



# Distinguishing thermal from non-thermal contributions to plasmonic hydrodefluorination

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ARISING FROM Hossein Robotjazi et al. *Nature Catalysis* <https://doi.org/10.1038/s41929-020-0466-5> (2020)

In a recent paper<sup>1</sup>, Robotjazi and colleagues demonstrate hydrodefluorination on Al nanocrystals decorated by Pd islands under illumination and under external heating. They conclude that photocatalysis accomplishes the desired transformation  $\text{CH}_3\text{F} + \text{D}_2 \rightarrow \text{CH}_3\text{D} + \text{DF}$  efficiently and selectively due to non-thermal (hot) electrons, as evidenced by an illumination-induced reduction of the activation energy.

Some of the problems identified in earlier work by the same group<sup>2,3</sup> have been addressed. In particular, unlike the procedure employed in previous work by this group<sup>4</sup>, the reaction data were not normalized to different effective volumes in the current work, but rather by the same total catalyst mass (see related discussion in refs. <sup>2,3,5</sup>). In that sense, the authors implicitly acknowledge the error we identified<sup>2,3,5</sup> in their previous work<sup>4</sup>. However, scrutiny of the data in ref. <sup>1</sup> raises doubts about both the methodology and the central conclusions.

We first show that the thermal control experiments in ref. <sup>1</sup> do not separate correctly thermal from non-thermal (hot-electron) contributions, and therefore some of the conclusions drawn from these experiments are questionable. We then show that an improved but still non-ideal thermal control implies that the activation energy of the reaction does not change and, finally, that an independent purely thermal calculation (based solely on the sample parameters provided in the original manuscript<sup>1</sup>) explains the measured data perfectly. For the sake of completeness, we also address technical problems in the calibration of the thermal camera, question the disqualification of some of the measured data and discuss concerning aspects of the rest of the main results, including the mass spectrometry approach used to investigate the selectivity of the reaction, and claims about the stoichiometry and reaction order. Accordingly, the burden of proof for involvement of hot electrons has not been met. Instead, it seems likely that the proposed approach suffers from all the known problems associated with mere thermocatalysis.

## Extraction of the hot-electron contribution

One of the central results of ref. <sup>1</sup> is shown in its Fig. 6a. It purportedly demonstrates that the activation energy decreases under illumination by plotting the hot carrier contribution to the rate versus the (intensity-dependent) surface temperature and performing Arrhenius fits.

To explain the possible flaws in Fig. 6a, we must first explain the procedure used to construct it, as described in the manuscript and in the response to the current Matters Arising. First, the reaction rate is measured in the dark ( $R_{\text{dark}}$ ). The sample was then illuminated and the reaction rate,  $R_{\text{illum}}$ , was measured as a function of  $T_{\text{S}}$ , the surface temperature measured under illumination.

However,  $R_{\text{illum}}$  is not what is plotted in Fig. 6a. Instead, to isolate the photocatalysis (that is, the hot-electron) contribution to the reaction rate under illumination, denoted by  $R_{\text{photo}}$ , the authors take the difference between the reaction rate under illumination and the reaction rate in the dark, that is,  $R_{\text{photo}}(T_{\text{S}}) = R_{\text{illum}}(T_{\text{S}}) - R_{\text{dark}}(T_{\text{dark}})$  (see ref. <sup>1</sup>, Supplementary Information, p. 30). The temperature  $T_{\text{dark}}$  is the temperature without illumination (the value is undisclosed in the manuscript) rather than the same temperature at which the illuminated experiments were conducted. Fitting  $R_{\text{photo}}$  to the Arrhenius equation gives  $E_{\text{a,photo}} = 0.59$  eV and 0.67 eV for continuous-wave (c.w.) and white-light illumination, respectively, both smaller than the activation energy in the dark,  $E_{\text{a,dark}} = 0.8$  eV. The authors conclude that the apparent reduction of activation energies is due to hot electrons. We note in passing that the extraction of exponents is based on a surprisingly limited number of data points and a narrow temperature range (Supplementary Note 1), such that the differences between activation energies lie within the margin of error. At this stage it is already evident that the thermal control experiment in ref. <sup>1</sup> is inadequate, because it does not account for the heating caused by the illumination. As a result, the activation energy extracted from  $R_{\text{photo}}$  is misleading, because it includes the thermal contribution to the reaction rates. In that regard, unlike what the authors of ref. <sup>1</sup> write, the practice of an Arrhenius fit that convolutes thermal and non-thermal contributions is in direct contradiction of earlier work by some of the authors of the current manuscript<sup>4,6,7</sup>, as well as their (and our) thermal calculations, and other recent work<sup>8–10</sup>.

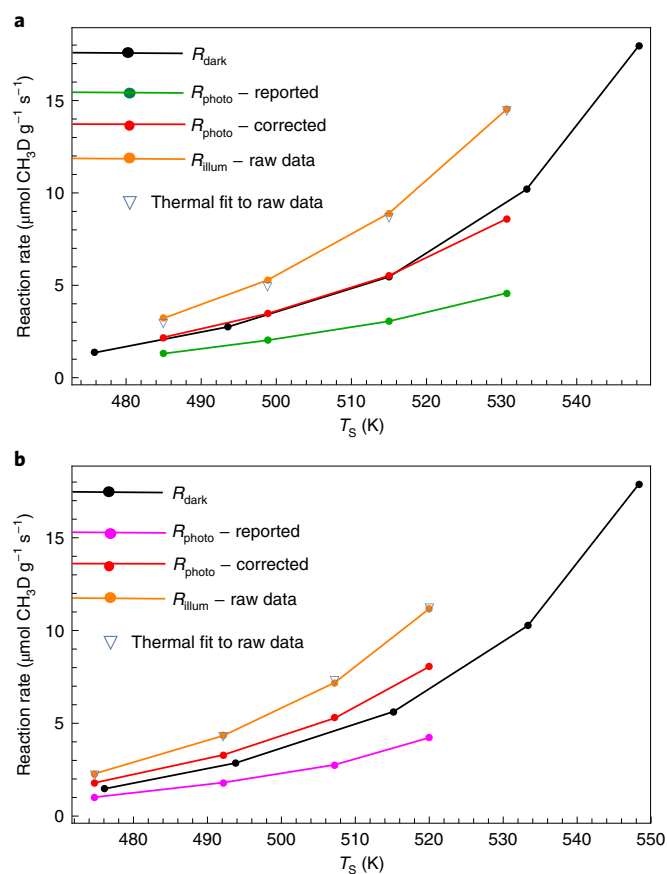
A more adequate thermal control experiment would be to measure the reaction rates while heating the sample to the same  $T_{\text{S}}$  and account for the thermal gradients. However, as we demonstrate in the following, this control experiment conclusively shows that there is no contribution of non-thermal electrons to the reaction.

To show this, we first obtain, using the data points of ref. <sup>1</sup> (black and green points), the total reaction rate under illumination,  $R_{\text{illum}}$  (orange points, Fig. 1). Next, to obtain the correct contribution from the photocatalysis ( $R_{\text{photo}}$ ; red points, Fig. 1), we subtract from  $R_{\text{illum}}$  not the reaction rate in the dark (as was done in ref. <sup>1</sup>), nor the thermal reaction rate assuming a uniform temperature  $T_{\text{S}}$  in the sample volume, but rather the thermal reaction rate due to a temperature distribution that has a surface temperature  $T_{\text{S}}$  identical to the one measured as well as the associated thermal gradients (calculated in Supplementary Note 2), namely

$$R_{\text{photo}} \approx R_{\text{illum}}(T_{\text{S}}) - \int R_{\text{dark}}(T(\mathbf{r}); T_{\text{S}}) d\mathbf{r}. \quad (1)$$

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**Fig. 1 | Reaction rates for c.w. and white-light illumination as a function of surface temperature.** **a, b**, Reaction rates for c.w. (**a**) and white-light illumination (**b**) as a function of the measured surface temperature,  $T_s$ . Black points: reaction rate in the dark,  $R_{\text{dark}}(T_s)$ , giving (from an Arrhenius fit) an activation energy of 0.8 eV. Green (**a**; c.w.) and magenta (**b**; white light) points: the contribution of ‘hot’ electrons to the reaction rate under illumination,  $R_{\text{photo}} = R_{\text{illum}}(T_s) - R_{\text{dark}}(T_s)$ , as evaluated in ref. <sup>1</sup>, disregarding the temperature difference between the bulk and surface reported by the authors themselves. Red points: corrected contribution of ‘hot’ electrons to the reaction rate under illumination (equation (1)), with a much smaller change in the activation energy. Orange points, total reaction rate (black + green/pink points; raw data); triangles, fit to raw data using a purely thermal model with a slightly shifted surface temperature. Perfect agreement is observed.

Here  $T(\mathbf{r}; T_s)$  is the calculated temperature throughout the sample (with the surface temperature identical to the one obtained under illumination), and  $R_{\text{dark}}(T) = R_0 \exp\left(-\frac{E_a}{k_B T(\mathbf{r})}\right)$  is the Arrhenius law, with  $E_a \approx 0.8$  eV extracted from the data in the dark (black points in Fig. 1).

The Arrhenius fit to equation (1) (red points, Fig. 1) gives  $E_{a,\text{photo}} \approx 0.7$  eV and 0.72 eV for c.w. and white-light illumination, respectively. Both changes are much smaller than the reported reduction; the obtained values are also well within the reported error bars, such that they cannot serve as conclusive evidence of any hot-electron-driven mechanism. Put simply, even if one assumes that there is hot-electron photocatalysis, its activation energy is roughly the same as the thermal one.

**A pure thermal analysis.** We have shown above that a re-examination of the control experiment and data analysis<sup>1</sup> brings into question the conclusion of the paper. Now, we continue and

show that a pure thermal analysis can explain the data perfectly. This requires pointing out yet another possible flaw in ref. <sup>1</sup>, namely, the setting of the sample emissivity. As in the authors’ prior work<sup>4</sup>, a surprisingly high value (0.95<sup>1</sup>; Supplementary Information, p. 28) was used, which we showed previously to be insufficiently accurate by the authors’ own calibration experiment<sup>3,5</sup> (in particular, a small difference in the reading of the thermal camera and a thermocouple causes high uncertainty in the reaction rate).

Moreover, not only is this value the default value of the camera, a calculation based on the composition of the sample in the current study (as done in refs. <sup>2,3</sup>) predicts an emissivity of  $\sim 0.17$ , significantly lower compared to the setting in the experiment. It is also worth mentioning that our previous work<sup>2,3</sup> showed conclusively that the infrared camera was not operated properly in previous work by this group (the camera–sample distance was unrealistically high and the image out of focus)<sup>4,8</sup>. Given that the authors do not provide any detail regarding the camera-to-sample distance, nor evidence for proper focusing, it is impossible to know if the camera was operated correctly in the current experiment. The nonlinear photothermal response<sup>11</sup> ensures that the overall temperature would not reach thousands of degrees even for the lower emissivity values.

Furthermore, a thermocouple embedded into the sample measured 10–20 °C higher in the dark and up to 200 °C lower under illumination compared to the thermal camera (Supplementary Figs. 13c and d, respectively; the former confirms the inaccuracy in the chosen emissivity). Remarkably, in ref. <sup>1</sup> (Supplementary Information, p. 27), the authors question the validity of the thermocouple reading, and disregard it. Their reasoning is that the disagreement between the thermocouple and camera readings results from the inability of the thermocouple to measure surface temperature ‘due to the limited light penetration into the catalyst bed and the heat localization on the surface of the irradiated catalyst’. Not only does the second part of this statement contradict an underlying assumption of the analysis (of a uniform sample temperature), but in fact the entire argument is physically inaccurate—the limited light penetration does not prevent heat diffusion to the lower parts of the sample (for example, ref. <sup>12</sup>). The argument also seems to be logically flawed—the disagreement in the two temperature readings indicates that either one (or both) of the measurements is flawed, or that both are correct, but measure somewhat different quantities.

It seems more than plausible that not only is the camera reading likely to be inaccurate, but also that the difference between the two temperature readings is to be expected. Indeed, there is no denying that vertical temperature gradients do exist in such heated or illuminated catalyst structures. Again, such gradients were measured by some of the authors of the current manuscript<sup>7</sup> and by others (for example, refs. <sup>10,13</sup>); they can also be extrapolated from the numerical simulations presented in Supplementary Fig. 14 of ref. <sup>1</sup> (performed over small voxels), and were described in detail in refs. <sup>5,12</sup> (also Supplementary Note 2).

Now, because the high emissivity setting may result in a temperature reading that is colder than the actual surface temperature, we now show that the data can be fully reproduced with only thermal reactions. To do so, we evaluate the reaction rate by again integrating the Arrhenius law over the entire sample, taking into account the calculated gradients  $T(\mathbf{r})$  (Supplementary Note 2) and this time assuming also that the real surface temperature is  $T_s$  plus some temperature shift  $\delta T$ , that is,  $\int d\mathbf{r} R_0 \exp\left(\frac{E_a}{k_B(T(\mathbf{r}; T_s) + \delta T)}\right)$ , with  $R_0$  and  $E_a$  taken from an Arrhenius fit to the reaction rate in the dark. We emphasize that the value for  $R_0$  is, in that sense, the same for all experimental data.

In particular, if the temperatures are shifted by  $\delta T = 27$  K (c.w.) and 36 K (white light), one obtains perfect predictions of the measured reaction rate without modifying the activation energy nor the prefactor (open triangles, Fig. 1). Such a shift is of the same order of

magnitude as the discrepancy between the thermocouple and camera readings reported by the authors themselves<sup>1</sup> (Supplementary Fig. 13c), and it is much smaller than the estimated error due to the emissivity and is comparable to the independent thermal calculations shown in Supplementary Note 2.

Thus, by Occam's razor, it seems far more likely that our simple yet remarkably quantitative thermal argument is the correct explanation for the faster chemistry reported compared with the speculative non-quantitative explanation provided in the original paper. Definitive proof of hot-electron-driven catalysis, particularly in light of the issues discussed above, will require approaches that can more precisely isolate thermal effects.

**Mass spectrometry, reaction order and stoichiometry.** Aside from the analysis of the purported photocatalysis contribution to the reaction rate, the authors reported other results that they claim support the involvement of hot electrons. We find these mass spectrometry observations and reaction order analyses unconvincing, especially as originally reported in ref. <sup>1</sup>. Our reservations are described in detail in Supplementary Notes 3 and 4. In brief, we believe that, here too, overly simplistic and optimistic assumptions were made in conflating experimental observations with scientific conclusions:  $m/z$  is not an unambiguous identifier, and neither is intensity at a given  $m/z$  necessarily a direct measure of concentration, especially when fragmentation and isotopologues must be considered. The carbon balance in the final products and reaction order in the reactants are inadequate to prove a mechanism, especially when the stoichiometry evidently evolves over the course of the reaction.

Finally, we would like to emphasize yet again that our purpose here is not to disprove contributions from photocatalytic mechanisms, but rather to argue that the experiments and analysis of Halas and colleagues, as originally published in ref. <sup>1</sup> do not meet the burden of proof.

### Data availability

All data are available from the authors upon reasonable request.

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### Competing interests

The authors declare no competing interests.

### Additional information

**Supplementary information** The online version contains supplementary material available at <https://doi.org/10.1038/s41929-022-00767-6>.

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