNP colloidal dispersion. However, **even within the same batch of chips, there are differences in the distribution of AgNPs, leading to variations in photothermal power with the same light source.** Therefore, representing the photothermal power of individual AgNPs in terms of **a range is more scientific than using a standard deviation**. All the data are in the same order of magnitude. Here we modified the manuscript.

Furthermore, even though we used a very advanced facility in the National Institute of Standards and Technology in Gaithersburg, MD, USA, to fabricate our bolometer chips, we did face a big problem with large device parameter spreading which probably caused this error. We employed an i-line ASML stepper series 5500/100 to conduct lithography of our chip follower patterning using reaction ion etching of Ti layer for the bolometer temperature sensor, its parameter variation was almost 50%. We do not know how to suppress or eliminate this problem and besides that, we do not have access to that

facility anymore, thus making new chips there will not be happening, even if we do like to get more. We added a comment to the text discussion section about potentially optimizing the devices to get smaller errors.

3) The number of bolometers was labeled based on the position of the chip. So, why the others are skipped?

This point has been partially answered above. Some devices had problems due to issues related to their fabrication, thus we selected a few based on their *G* value measurement having similar performance. We added a comment to the text.

4) As I understand, the difference between different bolometers is the amount of Ag NPs on them. It is meaningful to measure the relationship between NP amount and properties of the bolometer, i.e., change the NP amount and add more data. If the final aim is not to use it as a calculator but only to improve the bolometer property, why four devices are shown here?

The reviewer is correct that the measured photothermal power of the bolometer is related to the AgNPs distribution on its surface. It's our fault that the content is unclear. We have modified the text.

We agree with the reviewer that it can be used as a calculator for AgNPs in the future. We have also added this discussion as the reviewer suggested. However, the relationship and the amount of the AgNPs at the bolometer surface is not a subject of this manuscript. We used one chip with 48 bolometers for measurement, all those bolometers were subject to the same pH solution value during AgNPs adsorption. Ideally, all bolometers on the same Si chip should be identical as well as the AgNPs distribution, **which is unfortunately not the case caused by the fabrication process** as described in the previous comment. In this paper, all bolometers with AgNPs for photothermal measurement were deposited in an AgNP solution with a pH of ≈ 3.5. **We aimed to demonstrate a method to detect the presence and photothermal effect of AgNPs on the bolometer membrane.** The four different bolometers were measured to show the repeatable results, not the change in AgNPs amount. The difference of AgNPs on the bolometer membrane was caused by the deposition process, resulting in the difference in amount, uniformity, and distances between AgNPs.

I think more work should be done before publishing rather than simply explaining. Otherwise, innovation is lacking in this manuscript. In addition, the author should revise the work with a more serious attitude. For example, the font size of a sentence near Eq. (1) is different from others. And there are some spelling mistakes in the response letter. The Supplementary file is also missing.

We are sorry that the reviewer got the impression that we have not taken his/her comments seriously. We have followed the review's comments to improve the quality of this paper and added the innovation of this work. Our study revealed a single AgNP can dissipate power with an amplitude between 101.3 fW to 205.3 fW, demonstrating the efficiency of its energy conversion from photon to heat. We also demonstrated the approach for thermal analysis in micro/nanoscale using an ultra-sensitive bolometer that possesses a power resolution of ≈ 26 pW.

We also fixed the font size and checked other spelling mistakes. It is our fault for missing the supplementary file in the last revision. We did modify the supplementary and take serious to the submission.

Reviewer #3 (Remarks to the Author):

The authors have addressed most of my comments however the title is still a bit lengthy. It is suggested to use a title like "Collective photothermal effect of silver nanoparticles probed by a microbolometer".

Thank you for all the comments from the reviewer to improve the quality of the manuscript. The title was modified as suggested.

Decision letter and referee reports: third round

5th Apr 24

Dear Professor Neuzil,

Your manuscript titled "The collective photothermal effect of silver nanoparticles probed by a microbolometer" has now been seen again by our referees, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Materials under the open access CC BY license (Creative Commons Attribution v4.0 International License).

We therefore invite you to edit your manuscript to comply with our journal policies and formatting style in order to maximise the accessibility and therefore the impact of your work.

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Best regards,

Aldo

Dr Aldo Isidori

Senior Editor

Communications Materials

REVIEWERS' COMMENTS:

Reviewer #2 (Remarks to the Author):

The authors have addressed most of my comments in the previous round of review. I recommend the manuscript for publication.