**Reviewer: 1**

Recommendation: It appears that publication in any form would be premature at this time.

Comments:

Dear Editor,

I'm sorry to tell you that this article reproduces the method reported in 2016 by Xu Xie and David G. Cahill.

APPLIED PHYSICS LETTERS 109, 183104 (2016)

Thermometry of plasmonic nanostructures by anti-Stokes electronic Raman scattering

The authors are not mentioning this article.

I can't obviously recommend this article for publication for this reason.

Apart from that, this manuscript really lacks information to enable the reader to reproduce their experiments (in this respect, the article of Cahill's group is much better). I think it is now unnecessary, but I had prepared a long review of this submitted manuscript before pointing out the novelty issue. If need be I can still send you this review.

Additional Questions:

Are there elements of novelty in the research reported?: No

Is the manuscript likely to be of interest to a reasonable number of scientists working in the field of nanoscience and nanotechnology?: Yes

Are the conclusions technically sound and adequately supported by the data presented?: Yes

Is sufficient information included to allow other workers in the field to test and reproduce the results?: No

Rate the overall importance of this paper to the field of nanoscience and nanotechnology (5 - Highly Important / 1 - Unimportant): 1

Significance: High (suitable for Nano Letters)

Novelty: Lowest (not suitable for Nano Letters)

Broad interest: Moderate (not suitable for Nano Letters)

Scholarly presentation: Lowest (not suitable for Nano Letters)

**Author’s response**

We thank the reviewer for pointing out this very relevant paper by Xie and Cahill. We did not know about this work and we comment on it in the revised version of our manuscript (page --, reference number --).

Indeed it presents the use of anti-Stokes emission for temperature determination of gold nanostructures. However, we think that there are significant differences both in the approach of the problem and in the solution that make our work worth publishing. First of all, the origin of light emission by gold nanostructures is still under debate in the community []. We do not aim to solve this discussion thus we aim to use a general approach and a simple model for the emission. Our interpretation for the photoluminescence is more general electronic Raman Scattering the since we do not make any assumptions on the number of interactions between the carriers and the bath phonon. For the case of electronic Raman scattering, only one interaction is consider while we relax that condition to allow one or more interactions. Certainly, one-interaction contributions are important but we also include the contribution from more than one interaction.

Secondly, our model explicitly includes the presence of the plasmonic resonance and instead of normalizing with a reference spectra taken at a known particle temperature or a self-consistent fitting of many data points in combination with a room temperature measurement. I our approach we just require the knowledge of the plasmon resonance spectra, that can be obtained, for example, with a photoluminescence spectra recorded with a high energy laser (in our case, 532nm laser). This could be simplified for example using monodisperse colloidal particles such as gold bipyramids, where the plasmonic resonance can be measured in bulk.

Finally, we present a more clean set of measurements to support our conclusions and we work with a sample that is more relevant for applications:

* We use bare wet-synthetized colloidal gold nanorods dispersed on a glass surface by spin-coating without any further treatment for temperature stabilization, as opposed to the lithography made structures with an extra annealing process presented by Xie. Our structures do not require a substrate, they can be used in colloidal solutions and even they can be up-taken by cells, a crucial property for photothermal therapy applications.
* Concerning the spectral measurements, we present much more neat results, without any observable background contribution, nor from the glass substrate or the solvent (water), even though the volume of our nanorods is 18 times smaller (VND = 3.17 105 nm3 while VNR =1.69 104 nm3). We use one order less excitation intensity (for us it ranges from 0.107 to 0.43 mW µm-2, compared to 1.33 to 7.89 mW µm-2) and our acquisition time for spectra is 3.3 times smaller (60s against 200s) and we still get reasonable signal levels. One striking difference between our spectra and the reported is the presence of huge contributions from the from the glass substrate, seen in the peaks at 207cm-1 and 467cm-1 in the case of Xie and Cahill. On top of the intensity and integration time differences, which lead to at least two order of magnitude improvement in signal, the detection volumes are quite different. Assuming a diffraction limited spot and confocal detection we estimated their detection volume V = 45.1 µm3 while in our case the volume is 0.18 µm3. Therefore, we expect to have 3 orders less contribution of Raman signal from the glass substrate, even in the case of equal illumination intensity and integration time in the spectrometer (which is not the case). This explains why our spectra show no contribution from the glass or the solvent.
* The temperature range explored in our work is much smaller.
* We estimated the expected improvement of our results if use the same integration time for spectra acquisition as Xie and Cahill, 200s. In such case we expect an accuracy of %, which shows that our method is more sensitive.

We also improved the manuscript to make it more clear and added more experimental details also required by other reviewers.

**Reviewer: 2**

Recommendation: Publish as is; no revisions needed.

Comments:

Carattino et al. describe very clearly how the absolute temperature of gold nanorods can be measured with an accuracy of 6K by measuring the anti-Stokes to Stokes ratio of luminescence of single nanorods.

Measuring the accurate temperature increase of plasmonic nanoparticles upon irradiation with laser light is not an easy task. Carattino and colleagues report on a very elegant solution to this problem. Importantly, this approach does not require any prior calibration. I am convinced that this method will be of interest for many researcher working on plasmonics or temperature effects at the nanoscale.

I recommend the paper for publications with no further revisions. I have only three small suggestions, but I leave it up to the authors to apply these changes:

1. On page 3 at the end of the introduction the authors write that they "... measure their temperature with relatively high accuracy...". The question is relative to what. The authors could think about being more specific at this point.

2. Figure 4: It says in the Figure caption that "The circles in the inset plot show the local temperature ..." - to me they appear to be squares. The authors might consider to plot the data points a big larger to avoid any confusion (circles are actually used for the plot of the extracted temperatures at 20°C in the same Figure).

3. The authors explain that the dimensions of the nanorods were derived from the mean values from TEM images (page 12, last paragraph). An accurate measurement of the particle size is important to calculate the temperature but no TEM images of particles are shown. The authors might consider to show a few examples of TEM images in the supporting information to give the reader a better idea what the rods look like. This could be important for reader, who are not familiar with the field.

Additional Questions:

Are there elements of novelty in the research reported?: Yes

Is the manuscript likely to be of interest to a reasonable number of scientists working in the field of nanoscience and nanotechnology?: Yes

Are the conclusions technically sound and adequately supported by the data presented?: Yes

Is sufficient information included to allow other workers in the field to test and reproduce the results?: Yes

Rate the overall importance of this paper to the field of nanoscience and nanotechnology (5 - Highly Important / 1 - Unimportant): 5

Significance: Top 5% (suitable for Nano Letters)

Novelty: Top 5% (suitable for Nano Letters)

Broad interest: High (suitable for Nano Letters)

Scholarly presentation: Top 5% (suitable for Nano Letters)

**Author’s response**

We thank the reviewer for the kind words about our paper.

The comments are addressed as follows

1. On page 3 at the end of the introduction the authors write that they "... measure their temperature with relatively high accuracy...". The question is relative to what. The authors could think about being more specific at this point.

We changed the phrase adding a more specific value: ‘measure their temperature with less than 6% relative error and the temperature of the surrounding media with less than 2%’

2. Figure 4: It says in the Figure caption that "The circles in the inset plot show the local temperature ..." - to me they appear to be squares. The authors might consider to plot the data points a big larger to avoid any confusion (circles are actually used for the plot of the extracted temperatures at 20°C in the same Figure).

We improved the plot to make it more clear and avoid the ambiguity presented by the reviewer.

3. The authors explain that the dimensions of the nanorods were derived from the mean values from TEM images (page 12, last paragraph). An accurate measurement of the particle size is important to calculate the temperature but no TEM images of particles are shown. The authors might consider to show a few examples of TEM images in the supporting information to give the reader a better idea what the rods look like. This could be important for reader, who are not familiar with the field.

We added the SEM images and the bulk spectral characterization in the supplementary material.

**Reviewer: 3**

Recommendation: Publish after minor revisions noted.

Comments:

The authors have found a novel way to use gold nanorods not only as local heat source but at the same time as nano-thermometer. They determine the temperature of single gold nanorods by measuring their anti-stokes emission luminescence. Normalizing the anti-stokes to the normal luminescence gives them an absolute temperature scale.

The authors have conducted a very nice study to demonstrate this novel concept with beautiful experiments supported by extensive theoretical calculations. On the side, the PL of gold nanorods is explained in more detail (which should be emphazied more in the title and abstract). The figures present the data nicely and the text explains well the experimental methods. The novel way to measure local temperatures will be interesting for many readers of Nano Letters. I recommend the rapid publication after some improvements to the manuscript as outlined below.

Detailed comments:

1. It is unclear how local temperature probes would help to understand intracellular processes. The authors should either remove this claim from the introduction and abstract or specify further.

2. It is not easy to understand the physical principle behind the new method. It looks to me as if the ratio of Stokes and anti-Stokes PL is used as temperature measure but this is somewhat hidden in the manuscript (in equation 2). It would be nice if the new concept is explained in more simple words (without equations) at the beginning of the manuscript, before the authors develop a model for the plasmon PL intensity. Please explain if entire spectra are measured (and why) or if the total intensity is integrated at two different excitation wavelengths.

3. Please explain the error for the temperature calculations in more detail

4. Please provide information on the laser fluence.

5. In figure 3 and 4 the error bars in the inlet are a little confusing.

6. On page 12 line 18, “The error bar in figure 3 and in the following figures is the result of the estimation of the temperature uncertainty because of variations in the plasmon resonance fit”. The authors should explain how they estimated this and deduced the error bar.

7. Please provide TEM images that support the particle dimensions listed on page 6 line 54

8. Please provide an ensemble extinction spectrum to show the polydispersity of the sample and show how the exciting lasers agree with the transversal and longitudinal plasmon resonance positions.

9. On page 7 line 28, “Several accumulations of the spectra at the same laser power were recorded”. The authors should name a concrete number.

10. Same goes for page 10, line 19, “The absorption cross section of several particles was calculated…” and page 12 line 38, “At each temperature several spectra were acquired…”.

11. On page 7 line 32, “…because of a longer exposure time…”. It would be interesting to know what exposure time was used for the experiments, since this would also show how long a cycle was until the reshaping was controlled by measuring a spectrum with the 532 nm laser.

12. Please give the definitions of all variables on first use, especially for eq. 1.

13. The general idea to use Anti-Stokes PL as temperature sensor has probably been used with dyes before. The authors should include a discussion of this work, if it exists. If not, they should indicate how the concept would work for dyes.

Additional Questions:

Are there elements of novelty in the research reported?: Yes

Is the manuscript likely to be of interest to a reasonable number of scientists working in the field of nanoscience and nanotechnology?: Yes

Are the conclusions technically sound and adequately supported by the data presented?: Yes

Is sufficient information included to allow other workers in the field to test and reproduce the results?: Yes

Rate the overall importance of this paper to the field of nanoscience and nanotechnology (5 - Highly Important / 1 - Unimportant): 5

Significance: Top 5% (suitable for Nano Letters)

Novelty: High (suitable for Nano Letters)

Broad interest: Top 5% (suitable for Nano Letters)

Scholarly presentation: High (suitable for Nano Letters)

**Author Comments**

We thank the reviewer for the positive review or our work. Bellow we address the specific comments.

1. It is unclear how local temperature probes would help to understand intracellular processes. The authors should either remove this claim from the introduction and abstract or specify further.

We changed the first paragraph and say that ‘measuring and controlling temperature at a sub-cellular scale still remains a challenge and it will also contribute to a better understanding of the mechanisms involved in new therapies such as photothermal tumor ablation’

2. It is not easy to understand the physical principle behind the new method. It looks to me as if the ratio of Stokes and anti-Stokes PL is used as temperature measure but this is somewhat hidden in the manuscript (in equation 2). It would be nice if the new concept is explained in more simple words (without equations) at the beginning of the manuscript, before the authors develop a model for the plasmon PL intensity. Please explain if entire spectra are measured (and why) or if the total intensity is integrated at two different excitation wavelengths.

To explain our model in simple words, we added the paragraph:

‘In a nutshel, we model the luminescence emission as the radiative recombination of electron-hole pairs created by the decay of the plasmon. Before the recombination, the carriers may interact with the phonon bath a certain number of times and change their energy, leading to secondary light emission at a different energy. The anti-Stokes spectral part comes from interactions that transfer the energy from a phonon into the carrier, effectively increasing their energy, while the Stokes part involves the inverse case. Naturally, the emission process will also be enhanced by the presence of the plasmon, thus leading to the luminescence spectra that with the plasmon shape.’

Also, we emphasize that we are not using the ratio of Stokes to anti-Stokes in the following paragraph:

’We emphasize that our method is not simply using the anti-Stokes to Stokes intensity ratio to obtain the temperature of the particle, as it is commonly done with Raman lines for molecules, but modeling the many excited carrier interactions with the phonon bath with a Bose-Einstein statistics modulated by the plasmonic resonance of the particle. The latter can be obtained, for example, by measuring the photoluminescence spectra exciting the particlesat a different sorter wavelength.’

In order to obtain a temperature value we follow this steps:

1. Obtain the plasmon resonance spectra of the particle. This is done detecting normal photoluminescence, exciting with the 532nm laser. Fit this with a lorentizan to get ISPR(ω) appearing in equation (2) in the main text.
2. Excite near resonance (with the 633nm laser) and detect the blue-shifted anti-Stokes emission.
3. Fit this high-energy part of the spectra using equation 2 and ISPR(ω) from 1) with T as the ONLY free parameter.

3. Please explain the error for the temperature calculations in more detail

We added a section in the supplementary information discussing the error determination for the temperature.

4. Please provide information on the laser fluence.

We use a 633nm HeNe laser that delivers a maximum power of 100 µW at the objective, which corresponds to 0.43 mWµm-2 excitation intensity on the sample. This is equivalent to 1.37 1015 photons s-1 µm-2, which leads to a fluence of 82.2 photons µm-2 in one minute integration time used for the spectra acquisition. We added this information in the supplementary material in the experimental section.

5. In figure 3 and 4 the error bars in the inlet are a little confusing.

We modified the figure to make it more clear.

6. On page 12 line 18, “The error bar in figure 3 and in the following figures is the result of the estimation of the temperature uncertainty because of variations in the plasmon resonance fit”. The authors should explain how they estimated this and deduced the error bar.

We added a section in the supplementary material discussing this point.

7. Please provide TEM images that support the particle dimensions listed on page 6 line 54

We added a section in the supplementary material showing the TEM images for the AuNR samples.

8. Please provide an ensemble extinction spectrum to show the polydispersity of the sample and show how the exciting lasers agree with the transversal and longitudinal plasmon resonance positions.

We added a section in the supplementary material showing the bulk spectra and the lasers used.

9. On page 7 line 28, “Several accumulations of the spectra at the same laser power were recorded”. The authors should name a concrete number.

We changed several for the concrete number.

10. Same goes for page 10, line 19, “The absorption cross section of several particles was calculated…” and page 12 line 38, “At each temperature several spectra were acquired…”.

We changed several for the concrete number.

11. On page 7 line 32, “…because of a longer exposure time…”. It would be interesting to know what exposure time was used for the experiments, since this would also show how long a cycle was until the reshaping was controlled by measuring a spectrum with the 532 nm laser.

We added the specific values in the revised version of the manuscript.

12. Please give the definitions of all variables on first use, especially for eq. 1.

We added the needed definitions.

13. The general idea to use Anti-Stokes PL as temperature sensor has probably been used with dyes before. The authors should include a discussion of this work, if it exists. If not, they should indicate how the concept would work for dyes.

NEED to think this!

**Reviewer: 4**

Recommendation: Publish after minor revisions noted.

Comments:

This manuscript describes how the absolute temperature of a metal nanoparticle and its surrounding medium can be measured without calibration by analyzing the relative intensities of the Stokes and anti-Stokes emission bands when excited at the longitudinal surface plasmon resonance. The authors first developed a model that simulates the experimentally measured Stokes and anti-Stokes emission of single gold nanorods and extracted through a pump power dependence the nanorod temperature. They furthermore show that if the surrounding medium was independently heated above room temperature, these nano-thermometers recorded the correct temperature within a few percent. This is excellent work. The emission mechanism itself is of interest and important considering the recent debate on the origin of the emission in plamonic nanostructures. In addition, the authors have developed a clever way of measuring the local temperature using probes that are extremely stable and can be employed over extended observation periods. I therefore recommend publication in Nano Letters. I only have a few comments that the authors should address by mostly expanding their discussion in a revised version.

1) Figure 3: Are these spectra simply the anti-Stokes part of the spectra shown in Figure 1 (for different pump power and maybe a different nanorod)? It would be worth pointing this out more clearly. The energy axis might be confusing, but presumably needed for the fit, considering that the spectra in the Figures 2 and 3 are plotted against wavelength. Adding a top wavelength x-axis might make the comparison to Figure 1 easier.

2) The single nanorod scattering spectrum is often much better fitted by a Lorentzian function. Would the proposed method work better/yield more accurate temperatures if the scattering spectrum were used for the plasmon spectrum (neglecting small wavelengths shifts between gold nanorod absorption and scattering)? That would certainly add to the complexity of the measurement, but the authors should comment on it given that they specifically have addressed sources of error and identified the Lorentzian fit of the 532 nm excited emission spectrum as one such source.

3) On page 4, the authors mention that ‘but can also be interpreted in part as a Raman scattering process’. In light of recent reports that all emission from plasmonic nanoparticles is due to electronic Raman scattering (Nano Lett., 2017, 17 , 2568), it would be important to further elaborate especially in the discussion section. Specifically, how is the authors’ model consistent or inconsistent with electronic Raman scattering? The way this reviewer understands the suggested mechanism is that emission is due to radiative recombination of electrons and holes and that furthermore at least partial relaxation of the charge carriers is assumed (Fig. S1), therefore being mostly inconsistent with Raman scattering.

4) Regarding the power dependence shown in Figure S3, the authors argue that both Stokes and anti-Stokes emission follow a one-photon-process based on their slopes being close to 1. However, the slopes of 0.88 and 1.20 appear significantly different unless the error for these measurements is about +/- 0.2. What is the error? The authors should mention that. The explanation given is that equation 2 depends on temperature. Can the authors maybe expand that discussion? At first glance it would make sense that an anti-Stokes event requires more energy than just that supplied by a single photon. Considering that most excitations decay non-radiatively, the energy supplied by previous excitations have raised the energy content of the bath. Should that not give rise to a larger slope or is that line of thought equivalent to the authors’ model? Please expand the discussion here.

Additional Questions:

Are there elements of novelty in the research reported?: Yes

Is the manuscript likely to be of interest to a reasonable number of scientists working in the field of nanoscience and nanotechnology?: Yes

Are the conclusions technically sound and adequately supported by the data presented?: Yes

Is sufficient information included to allow other workers in the field to test and reproduce the results?: Yes

Rate the overall importance of this paper to the field of nanoscience and nanotechnology (5 - Highly Important / 1 - Unimportant): 5

Significance: Top 5% (suitable for Nano Letters)

Novelty: Top 5% (suitable for Nano Letters)

Broad interest: Top 5% (suitable for Nano Letters)

Scholarly presentation: Top 5% (suitable for Nano Letters)

**Author Comments**

We thank the reviewer for the positive review or our work. Bellow we address the specific comments.

1) Figure 3: Are these spectra simply the anti-Stokes part of the spectra shown in Figure 1 (for different pump power and maybe a different nanorod)? It would be worth pointing this out more clearly. The energy axis might be confusing, but presumably needed for the fit, considering that the spectra in the Figures 2 and 3 are plotted against wavelength. Adding a top wavelength x-axis might make the comparison to Figure 1 easier.

We agree that it is certainly interesting to point this out in a more clear way in the text. We do this by… (NEED TO ASK AQUI)

2) The single nanorod scattering spectrum is often much better fitted by a Lorentzian function. Would the proposed method work better/yield more accurate temperatures if the scattering spectrum were used for the plasmon spectrum (neglecting small wavelengths shifts between gold nanorod absorption and scattering)? That would certainly add to the complexity of the measurement, but the authors should comment on it given that they specifically have addressed sources of error and identified the Lorentzian fit of the 532 nm excited emission spectrum as one such source.

We totally agree with the reviewer: an important source of error is the fit of the plasmon resonance spectral shape, therefore, improving this measurement and fit will definitely improve the method. It is indeed a technical complication for our current setup to measure the scattering spectra, for example, with dark field spectroscopy, while it is easier to detect photoluminescence with an extra laser, as we presented in the manuscript. We add the following text to discuss this point in the revised manuscript: ‘Another possible way to improve this point is to measure ISPR(ω) using another technique, for example dark-field spectroscopy, which gives access to the scattering plasmonic resonance. In this case, one should neglect the shift between absorption and scattering spectra, but the Lorentzian fitting for the plasmonic resonance should be better.’

3) On page 4, the authors mention that ‘but can also be interpreted in part as a Raman scattering process’. In light of recent reports that all emission from plasmonic nanoparticles is due to electronic Raman scattering (Nano Lett., 2017, 17 , 2568), it would be important to further elaborate especially in the discussion section. Specifically, how is the authors’ model consistent or inconsistent with electronic Raman scattering? The way this reviewer understands the suggested mechanism is that emission is due to radiative recombination of electrons and holes and that furthermore at least partial relaxation of the charge carriers is assumed (Fig. S1), therefore being mostly inconsistent with Raman

scattering.

NEED TO DO THIS

4) Regarding the power dependence shown in Figure S3, the authors argue that both Stokes and anti-Stokes emission follow a one-photon-process based on their slopes being close to 1. However, the slopes of 0.88 and 1.20 appear significantly different unless the error for these measurements is about +/- 0.2. What is the error? The authors should mention that. The explanation given is that equation 2 depends on temperature. Can the authors maybe expand that discussion? At first glance it would make sense that an anti-Stokes event requires more energy than just that supplied by a single photon. Considering that most excitations decay non-radiatively, the energy supplied by previous excitations have raised the energy content of the bath. Should that not give rise to a larger slope or is that line of thought equivalent to the authors’ model? Please expand the discussion here.

We added the errors to the slope, however the confidence interval does not include the unit value. For the case of stokes emission,

COMMENT: Is it BKG corrected? A constant intensity added to every point leads to a lower slope. This could explain the 0.88

For the case of anti-Stokes, we changed the text in the supplementary information to make our explanation clearer: ‘The anti-Stokes has a higher slope due to dependence on $T$ of the anti-Stokes emission: the higher the power, the higher the temperature of the particle and the higher the anti-Stokes signal is.’ This goes in the line proposed by the referee.

**Reviewer: 5**

Recommendation: It appears that publication in any form would be premature at this time.

Comments:

In this manuscript, Carattino et al. demonstrated the possibilities of measuring the absolute temperature of the gold nanorods without any pre-calibration from their anti-stoke emission spectra collected by irradiating them at their plasmon resonance wavelength. Even though these new insights will be helpful in nano-thermometry, the reviewer is not enthusiastic about publishing the paper in the present form due to the following reasons.

First, the abstract lacks clarity and the authors have to clearly express their main findings in the abstract. Moreover, the main text is bit vague and difficult to understand, which needs to be more focused and clear. The authors claim that they measured the temperature of the single nanorod. However, this needs to be supported by suitable microscopic techniques, which is not shown in the manuscript. Furthermore, the material characterization part is not described in the text, which needs to be incorporated including the optical extinction spectra and corresponding microscopic images of the gold nanorods used in this study. This will be helpful to validate the theoretical arguments. It is also important to do the experiments on gold nanorods of different aspect ratios to further validate the technique.

It may be considered if the authors can address these issues.

Additional Questions:

Are there elements of novelty in the research reported?: Yes

Is the manuscript likely to be of interest to a reasonable number of scientists working in the field of nanoscience and nanotechnology?: Yes

Are the conclusions technically sound and adequately supported by the data presented?: No

Is sufficient information included to allow other workers in the field to test and reproduce the results?: No

Rate the overall importance of this paper to the field of nanoscience and nanotechnology (5 - Highly Important / 1 - Unimportant): 3

Significance: High (suitable for Nano Letters)

Novelty: High (suitable for Nano Letters)

Broad interest: Moderate (not suitable for Nano Letters)

Scholarly presentation: Moderate (not suitable for Nano Letters)

**Author Comments**

We thank the reviewer for the review or our work. We modified the abstract and the text to make them clearer and added in the sporting material the required images for the nanorods. We are sure that we work with single gold nanorods since they appear as a diffraction-limited spot in the confocal image (i.e. the object has sub-diffraction dimensions) and we take the luminescence spectra to see the plasmonic resonance. Such spectra have a Lorentzian-like shape with the expected width for a single gold nanorod, supporting our claim.

We would also like to point out that we did study nanorods with different aspect ratio, within a certain range, as evidence in figure 2. We do not see any reason why this method should not work taking a different central wavelength for the resonance laser and a completely different range of aspect ratios.