**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 5, reference number 45).

Indeed Xie’s paper presents the use of anti-Stokes emission for temperature determination of gold nanostructures, as it was proposed by other authors before. 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 (see, for example, Ref. 34-36 in the main text). We do not aim to solve this discussion thus we use a general approach and a simple model for the emission. Our interpretation for the photoluminescence is more general than just 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 which *allows to extract the temperature from a single spectral measurement* once the plasmon resonance profile is known. In our paper we obtained such profile from a photoluminescence spectra recorded with a high energy laser (532 nm laser), but any other procedure to measure the SPR would suffice. In Xie’s paper, the authors need a baseline spectra at a known particle temperature to normalize the rest of the spectra. This is achieved in the ensemble case by exciting at low intensities where the heating of the particles is negligible. This is not the case for single particles, thus the authors extract the temperature for each laser intensity using a self-consistent fitting procedure with the complete set of data and the prior knowledge of the room temperature value.

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 et al. 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). 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 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, which is possible due to our high sensitivity. We should not that the achievable temperature range is limited by the thermal reshaping of the bare nanorods we used. This could be improved by stabilization treatments like the ones presented by Xie et. al.

Apart from these comments, 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 and we address below the points presented.

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 mentioning concrete values:

‘In this paper we show that the anti-Stokes luminescence of single gold nanorods can be used to measure their temperature upon resonant CW irradiation. The temperature error for a single measurement is less than 10K with an acquisition time of a few minutes; with a set of such measurements, the temperature of the surrounding medium can be determined with 4K accuracy or better.’

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 Supporting Information.

**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:

‘Notably in biology and medicine measuring and controlling temperature at a sub-cellular scale are the challenges that need to be overcome to achieve better understanding and control of the mechanisms involved in new therapies such as photothermal tumor ablation 4 or controlled drug delivery.’

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 nutshell, we consider the luminescence emission as radiative recombination of electron-hole pairs created by the decay of the plasmon, after their interaction with thermal baths. Before the recombination, carriers may interact with the baths one or more times, leading to secondary light emission with an energy different from the initial internal energy of the pair. The anti-Stokes spectral contribution arises from interactions that increase the energy of the pair, whereas the Stokes emission to a decrease in energy. The emission process will be enhanced by the surface plasmon; therefore the luminescence spectrum will be modulated 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 we cannot simply use the anti-Stokes to Stokes intensity ratio to obtain the temperature of the particle, as is commonly done with Raman lines of molecules, due to the presence of the strong plasmonic enhancement of the emission that must be considered in addition to the Boltzmann factor.’

We also clarify our procedure by adding explicitly the steps needed to extract the temperature from the anti-Stokes spectra:

1. Obtain the surface plasmon resonance spectrum of the particle. This is usually expressed as a Lorentzian function, i.e.

Where is the photon energy frequency, is the resonance frequency and is the width of the surface plasmon resonance. In our case, we detect the spectrum of photoluminescence excited at 532nm to extract and , with the procedure explained in the Supporting Information.

1. Excite near the longitudinal plasmonic resonance and detect the blue-shifted anti-Stokes emission spectra. For this we employed a 633 nm laser as a source.
2. Fit the high-energy part of the spectrum using equation 2 with T as the only free parameter.

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

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

4.Please provide information on the laser fluence.

When we use the 60x NA1.4 the 633nm HeNe laser maximum power reaching the objective is 100 µW, 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 also 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!

Note reference

Deprédurand, Valérie, et al. "A temperature-sensitive tracer suitable for two-colour laser-induced fluorescence thermometry applied to evaporating fuel droplets." *Measurement Science and Technology* 19.10 (2008): 105403.

It is still ratiometric: https://hal.univ-lorraine.fr/hal-01570410/document

**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.

The data shown in figure 3 is from a different nanorod than the one presented in figure 3. We added the wavelength scale on the top axis in figure 3 and the energy scale in figure 1 to help the reader relate the tow scales.

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: a source of error is the fit of the plasmon resonance spectral shape, therefore, improving this measurement and fit will improve the method. The added section ‘’ in the Supporting Information analyzes this point in detail. It is 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.

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.

Triggered by this comment we added the following paragraphs to discuss this point:

‘In this work, we call “photoluminescence” any secondary light emission 39 at energies different from the excitation laser energy, . After (virtual or real) absorption of an excitation photon, the excited electronic state31,37 may interact and exchange energy with the phonon bath or, in the case of metals, with the bath of thermally excited charge carriers around the Fermi level. After a number of interactions, the excited electronic state will re-emit a photon which can possess a lower or higher energy than that of the excitation photon40-42. For a non-resonant excitation, the probability of more than one interaction is negligible and the main contribution to secondary emission is Raman scattering34. This is the case, for example, of insulators excited well below their electronic absorption edge. For resonant excitation, a relatively long-lived excited state is prepared. It will have enough time to interact repeatedly with thermal baths, particularly with phonons. This is the case of organic dye molecules or semiconductors, in which relaxed fluorescence is observed. We also note that fluorescence always presents hot bands on the anti-Stokes side of the excitation laser. In most fluorescence detection schemes, however, these hot bands are ignored, but they are far from negligible in heavily doped samples.

Metal nanoparticles fall between those two extremes because the excited electronic state, an electron-hole pair, relaxes very rapidly by interacting with other charge carriers and with phonons. The photoluminescence lifetimes are on the order of tens of femtoseconds44 and therefore there is not enough time to obtain a fully relaxed luminescence. In other words, the photoluminescence is always “hot”. It is worth noting that Raman scattering, corresponding to the lowest order of interaction with baths, will be an important contribution to photoluminescence34,36. However, second and higher orders may also contribute significantly. Because all these processes obey a Boltzman-type of relation between anti-Stokes and Stokes emission, they cannot be easily distinguished from each other on the basis of their temperature dependence.

The anti-Stokes emission is highly sensitive to temperature and thus it can be used for thermometry45. In this letter we present a simple procedure to extract the absolute temperature from the anti-Stokes photoluminescence spectrum of individual gold nanorods without the need of any previous temperature calibration. We show that we can determine the particle temperature in-situ with an accuracy of 6% by recording a single anti-Stokes spectrum (with an acquisition time of 3 minutes). Moreover, by performing this measurement at different excitation powers we can obtain the temperature of the surrounding medium with an accuracy better than 2%.’

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 changed the text to clarify this point:

‘In order to achieve photon emission at higher energy than the excitation, i.e. an anti-Stokes band, the interactions with the thermal baths has to provide the extra energy required. Since most excitations decay non-radiatively, the energy available in the thermal bath also depends on the previous excitations. Thus, the energy content of the bath also presents on the excitation power, leading to a slope > 1 in Figure S6. In other words, the higher the power, the higher the temperature of the particle and the higher the anti-Stokes signal is.’

**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 Supporting Information 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 when we take the luminescence spectra we see the typical shape that corresponds to a single gold nanorod.

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 if the aspect ratio and the resonance laser are changed to a different wavelength.