



Experimental practices required to isolate thermal effects in plasmonic photo-catalysis: lessons from recent experiments

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Abstract: Metal nanoparticles have recently been shown experimentally to speed up chemical reactions when subject to illumination. The mechanisms of this phenomenon have been under debate. A dominant role for high energy non-thermal (typically but imprecisely referred to as “hot”) electrons was proposed in a study by the Halas group [*Science* **362**, 69 (2018)]. However, evidence that the faster chemistry has a purely thermal origin has been accumulating, alongside the identification of methodological and technical flaws in the theory and experiments claiming the dominance of “hot” electrons [*Science* **364**, 9367 (2019)]. Here, we advance this discussion towards the possibility of isolating thermal from non-thermal effects. We detail a series of experimental aspects that must be accounted for before effects of “hot” electrons can be distinguished from thermal contributions in plasmonic photocatalysis.

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1. Introduction

Experimental demonstrations of faster chemistry in the presence of illuminated metal nanoparticles have sparked a great deal of interest among researchers in the fields of nano-plasmonics, nanophotonics, and chemistry. Modifications to reactivity and selectivity that were discovered in such plasmon induced catalysis were discussed thoroughly in various previous reviews [1–5]. Early works associated these effects with non-thermal carriers (having energies high above the Fermi energy, see Fig. 1) generated upon photon absorption in the metal. However, the role of regular heating in these systems (associated with electrons with low energies with respect to the Fermi energy, also shown in Fig. 1), an effect that is undesirable due to the resulting lack of selectivity and high practical costs, was not fully elucidated.

In Ref. ([6]), Zhou *et al.* described an experiment that aimed to provide conclusive evidence for non-thermal effects. However, a brief Technical Comment [7] we published shortly after the publication of the original work identified technical and methodological errors in [6]. Specifically, we showed that inaccurate measurements of the temperature likely led to an underestimation of the catalyst temperature, and that the catalytic enhancement of the reaction rates can be simply and directly attributed to illumination-induced heating using the well-known Arrhenius Law. Similar problems in additional related papers, as well as a more comprehensive discussion that includes an alternative interpretation of the experimental data, were presented in Ref. ([8]).

The constructive criticism we raised in [7] was met by a reply from Zhou *et al.* [9], and the rest of the current paper does discuss difficulties in said response and the original paper [6]. However, we urge the reader to view this paper as much more than an “ongoing argument”. Rather, this manuscript contains a set of experimental (and conceptual) conditions that must be met, if indeed non-thermal photo-catalytic effects are to be isolated from the thermal ones. We hope that these

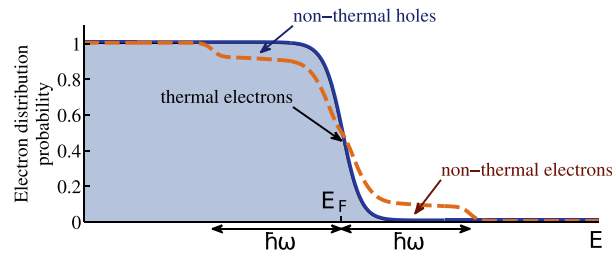


Fig. 1. Schematic illustration of the electron distribution in a metal illuminated by continuous wave (CW) radiation. The blue solid line represents the equilibrium electron distribution in the absence of illumination. The orange dashed line represents the electron distribution under illumination. It consists of thermal electrons near the Fermi energy that obey the Fermi-Dirac statistics, and non-thermal (the so-called “hot”) electrons in two $\hbar\omega$ -wide shoulders far from the Fermi energy, which are not part of the Fermi-Dirac distribution.

conditions will serve as guidelines for future experiments, and that this will aid the design of future control experiments in this field.

This paper is thus organized as follows. In Section 2, we provide relevant background, describing the experiments of Zhou *et al.* [6] in detail, and summarizing their main findings and our central criticism, as discussed in [7].

In Section 3 we discuss some guidelines that future experiments must consider, if thermal imaging is to be used to try and differentiate heating from “hot-electron” photocatalysis. Section 4 is devoted to a detailed response to Zhou *et al.*’s response to our Comment. This section may read like a review rebuttal, but it is not. Rather, it is a clarification of errors made in [6] and compounded in [9], roughly in the order presented in [9]. The reader is encouraged to first read our Comment, [7], and then [9] and Section 4 paragraph by paragraph.

In Section 5, we outline several additional problems in the data acquisition and processing of [6] (not mentioned before), which call into question the very validity of the data. We summarize in Section 6, and re-iterate the potentially most important message of our own set of studies on plasmon-assisted photocatalysis, namely, the limitations of the methodology adopted in [6] (and many others, see [8]) that render it unsuitable as means to distinguish thermal vs. non-thermal effects. Specifically, in the approach pursued in [6], any small difference between the temperature profiles of the photocatalysis experiment and its thermocatalysis control is bound to be erroneously interpreted as a non-thermal effect. In other words, the methodology of [6] can allow one to detect non-thermal effects only if they are far stronger than the reaction rate uncertainty associated with the temperature inaccuracy of the thermocatalysis control experiments. Our theoretical predictions [10,11] show that this scenario is very unlikely.

2. Review of experiment and criticism

The experiments performed by Zhou *et al.* [6] are conceptually simple, and similar in spirit to experiments reported by the same group [12] as well as other groups [13–16]. A catalytic pellet, composed of hybrid plasmonic nanoparticles (Cu and Ru in their case) embedded in an oxide porous substrate, is placed in a reaction chamber which has a window, through which the sample is illuminated. Temperature is measured using a thermal camera (in [6]) and/or a thermocouple, placed well below the catalytic bed (see schematic experimental setup, taken from [9]). The reaction rate is measured in the dark and under illumination, and the photo-catalytic enhancement is determined in the following manner. Under illumination, typically both the reaction rate and the measured temperature increase. Then another measurement is performed, where the system is not illuminated, but the temperature is increased to the level measured under illumination. If

the reaction rate is not the same under illumination and under heating to the same temperature, the hypothesis is then that additional, non-thermal effects presumably take place. The suggested mechanism for such a non-thermal effect was “hot-electron photocatalysis”, where non-thermal high-energy electrons tunnel from the nanoparticle to the reactant and place it on an excited state potential energy surface, thereby lowering the energy barrier for the dissociation reaction.

In our Comment [7] we suggested that there is a flaw in this argument, because of three simple observations. First (as was indeed demonstrated experimentally [14,17]), the temperature of the catalytic pellet is not uniform, and temperature gradients are formed, both in the dark and under illumination. Second, the measured temperature is thus not the true temperature of the nanoparticles themselves, but rather depends on the experimental setup (for instance the position of the thermocouple, or the parameters of the thermal imaging camera). Third, thermal reaction rates are exponentially sensitive to temperature (reflected in the well-known Arrhenius form of the reaction rate).

Considering these three points, we argue that the measured temperature underestimates the nanoparticle temperature, leading to an over-estimation of non-thermal effects. Moreover, we demonstrated that under this assumption, as we showed in [7], the experimental data of Zhou *et al.* can be fully reproduced as a pure thermal effect. This was later demonstrated to hold for other experimental data claiming similar non-thermal photocatalysis [8].

3. Guidelines for future experiments

Our analysis, based on the three points mentioned above, leads to a very simple conclusion: in order for a thermal control experiment to be valid (and to demonstrate non-thermal photocatalytic effects unequivocally), the full, 3-dimensional temperature profile of the catalytic pellet must be reconstructed (without illuminating it), and only then can the comparison to the illuminated reaction rates be relevant. This is because (as discussed in [7]), reaction rates are exponentially sensitive to the local temperature. Thus, the spatial average of the temperature will be very different from a temperature inferred by the reaction rate. This is equivalent to the simple mathematical statement that the average over an exponent is not the same as the exponent of the average; if the chemical reaction obeys an Arrhenius law, then it is defined by the activation energy E_a and the position-dependent temperature $T(r)$. Then, $\langle \exp\left(-\frac{E_a}{k_B T(r)}\right) \rangle \neq \exp\left(-\frac{E_a}{\langle k_B T(r) \rangle}\right)$, unless the temperature is uniform over space (but in some photocatalytic experiments it has been proven to be position-dependent [13]). Thus, it is critical to be able to determine the temperature distribution of the sample properly. Below, we give several simple guidelines for the use of thermal imaging to understand the temperature profile of the illuminated sample. These should be a useful checklist for all groups who wish to use thermal imaging for evaluating temperatures of a catalytic surface. It may very well be that innovative solutions beyond thermal imaging are necessary to truly overcome this challenge.

3.1. Stay focused

A thermal camera is, among other things, a camera. It has optics, and one has to be extremely cautious that it is kept in focus. When the sample is out of focus, photons from different parts of the sample end up at the same position on the camera detector. Since the amount of photons hitting the detector is converted into temperature, an out-of-focus camera essentially averages or “blurs” temperature readings over a certain width, which yields the error discussed above.

3.2. Check the emissivity

An ideal blackbody emits thermal radiation according to Planck’s law, which then allows temperature determination via the Stefan–Boltzmann law. But real samples are never ideal black bodies, and do not actually emit in accordance with Planck’s law. The emissivity is a measure

of how well a graybody sample performs as a blackbody (a perfect black body will have an emissivity of unity at all wavelengths; a graybody has a constant emissivity less than one). While many materials are reasonably approximated in this way, especially in the far-IR, metals are very poor blackbodies, and polished metal surfaces tend to have emissivities of <0.1 .

Thermal cameras can, in principle and within a certain range, correct for low emissivity. However, for this to be accurate, the surface emissivity has to be determined a priori. Many materials and surfaces are tabulated (typically even in the camera manual), but for a specific system, there is no better solution than to actually measure the emissivity directly. Note that in some cases, the emissivity can be wavelength- and temperature- dependent, thus complicating the thermal camera calibration [18].

3.3. *Insist on resolution*

As was pointed out above, spatial averaging of the temperature may lead to a discrepancy between the temperature measured via the thermal camera and the temperature inferred by the chemical reaction rate. This will happen automatically if the spatial resolution of the thermal camera is larger than the scale of the temperature changes on the surface of the sample. It is thus imperative that the resolution of the camera and associated optical system is adequate for the system under study.

3.4. *Steady-state or pulsed illumination*

There can be a substantial difference in the response of the system to continuous wave illumination vs. pulsed illumination. Since time-scales for the pulse and for thermal relaxation can be similar, the electronic and phonon temperatures can be drastically different, depending on whether the system is illuminated continuously or not [10,19].

3.5. *Calculate the expected temperature*

The theoretical approach for evaluating the temperature rise of illuminated nanoparticles has been specified in Ref. [20,21], and it is rather straightforward. However, it requires extracting information on the properties of the nanoparticles, including size, nanoparticle density, thermal conductance, absorption cross-section etc. If this is done properly, it can provide useful intuition of the mechanism of photocatalysis, while if done improperly can lead to the wrong conclusions (see, e.g., Ref. [16], where single nanoparticles were considered instead of many billions of nanoparticles, leading to an error of five orders of magnitude in the local temperature estimation).

4. **Response to response of Zhou *et al.* [3]**

Once we have established some key experimental points which must be addressed, we devote the rest of this paper to a detailed discussion of how, unfortunately, they were not addressed properly in Ref. [6]. Some of these points were raised in [7], and so in order not to be repetitive, we do this by a detailed analysis of the response of Zhou *et al.* to our Comment [9]. While this is not a standard format for a paper, nevertheless we believe that the readers, especially those keen to understand the origins of the misinterpretations of Zhou *et al.*, will find this format useful and informative.

4.1. *Discrepancy between temperature readings from their thermal camera and from a thermocouple*

In their Response [9] to our Comment, Zhou *et al.* defend their original paper by, among other things, providing additional results not reported previously. We wish to begin by noting that the newly presented data in the Response in fact *supports* our criticism. Specifically, the Response reports a roughly 5% discrepancy between temperature readings from their thermal camera and from a thermocouple, whereas in [6] they claim that the readings were identical. This $\sim 5\%$ error

in the temperature measurement alone adds a factor of ~ 5 to the thermal reaction rate, due to the exponential dependence of the reaction rate on the temperature; this error is certainly an underestimate, and as discussed below, the remainder of the originally claimed photocatalysis enhancement of $30\times$ could easily be erased by any of a plethora of factors.

4.2. Incorrect value for the emissivity

The first item in the Response [9] is the chosen emissivity value. The authors of Ref. [6] used the *default setting* of their thermal camera, an emissivity of 0.95 (almost an ideal black body; compare the FLIR A615 camera manual [22] to the settings seen on the right-hand-side of the camera image, Fig. S11 of the original work [7], Fig. 3 below) rather than adjusting the settings to the actual experimental conditions! Indeed, their sample seems to have a much lower emissivity. Specifically, we estimated 0.02 – 0.2 based on composition and structure of their sample as described in the SI of [6]. Unlike what is claimed in the Response [9], the values we used in our estimate of the emissivity of the sample *were not* taken for polished surfaces, but rather for small grains, see for example the MgO content values (see Fig. 18 of Ref. [3] of [7]).

To answer this, Zhou *et al.* state that in porous beds of powdered materials the emissivity is much larger, and refer to an example of samples consisting of Ni nanoparticles on a Al_2O_3 substrate. What Zhou *et al.* fail to point out is that Al_2O_3 comprises just ~ 20 percent of their sample (see page 1 of their SI). Thus, conducting a weighted sum of the emissivities (taking the extreme limit of unity emissivity for Al_2O_3) gives a contribution of ~ 0.2 , which is effectively the upper limit we provided in our Comment [7]. But, this is also probably an overestimate – the user manual for their thermal camera [23] clearly states the emissivity of powdered alumina as 0.16 – 0.46. To avoid this issue, the authors of [6] should have measured the emissivity (for each different sample) and set the thermal camera parameter to that value. No such attempt was made in the original paper [6], nor in the Response [9], even though the authors did change the value for the external optics transmission factor.

As explained in our Comment, the exceedingly high emissivity setting in [6] means that the temperature readings of the thermal imaging camera underestimate the actual temperature of the sample. As shown in Section 4.4 below, this claim is well correlated with the incorrect choice of the thermocouple position in the newly reported benchmarking experiments (see Sec. 4.4 below).

4.3. Incorrect focusing and choice of camera-sample distance

Further consideration of Fig. S11 of the original work [7] (Fig. 3(b)) gives rise to additional concerns. Comparison of the FLIR A615 camera manual (<https://www.flir.eu/products/a615/>) to the settings seen on the right-hand-side of the camera image reveals that the (rather blurry, especially compared to the regular image in Fig. 3(a)) images were taken with the camera-to-sample distance set to the unlikely large distance of 3.3 feet, which is, again, the *default* setting of the camera software. As a comparison, Fig. 3 shows also an image of an object of the same size as the pellet (2 mm) taken by the *same* camera model. The far better achievable resolution is clearly seen. Simply put: the images in [6] were out of focus, hence, inevitably led to an underestimation of temperature. The Response [9] does not refer to the unlikely choices of settings for both the emissivity and camera-sample distance.

4.4. Improper thermocouple positioning

To validate the readings of the thermal camera, Zhou *et al.* compare them to those of a thermocouple, placed well below their catalytic pellet (specifically, 3 – 5 mm away, see Fig. 2, a copy of a new plot that appears in the Response [9]). Quite intuitively, the temperature at that position differs from the catalyst temperature: for external heating (from below), it records a temperature which is higher than the catalyst temperature, whereas for optical heating (from above), it records a lower temperature. Indeed, as we showed in [8], and as demonstrated

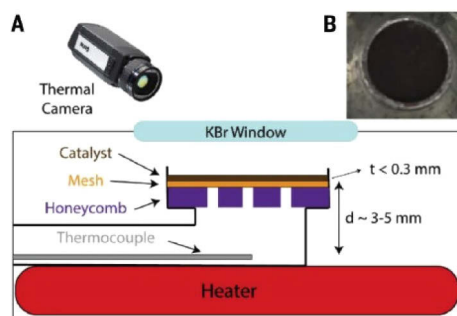


Fig. 2. Fig. 1 of [9], showing a schematic of the experimental setup. The distance between the thermocouple and the sample is 3 – 5 mm. The distance from the camera to the sample is not specified.

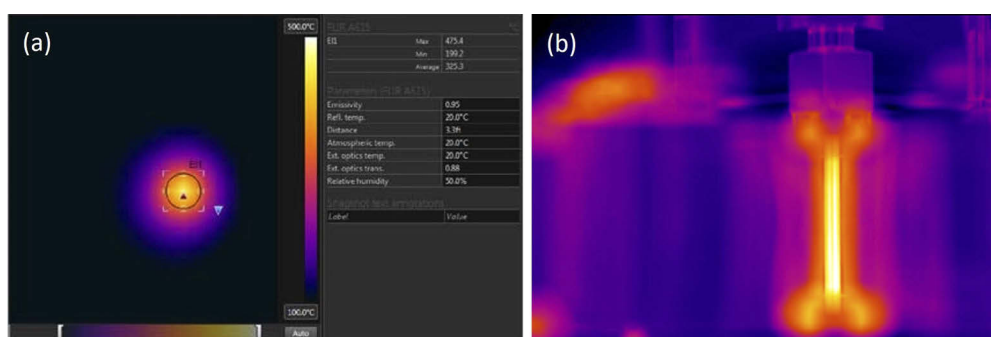


Fig. 3. (This image is best viewed as a high resolution color image) (a) Fig. S11 of [6]. The image is clearly blurred (out-of-focus) and the camera settings are clearly left at their default values (Distance = 3.3 ft and Emissivity = 0.95). As explained in the text, these are very unlikely to be suitable for the experimental conditions. (b) As a comparison, we show an image of an object [24] of the same size as the pellet (2 mm diameter tube, seen yellow-white in the center-right of the image) taken by the *same* camera model (equipped with a 100 μm closeup lens, to boot). Improved image sharpness is apparent with correct focusing, but note the difficulty of obtaining sufficient resolution (and therefore accurate temperature measurements) even with the magnifying lens. Other hot(ter) objects that are out of focus seem to be cooler than their actual temperature.

experimentally by the Liu & Everitt teams [13,14], even if the thermocouple is placed right at the bottom surface of the catalytic pellet in the photocatalysis experiments, it measures lower temperature compared to the top surface temperature (where the photon absorption takes place, hence, where the heat is generated), all the more so if the thermocouple is placed some 3 mm below the pellet, as in [6].

As shown in [8], the lower temperatures arising from the improper positioning of the thermocouple are likely to be the origin of the incorrect claims on dominance of non-thermal effects in [25] and [12]. In the current context, the fact that the temperature readings of the thermocouple and thermal camera are roughly the same only *strengthens* our claim that these readings refer to a temperature which is lower than what is felt by the illuminated nanoparticles (hence, of the reactants) and provide further support of our criticism on the data acquisition in [6]. Put simply, Zhou *et al.* compare two temperatures which *both* underestimate the true temperature of the catalytic pellet. The accuracy of the temperature readings is likely to be worse under illumination, where the energy is deposited in the nanoparticles on the upper surface of the

pellet, leading to more pronounced temperature gradients. The authors of the Response [9] did not report such a comparison of two thermometry methods under photocatalytic conditions.

What the authors *do* report is a $\sim 5\%$ discrepancy between the temperature readings from their thermal camera and from the thermocouple. We point that this $\sim 5\%$ error in the temperature measurement alone adds a factor of 5 to the thermal reaction rate, due to the exponential dependence of the reaction rate on the temperature. Such a factor cannot be dismissed, especially in light of the possibility that the observed enhancement factor is largely artificial, see Sec. 5.2 below.

4.5. More on temperature measurements

4.5.1. Temporal non-uniformity

Next, Zhou *et al.* discuss the uniformity of the temperature in their sample. First, considering the temperature uniformity in time (i.e., the fact that the temperature is eventually nearly constant over time even though the illumination has a pulsed nature), they refer to their Fig. S12E in the SI. This is a *schematic figure*, not a measurement nor a calculation. Nevertheless, the emphasis on this issue is misleading since never in our Comment did we argue differently. In fact, we had performed the corresponding calculation and indeed found a fairly temporally-uniform temperature, see [8](p. 270 and on).

4.5.2. Surface non-uniformity and spatial resolution

After that, Zhou *et al.* discuss spatial variations of the temperature and point out that the values indicated in their plots is the highest surface temperature. Here, they are referring to temperature variations along the surface plane, which we never mention in our Comment, so this is, again, not particularly relevant. For the sake of completeness, we note that we treated this issue at length in [8], and did find significant in-plane non-uniformity. Such non-uniformities might prove to be important in future studies.

However, this topic is intimately related to the crucial issue of spatial resolution, and demonstrates the unreliability of the claims made in [6]. Insufficient spatial resolution or incorrect focusing of the thermal camera (see Section 4.3) necessarily leads to temperature readings lower than the actual temperature. Zhou *et al.* claim a resolution of $\sim 100 \mu\text{m}$; this contradicts the manufacturer's specifications [26], where the resolution is given as $690 \mu\text{m}$ at the working distance of 3.3 ft. indicated in Fig. S12 of [6] (our Fig. 3). Worse, a resolution of $\sim 100 \mu\text{m}$ with this camera is impossible at any working distance, according to the manufacturer. Using the correct $\sim 0.69 \text{ mm}$ value, we can see that a properly focused image would achieve less than 3 pixels across the 2 mm diameter pellet, which is not adequate for accurate temperature measurement, again, according to the recommendations of the manufacturer.

4.5.3. Depth non-uniformities

Nevertheless, even if one ignores all the above, a less obvious yet crucial problem arises from temperature gradients along the depth of the pellet. The thermal camera gives no information about this dimension, and so we are left to rely on calculations and common sense. Our detailed temperature calculations in [8] show that there are gradients of several *hundreds* of degrees across such a distance. Such gradients were also shown to exist experimentally by the Liu team [13,14]. While it is true that, given only surface temperature information, thermocatalysis control experiments should be carried out at the highest measured temperature in order not to underestimate thermocatalytic effects, this is still inadequate in case the gradients have opposite signs, since the (top) surface temperature is lower than the bottom surface temperature in the thermocatalysis case, see Fig. 4; this is exactly the case in [6], so that clearly the control thermocatalysis experiment does not overestimate the thermal contribution in the photocatalysis case. Moreover, the Liu/Everitt teams [13,14] discussed additional consequences in the reaction

rate caused by these opposing gradients. Thus, an effective control experiment must ensure the temperature profiles in the photocatalysis and thermocatalysis experiments are exactly the same.

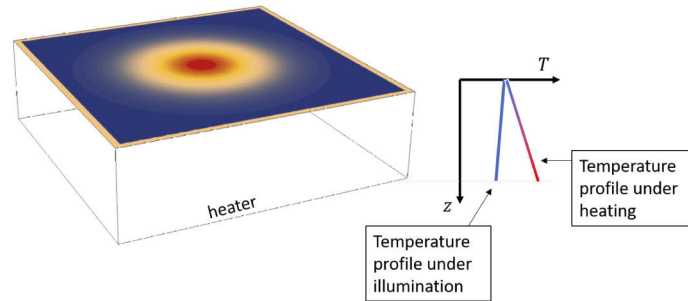


Fig. 4. A schematic illustration of the temperature profile in the photocatalysis and thermocatalysis experiments. The vertical gradients are opposite in the two experiments, such that the thermocatalysis control experiment does not mimic correctly the conditions of the photocatalysis experiment.

4.6. Intensity-dependence of temperature

Zhou *et al.* continue their Response by criticizing the intensity-dependence of the temperature in our model, specifically, that our model *a priori* assumes an incorrect linear relation between the temperature and the illumination intensity. Here, they commit a few factual and physical *faux pas*.

First, unlike what is claimed in the Response, in our model we never assume *a priori* that the temperature is linear in intensity. Quite the opposite – we start by assuming a general form,

$$T(I_{inc}) = T_0 + aI_{inc} + bI_{inc}^2. \quad (1)$$

Clearly, T_0 is the temperature of the sample in the dark. What we find from fitting this expression (placed in the Arrhenius formula) to *their* data (specifically, Figs. 2(a)-(b) in [6]), is that the nonlinear term is vanishingly small. Therefore, the linear dependence in Fig. 1 of our Comment [7] comes out of the data rather than being pre-assumed.

In this context, the linear model works perfectly well for most of the data presented in [6] (as well as for all the data of several other papers we criticize in [8], see discussion in page 270-271 of [27]). However, like any other physical system, the range of validity of the linear response is finite. Zhou *et al.* quote several papers (Refs. [10,11] in their response [9]) as stating that a linear dependence of the temperature on the illumination is only applicable for temperature rises smaller than about a 100K. This is never stated in neither of these references.

An additional error made by Zhou *et al.* is the formula they suggested for analyzing the dependence of the temperature on illumination, namely,

$$\alpha I = h(T)(T - T_0) + A(T)(T^4 - T_0^4). \quad (2)$$

This equation is essentially energy conservation - it equates absorption of photons (left-hand-side) to radiative (quartic term) and non-radiative (linear term; heat conductance) heat loss (right-hand-side). What Zhou *et al.* get wrong is that the latter is extremely small. In particular, a quick evaluation (see Appendix A) reveals that heat radiation is at least about $10^4 - 10^5$ times smaller than the power that is lost via thermal conductance - because their nanoparticles are not isolated. Put simply - the power that is lost due to radiative heat losses is only a tiny fraction of the power that is lost through direct contact between the nanoparticles and the substrate, so that the nonlinearity has nothing to do with radiative heat losses.

Instead, the nonlinearity has two main sources, both much stronger than radiative losses. First, the absorption coefficient α depends on the temperature *via* the temperature dependence of the metal permittivity, an effect studied in countless papers, see e.g., [28,29] for the ultrafast temperature dependence of the metal permittivity; many other papers, including various ellipsometry papers, studied the corresponding steady-state temperature dependence, see e.g., [30–34], to name just a few. Second, the heat transfer coefficient $h(T)$ also depends on the temperature *via* e.g., the thermal conductivity, Kapitza resistance etc. (see e.g., [32,33]). The exact quantification of these nonlinear thermo-optic effects is a topic which has occupied the Sivan group in the last few years [32–35]; we are currently in the process of quantifying these two effects in the current context of plasmon-assisted photocatalysis (namely, a calculation of a and b from first principles modelling and matching them to the experimental data), and expect to publish initial results soon.

4.7. Nanoparticle melting

In a direct continuation of their reasoning, Zhou *et al.* point out that within the model we present, the temperatures would rise above the melting temperature of the copper nanoparticles, thus leading to sintering which was not observed. To answer this, one needs to consider the following points. (1) Melting is an ambiguous concept for the small NPs employed in [6]; one may argue that melting occurs even under the conditions reported in [6] itself. (2) Since the nanoparticles are embedded within a porous substrate, they are separated from each other by an oxide layer and air, which may prevent sintering. (3) The authors state that no sintering was observed, but do not show data to support this claim. (4) As explained in the previous section, the main results of the original paper [6] are limited to illumination intensities $I \leq 4 \text{ W cm}^{-2}$, which, according to our fitting, lead to temperatures still below an *approximate* melting point. In particular, it is not clear why the authors do not show data points for higher intensities (except in Fig. 1D of [6]). (5) The data that the authors do show that includes higher intensities (Fig. 1D and S11 in the SI of [6]) shows the onset of nonlinearity at roughly the intensity which presumably leads to heating by several hundreds of degrees, where melting might be expected. We refer the interested reader to a far more thorough discussion of this issue in [27] (p. 270 and on). Overall, all the above points out that even if melting occurred, it is not likely to have modified the thermal/optical/chemical performance of the pellet.

4.8. Intensity-dependent activation energy

In the final part of their response, Zhou *et al.* state that “the assumption of a light-independent E_a is not physical, because hot carriers modify adsorbate coverage on the catalyst surface and thus influence the apparent activation barrier, as we explained in our original paper”. It is hard to follow their reasoning here, since the only proof they provide for this statement is data that can be fitted – to remarkable accuracy – with a light-independent E_a .

Finally, Zhou *et al.* point that even if one assumes an intensity-dependent temperature, the evaluated activation energy E_a still depends on the illumination intensity. This is simply incorrect, because if one assumed both intensity-dependent temperature (e.g., $T(I) = T_0 + aI$) as well as intensity-dependent activation energy $E_a(I)$, then the data would not be sufficient to determine both of them. Simply put, one can choose any value for a , from $a = 0$ up to our value of $a \sim 180 \text{ K/W cm}^{-2}$ (and higher), and obtain - from the same data - a different curve for $E_a(I)$. These $E_a(I)$ curves changes for different values of a , from the curve shown in Fig. 2 of [6], up to E_a which is essentially intensity-independent, and all this with remarkable accuracy.

An example of this fitting procedure is shown in Fig. 5. On the left panels we plot the original data (reaction rate vs temperature) of [6] (blue points are reaction rate in the dark, and yellow, green, red and purple are for intensities $I_{inc} = 0, 1.6, 2.4, 3.2$ and 4 W/cm^2). The solid lines are fits to an Arrhenius form, $R = R_0 \exp\left(-\frac{E_a}{k_B(T_0 + aI_{inc})}\right)$, where a takes different values, from $a = 0$

(as chosen by Zhou *et al.*) up to $a = 180 \text{ K/W cm}^{-2}$ (left panels). The right panel shows the corresponding $E_{a(I)}$ -curves, ranging from a strongly intensity-dependent activation energy (at $a = 0$) to an essentially intensity-independent activation energy, all obtained with the same data and the same accuracy. This demonstrates that the last statement in the response of Zhou *et al.* is simply wrong. For the reader's convenience, we have added in Appendix B the data used to extract these fits (which was obtained by digitizing the original figures of [6]). The active reader can simply take these data, fit them to an Arrhenius form and see the remarkable agreement.

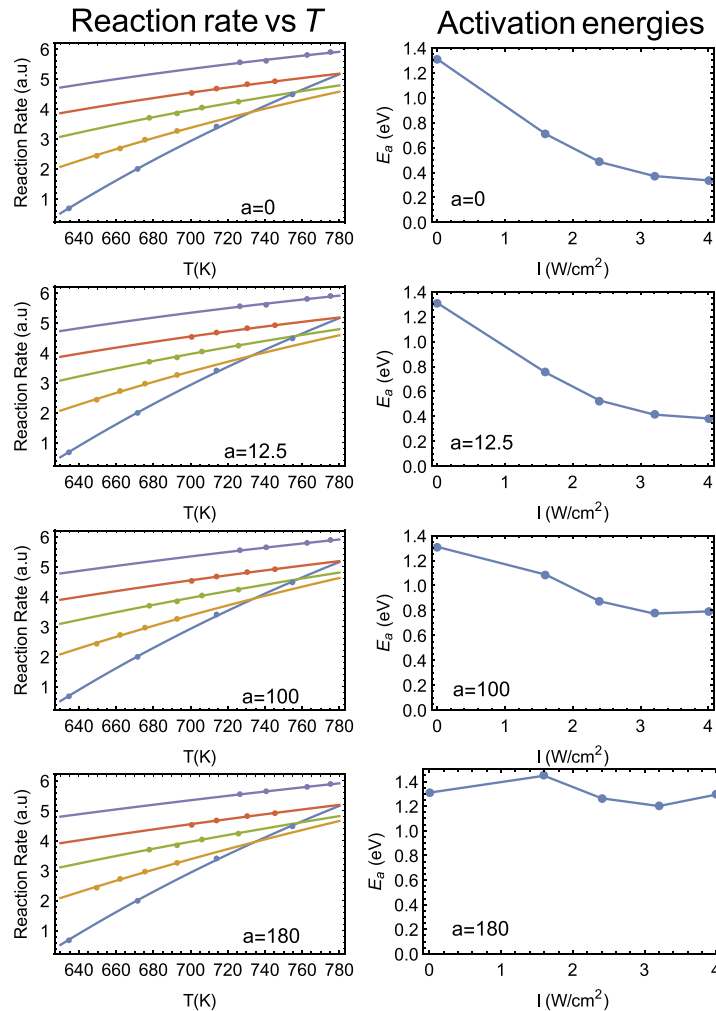


Fig. 5. Left panels: reaction rate as a function (inverse) temperature, points are data from Zhou *et al.* [6] (the data is available in Appendix B). The solid lines are fits to an Arrhenius form with varying values of a . Right panels: the resulting activation energy as a function of intensity, going from a strongly intensity-dependent activation energy (this is what is plotted in Fig. 2C of Ref. [6]), all the way to an essentially intensity-independent activation energy for $a = 180 \text{ K/W cm}^{-2}$.

5. Additional problems

Up till now, we have only addressed points mentioned in the Response of Zhou *et al.* to our Comment. We now discuss several issues which were not treated in our original Comment, yet cast further doubt on the original claims of Zhou *et al.* of isolating the non-thermal effects from the thermal effects.

5.1. Uncertainties in the illumination intensity

Here follow a few particularly concerning ambiguities regarding the illumination source used in [6].

In the Supporting Material of [6] (page 5), Zhou *et al.* write, “Direct illumination of the thermal camera with our light source did not cause any response to temperature, demonstrating that the illumination source has no mid-IR ($2 - 10 \mu\text{m}$) photons.” Given that (a) the long wavelength infrared camera’s response range is $7.5 - 14 \mu\text{m}$ [36], and (b) the specification sheet of the light source states and shows that the output extends well above $2 \mu\text{m}$ [37], this statement is both factually incorrect and logically indefensible. In particular, it is conceivable that a massive amount of infrared radiation also illuminated the catalyst pellet during these experiments. According to the manufacturer’s specifications, the light source outputs 8 W total power from <410 to ≈ 2400 nm [38]; Zhou *et al.* describe the use of a filter to reduce the power to 300 mW, but it is not clear if that value was explicitly measured, and if so, how. If the 300 mW value relied on the filter specifications, then an inspection of Edmund Optics’ catalog shows that their relevant filters are not specified past 1200 nm; none of the other optical components used (KBr window, N-BK7/SF5 lens) would have blocked the substantial infrared power ($3 - 4\times$ the UV/Visible power) produced by the laser.

Furthermore, the output beam profile is Gaussian, meaning that its peak intensity is roughly twice the average intensity value taken by Zhou *et al.* in their data analysis. This non-uniform illumination intensity would only exacerbate the problem of temperature gradients and non-uniform heating; again, that leads to more significant thermocatalysis effects in the photocatalytic experiments.

Finally, it is curious that the specified collimated output beam diameter of the laser in the visible is equal to or even smaller than ($1.5 \text{ mm} @ 530 \text{ nm}$) the 2 mm spot size to which Zhou *et al.* claim to have focused it with a fairly short focal length ($f = 100 \text{ mm}$) lens.

5.2. Normalization of the reaction rate

One of the most problematic aspects in the original paper [6] which was not raised in our Comment [7] (due to lack of space) is worth discussing now. The main claim in [6] relies on a single post-processing procedure - the rescaling of the volume contributing to the reaction according to the penetration depth of the electric field; this is justified by claiming that the contribution of non-thermal electrons can come only from the illuminated layer, whereas for thermocatalysis, the contribution to the reaction is supposed to come from the whole layer thickness. In particular, the authors estimate the penetration depth, and renormalize the reaction rate accordingly by a factor of ~ 30 according to [6] (or $20 - 100$ according to [9]). This estimate is rather crude - the electric field decays exponentially, and the electron distribution scales with its square (which means that the decay occurs at twice as short a distance); this is different from the step-like dependence assumed by this normalization. A proper integration is called for - it will show that the exponential weight makes the regions of highest field matter much more (see e.g., the procedure described in [13,14]). As shown above, even small errors associated with crude normalization might result in a very large effect on the reaction rate. Moreover, this approach ignores two additional complications. First, the temperature penetration is also finite (see our detailed calculations in [8]) so that a similar rescaling should have been applied to the

thermocatalysis. As discussed in Section 4.5.3, the experimental setup provides no information on this aspect, thus, introducing further significant uncertainties or even errors to the data. Second, these two penetration depths can vary significantly with the temperature due to the temperature dependence of the various thermal and optical parameters of the pellet constituents [32]. Indeed, changes of several tens of percent were observed in these quantities due to elevated temperatures (e.g., in [39,40]).

The bottom line is that the factor by which the authors claim that the photocatalysis is higher than thermocatalysis is very similar to the value by which the thermocatalysis was normalized. Thus, if this normalization procedure had not been used, essentially no difference between reactions rates under illumination or in the dark would have been observed. In that sense, the normalization should have been much more accurate in order to allow extracting valid conclusions. Moreover, the normalization voids the claims in the Response about overestimation of the thermocatalysis, see Section 4.5.3. In that sense, our alternative (normalization-free) explanation that there is a negligible contribution of the non-thermal electrons to the reaction sounds far more likely compared with the crude and even somewhat artificial rescaling of the reaction data.

6. Summary

To summarize, we have shown that the measurements of Zhou *et al.* are severely flawed, in several ways. These include (but are not limited to) their thermal camera being out of focus and being set to the default settings (which include the wrong emissivity and other limiting factors). Our original Comment [7] was augmented with specific details pertaining to [6] and a detailed response to their reply to our Comment [9].

We would like to reiterate once more our primary message, which was not addressed by Zhou *et al.* in [9]. In order to distinguish thermal from non-thermal effects in plasmonic photocatalysis, one cannot simply compare illuminated and heated samples. A true control experiment must make sure that the full temperature profile inside the catalytic pellet is the same under illumination and in the dark, because reaction rates are exponentially sensitive to temperature changes. Unless such an experiment is performed, one cannot fully isolate non-thermal from thermal effects.

A. Estimation of radiative vs non-radiative heat transfer

In the energy conservation equation of Zhou *et al.*, Eq. (2), the first term describes the contact thermal conductance, i.e., heat transfer via vibrations of the solid at contact (to be referred to below as “non-radiative” heat transfer), and the second term describes the radiative heat loss, i.e., the heat transfer due to black body radiation absorption and emission (the the Stephan-Boltzmann law). Zhou *et al.* claim that the second term is responsible for the apparent nonlinear dependence on the temperature observed in their data.

It is very easy to make an estimate of the importance of the two terms, to see that the second term is much smaller, and hence has nothing to do with the nonlinearity. Specifically, the radiative power output per unit area is

$$P_{rad}/A = \sigma(T^4 - T_0^4), \quad (3)$$

with $\sigma = 5.67 \cdot 10^{-8} \text{ W/m}^2 \text{ K}^4$. This is an upper limit, assuming that the emissivity is 1 (although it is likely not, see Section 4.2). The non-radiative heat transfer, which is the power per unit volume that goes from one hot body to another via the vibrations of the molecules, can be estimated by

$$P_{non-rad}/V = G_{ph-env}(T - T_0), \quad (4)$$

where G_{ph-env} is the typical thermal conductance of the host. The typical thermal conductance of the nanoparticles can be estimated as $G_{ph-env} \sim 5 \cdot 10^{14} \text{ W/m}^3 \text{ K}$ [10]. Thus, even if we take extremely small nanoparticles, with a typical dimension of 2nm, the contribution of the second

term is $P_{non-rad}/A \sim (T - T_0) \times 10^6 \text{ W/m}^2 \text{ K}$. Comparing these terms at, say, $T = 700\text{K}$, gives $P_{rad}/A \sim 13000 \text{ W/m}^2$, $P_{non-rad}/A = 4 \cdot 10^8 \text{ W/m}^2$, about 4 orders of magnitude difference in favor of non-radiative heat transfer. In fact, in contrast to the claim in the Response, these terms become comparable only for temperatures as high as 20,000K(!) (rather than for a few hundreds of degrees).

B. Reaction rate data

For the reader's convenience, we add here the data extracted from Ref. [6]. The intrepid reader who has made it this far is encouraged to repeat the calculation we present (which is very simple), and to reproduce the remarkable fits of the data to the Arrhenius form.

I=0		I=1.6 W/cm ²		I=2.4 W/cm ²	
T^{-1}	Reaction Rate	T^{-1}	Reaction Rate	T^{-1}	Reaction Rate
0.00132487	4.49512	0.00144277	3.24939	0.00137739	4.25341
0.00139989	3.39814	0.00148028	2.9705	0.00141597	4.04889
0.00148992	1.98507	0.00151029	2.71019	0.00144384	3.86296
0.00157674	0.683559	0.0015403	2.44989	0.00147492	3.7142

I=3.2 W/cm ²		I=4 W/cm ²	
T^{-1}	Reaction Rate	T^{-1}	Reaction Rate
0.00134094	4.92276	0.0012895	5.8896
0.00136881	4.8112	0.00131093	5.79663
0.00139989	4.68105	0.00135059	5.62929
0.00142669	4.5509	0.00137631	5.55492

Disclosures

The authors declare no conflicts of interest.

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