Lessons learned from recent experiments? A critical analysis of "Hot carrier multiplication in plasmonic photocatalysis"

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Abstract

In recent years, the origins of accelerated reaction rates in the presence of illuminated plasmonic nanoparticles have been hotly debated. In particular, popular early claims of "non-thermal" electron action were shown to be based on inaccurate temperature measurements and poorly designed control experiments; instead, a pure thermal effect was shown to successfully explain the measurements in many high impact studies. Here, we comment on the results in yet another recent high profile paper from the Halas group [1], and show that while some improvement has been made, several problems remain, so it still does not provide sufficient evidence for non-thermal electron action.

1 Introduction

One of the most promising applications of metal nanoparticles was predicted to be the speeding up of chemical reactions, usually referred to as plasmon-assisted photocatalysis, see, e.g., [2, 3, 4, 5, 6]. In particular, it was envisioned that the strong absorption of photons in these particles promotes the generation of a non-equilibrium (also known as non-thermal, or "hot") carrier distribution such that electrons in the high-energy tail of this distribution can tunnel out of the metal into high-energy orbitals of the surrounding molecules, and then catalyse the chemical reaction.

This approach was predicted to surpass the efficiency of traditional catalysis approaches [7, 8] and to circumvent the well-known limitations associated with catalysis using high temperatures. This conclusion led to a rapid growth of interest in plasmon-assisted photocatalysis, mostly as a viable pathway towards cheap and efficient way to produce "green" fuels [9, 10, 11, 12, 13, 14, 15, 16, 17].

Potentially because of the complex multi-disciplinary nature of this problem, the exact manner in which "hot" electrons assist the reaction rate was not supported by a quantitative, first-principle type theory, but instead, has remained at the phenomenological level. Moreover, the build up of temperature that follows the decay (thermalization) of the "hot"

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electrons [18] was frequently ignored. In particular, while in some works the importance of thermal effects was acknowledged and harnessed for useful applications [2, 4, 19], many early (experimental as well as theoretical) studies overlooked thermal effects or concluded that they were small. In some cases, this may have originated from the conceptually difficult distinction between thermal and non-thermal effects, or from the common incorrect conception that at low illumination intensity, non-thermal effects dominate over thermal effects [20, 21]. Other studies estimated thermal effects crudely and/or employed too simplistic control experiments, most likely because of the limitations of existing reliable thermometry techniques, especially in the early stages of this line of research. The fact that in the current publication climate quantum mechanical effects on the nanoscale are more attractive than "macroscale" thermal effects may have also offered some incentive for the downplaying of thermal effects.

In a series of recent works, we have shown how to separate theoretically thermal and non-thermal effects using a simple addition to standard theoretical approaches [20, 21]. This approach showed that generically, the "hot" electron generation efficiency is extremely small ($10^{-10} - 10^{-6}$ under most experimental conditions)[1]. Most importantly, we have also shown that standard modelling based on the Arrhenius Law and careful temperature measurements can provide a purely thermal quantitative explanation to many (although not all) reports of faster chemical reactions in the presence of illuminated metal nanoparticles [23, 24, 25, 26, 27].

The core of our observation, as discussed in great detail in [24], is that in order to prove "hot" electron action, one needs surpass two challenges - first, the theoretical prediction of very low "hot" generation efficiency, and the need to *perfectly* reproduce the temperature profile exactly in order to quantify the non-thermal contribution correctly. Several simple experimental procedures that are useful towards those ends were described in [22]. Without solid evidence for "hot" electron action, one is forced to adopt the Ockham razor, namely, to favour the simplest possible explanation (i.e., thermal effect, using the 19th century Arrhenius Law) over the sophisticated (and speculative and non-quantitative) claim for non-thermal electron action.

In [1], the Halas team describes a new set of intriguing experiments where the main novelty is that reaction rate (as well as the quantum efficiency) exhibits an "S"-shape (or maybe more simply, a rather mild kink shape) for the H_2–D_2 exchange reaction photocatalyzed by Cu nanoparticles; after subtraction of (what the authors believe to be) the thermal contribution, this effect was attributed to "multiplication of hot carriers", i.e., an external quantum yield that exceeds 100%.

A similar "S"-shape was observed in [28, Fig. 1c], but did not receive particular attention; that work reported a quantum efficiency of a few 10s of percent, at most. In [29], an "S"-shape was observed as well, but was associated with a quantum efficiency smaller than 10^{-5}. Thus, one is forced to ask - could the unusually high efficiency reported in [1] be a result of insufficiently accurate thermal control experiments? the answer seems to be (as in previous studies of the Halas group) positive.

Below, we point to potential technical and conceptual problems in [1] (Section 2), and conclude that the claims in the paper do not convincingly support the interpretation by

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[1]The same conclusion was reached in [22].

the authors. In Section 3, we offer several more conventional interpretations of the measurements. The unavoidable conclusion is that claims for "hot" electron dominance and multiplication should be considered only once the far simpler thermal explanation is ruled out. The alternative of matching the reported results to a thermal model is left to the interested reader.

2   Technical and conceptual problems in [1]

Temperature calculations and measurements. Following the success of previous extensive thermal modelling in the identification of the reaction mechanism (see e.g., [30, 31, 23, 32, 24, 26, 33, 34, 27]), the Halas team performed a thermal simulation of the *whole* reactor for th efirst time, and used the accepted recipe [35] for the calculation of the effective thermal conductivity of the host, within an effective medium approach (the very model we used previously to re-interpret results of the Halas group [23, 24, 26, 33, 34, 27]). However, unfortunately, an improper boundary condition for the outer edges of the simulation domain was used – the temperature on these boundaries was fixed to room temperature, while that temperature is supposed to be reached only at an "infinite" distance from the sample. Since the temperature profile decays slowly in space (inversely with the distance [36]), this means that the temperature at the simulated domain boundary (which seems to have been chosen insufficiently far from the reactor) was likely set to a lower value compared with the actual temperature in the experiment at that location. As a result, this inaccurate boundary condition effectively cooled down the simulated domain; a proper quantification of the associated error cannot be estimated from the information provided in the manuscript. The correct way to simulate the temperature distribution in such systems is to use a *heat flux boundary condition*[2], such that the outward heat flux equals the total heat generation in the sample [2, 34]. An alternative modelling approach can involve shrinking the infinite simulation domain using transformation optics [37].

The (likely inaccurate) thermal simulations in [1] were claimed to match the thermal measurements. These were based on a thermal camera, as in previous studies of that team, but this time, these were not corroborated with a thermocouple measurement. The latter measurement is important, as it can also be used to go beyond the capabilities of the thermal camera and probe the temperature away from the illuminated surface (i.e., deep inside the sample), hence, it provides much more information than provided by the thermal camera. Further, unfortunately, there is no mention of the emissivity setting, so it is difficult to assess the quality of the reported temperature readings. All the these relevant details were provided in earlier papers of that group; these, in fact, allowed us [23, 25, 24, 27] (and others [38, 22]) to identify several technical errors in the temperature measurements in these papers. Since no indication of fixing of these problems is given in [1], it is likely that the previous problems persist in the current work; indeed, the problems identified in [27] persisted in [23]). To be more specific, since the emissivity settings were exaggerated in previous work of the Halas group [23, 24, 27, 25], the temperature is likely to have been underestimated, giving rise to the seeming agreement between the measurement and simulation reported in [1]. As in

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[2]i.e., a Neumann rather than Dirichlet boundary condition.

previous work of the same team, this might have occurred because mistakes in *both* the experiment and simulation were made (see discussion in [23, 24, 27, 25]).

From the above, the subtraction of the thermal contribution from the total rate and isolation of "hot" electron contribution does not seem quantitatively convincing. A complementary approach would be to fit the experimental results to a thermal model, and if successful, to see how different is the temperature resulting from the simulation, or whether a reasonable adaptation of the parameters can yield the fitted temperature [23, 24, 27]. Such an approach may explain (or even eliminate) the surprising observation of "saturation" of the non-thermal effect and the vanishing of the thermal effect presented in [1, Fig. 3b].

The electronic calculations. The authors clearly write that their analysis involves "thermalized" (hot) carriers - this clearly refers to electrons that obey Fermi-Dirac statistics (i.e., when the electron distribution can be characterized by a single parameter, the electron temperature T_e), rather than to non-thermal electrons, whose contribution was supposedly isolated in the first part of the work; thus, the relevance of this analysis remains unexplained. Furthermore, the electronic analysis relies on the theory of [39] which was originally introduced as a replacement to a thermal theory that according to the authors of [39] failed to explain the measurement. However, in [24] we showed that this "failure" occurred because the authors of [39] ignored accumulation of heat from the many particles in their system [40, 22, 24, 26]; as a result, they underestimated the temperature rise by a factor of about 1,000,000. In that regard, there is, to our knowledge, no evidence that the model of [39] explains any measured data.

The theory also seems to rely on an unphysical assumption, namely, that there is a temporal regime in which $e - e$ interactions caused a thermalization of the electron cloud, but $e - ph$ interactions did not yet occur. This is the underlying assumption of the so-called 2 temperature model [41], which is known to give no more than a rough approximation suitable for long pulses. This also implies that according to the authors of [1], some chemistry occurs on the short picosecond time scale of their pulse; evidence for this unlikely possibility is lacking.

Effect of fluid flow. Many previous studies employed fluid flow as means to remove the optically-generated heat. However, until recently, no attempts were made to determine the efficiency of this mechanism. First estimates made in [24] indicated that the the flow rates used in previous work can modify the overall light absorption-induced temperature rise by only a few percent. Further attempts to model the fluid mechanics more accurately [33] showed that the flow is effective only when rapid stirring is employed (e.g., as in [31]).

Despite these discouraging results, in the current work, fluid flow is still used as means for reducing the temperature, again, without providing any quantitative indication to the effectiveness of the flow. Furthermore, the flow rate is varied with the illumination intensity. This is conceptually problematic - changing two parameters at the same time prevents one from being able to identify which of the two is responsible for the observed change. Yet, because of the expected smallness of the effect, it is hard to say how important this conceptual problem is.

3   Ockham again...

In addition to all the above technical concerns, an obvious concern arises again - before considering a peculiar mechanism like "hot" electron multiplication, one should explore a simpler mechanism (assuming the observation of an "S"-shape persists even under a corrected thermal control experiment). For example, there could be a change of the reaction pathway above some threshold temperature that causes a modification of the activation energy. This is, indeed, a widely accepted phenomenon, studied even in undergraduate textbooks. Specifically, for example, this seems to have happened in [42, Fig. 2a]. Alternatively, a competing reaction could have become less probable above a threshold temperature (e.g., due to damage to reactants). Surely other simple explanations are possible.

Another popular explanation to "S"-shaped reaction rate curves is the so-called diffusion limit, whereby the reaction becomes so efficient so that the reactant flow cannot prevent their depletion in the proximity of the reaction sites. This is known to lead to a much slower increase rate in the reaction rate (see, e.g., [29, 43]). This possibility can be tested by varying the flow speed at a constant intensity; this seems to be a feasible control experiment, yet, one which may (also) lead to slowing down the reaction because of the somewhat lower temperature rise, see above).

The same effect is also caused by the photothermal nonlinear response [34], which becomes relevant for heating by more than a 100 K or so. This very effect was already shown to enable the re-interpretation of the data in [44] quite accurately. Since the temperature rise reported in [1] is about 200K, the photothermal nonlinear response may be playing a role in the current work as well, leading to a slow down of the temperature rise rate by a few 10's of percent; this effect has been ignored in the calculations of [1]. Notably, if the fluid flow is somehow efficient, then increasing it with intensity should have made this slow down more pronounced. The absence of this slow down in the temperature rise should have been given proper physical justification.

Before those mechanisms are ruled out convincingly, and the much higher claimed quantum efficiency validated, it is hard to accept the "hot electron multiplication" explanation. In addition, without reference to the abysmal hot carrier generation efficiency and the experimental demonstration of far smaller quantum efficiencies [42, 29], it is hard to find the interpretation of [1] convincing.

4   Summary and outlook

Even if after a revision of the analysis of the results of [1] the explanation of a "hot" electron multiplication persists, one may ask why is carrier multiplication surprising or particularly interesting? After all, the photons have $1 - 2eV$, and the activation energy is claimed to be $\sim 0.5eV$. Thus, it is not impossible that one photon induces more than one reaction...

Either way, the concerns raised above would hopefully prompt the authors of [1] to clarify the open issues, provide the missing information necessary to reproduce all their results and correct the errors in the analysis and conclusions.

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