

Challenges in temperature measurements in gas-phase photothermal catalysis

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Conventional heterogeneous catalysis is the cornerstone of the modern chem-

ical industry producing a wide range of commodities, such as ammonia by the Haber-Bosch synthesis, propylene by the Ziegler-Natta polymerization, and hydrogen by steam reforming. Such processes typically require large reactors operating at high temperatures and pressures fed by non-renewable sources, which need to be replaced by alternative ones (such as solar energy) to meet the global challenges of decarbonization and climate change mitigation. At the laboratory scale, the field of photothermal catalysis has recently emerged.¹ The latter aims at driving industrially relevant chemical reactions through suitable photocatalysts that can efficiently convert photons both to charge carriers, as in photocatalysis, and to heat, as in thermochemistry. Notably, plasmonic materials have played a substantial role in this field because of the possibility of engineering their resonance wavelength by nanostructuring, thus increasing light absorption and generating high temperatures and excited carriers upon plasmon decay. Indeed, the sub-field of the so-called plasmonic (photo)catalysis has developed in the last 10 years,^{2,3} giving rise to exciting discoveries and vibrant debates to uncover the thermal or non-thermal (i.e., electronic or electromagnetic) effects in photocatalysis. More generally, these mechanistic aspects are critical for the development of the entire photothermal catalysis, including best practices in measuring precise reaction temperatures while employing conventional photocatalysts such as inorganic semiconductors, carbon nanohybrids, and catalytic metals supported on inert oxides.⁴⁻⁶

A reliable measurement of the sample temperature during photothermal catalysis experiments is of paramount importance in disentangling the thermal and non-thermal contributions to the overall process. Moreover, even small errors in the temperature value may lead to

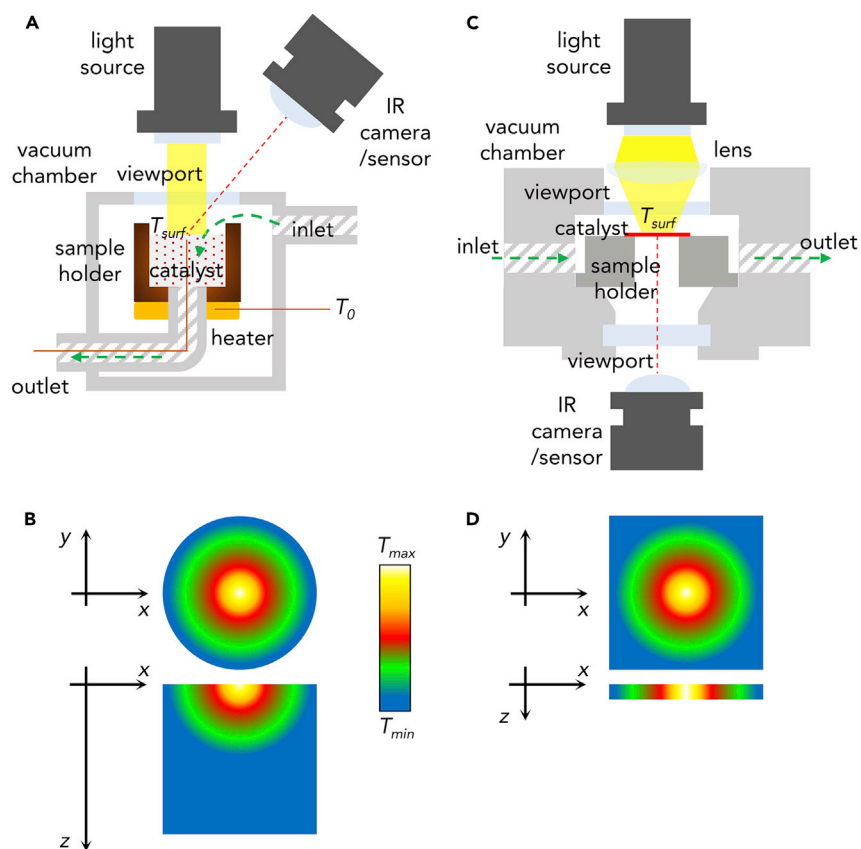


Figure 1. Examples of setups for photothermal catalysis experiments

(A and B) Typical setup (A) and thermal gradients (B) for photothermal catalysis experiments for catalysts in powdered form. The sample is compressed in a few-mm-thick pellet and placed inside a cup-shaped sample holder, both contained in a small vacuum chamber. Light irradiation from the light source travels through a front viewport to reach the sample surface. The reactive gas can travel through the catalyst thanks to its porosity, and the products are collected at the outlet by gas chromatography or mass spectrometry. The temperature at the catalyst surface can be monitored by a thermocouple just below the surface and/or by non-contact IR instrumentation viewing the surface from the front viewport. The thermal gradients schematically represented in (B) describe the situation under light irradiation without external heating, which can also be provided by a heater under the sample holder monitored by a thermocouple T_0 .

(C and D) Possible setup (C) and thermal gradients (D) for photothermal catalysis experiments for catalysts in thin-film form.

substantial mistakes in estimating the reaction rate due to the exponential dependence of the Arrhenius law. In this work, after general setup considerations, we discuss the challenges in reliably measuring the temperature of photocatalysts considering the case of thin-film titanium nitride (TiN), an emerging plasmonic metal, and of titanium dioxide (TiO₂), a benchmark semiconductor, under gas-phase conditions. By evaluating the effects of the gas flux, gas composition, and choice of instrumentation, we show how all these parameters can significantly

affect the values of the measured temperatures. This analysis highlights the critical points that researchers ought to consider when performing photothermal catalysis studies.

Setup considerations

Photothermal catalysis experiments are usually carried out in reactors derived from vacuum chambers. Typically, powdered catalysts consisting of a mixture of metallic nanoparticles (NPs, i.e., Pd, Pt, and Ru alone or combined with plasmonic metals such as Au, Ag,

and Cu) dispersed in an oxide matrix (i.e., an inert support, such as Al₂O₃, or an active one, such as TiO₂) are pressed in few-mm-thick pellets inside a cup-shaped holder, which is enclosed in a vacuum cell (Figure 1A). The latter is equipped with a front viewport that is transparent to the incoming irradiation (provided either by monochromatic or broadband light sources) and the outgoing radiation from the sample surface to be detected by an infrared (IR) thermal camera or sensor. The surface temperature is also monitored by a thermocouple inside the pellet just below the sample surface (T_{surf}). Another thermocouple controls a heater placed under the sample holder (T_0). The latter is employed to perform purely thermal experiments in the dark as a control. Additional thermocouples may be also placed along the sample thickness. The reactive gas mixture travels from the inlet through the porous catalyst pellet and is finally collected at the outlet. The products are thus analyzed by gas chromatography (GC) or mass spectrometry (MS). In this case, significant thermal gradients usually arise in the radial direction at the catalyst surface, depending on the light beam spot size (typically in the range of a few mm), and along the thickness, z (Figure 1B). Thermal gradients in the whole photocatalyst pellet should be accurately assessed, not only to reliably estimate the activation energy but also to identify unexpected effects.^{7,8} For example, ammonia synthesis by a Ru-Cs/MgO catalyst was enhanced under irradiation compared to the dark reaction due to the non-isothermal conditions of the catalyst along its thickness.⁸

Photothermal materials in thin-film form have been, by far, less investigated in this field. This is because powdered photocatalysts offer a high surface area favoring the contact with reactive gas molecules, while, in the case of thin films, only a fraction of the gas mixture is in contact with the catalyst and participates in the reaction. However, thin-film

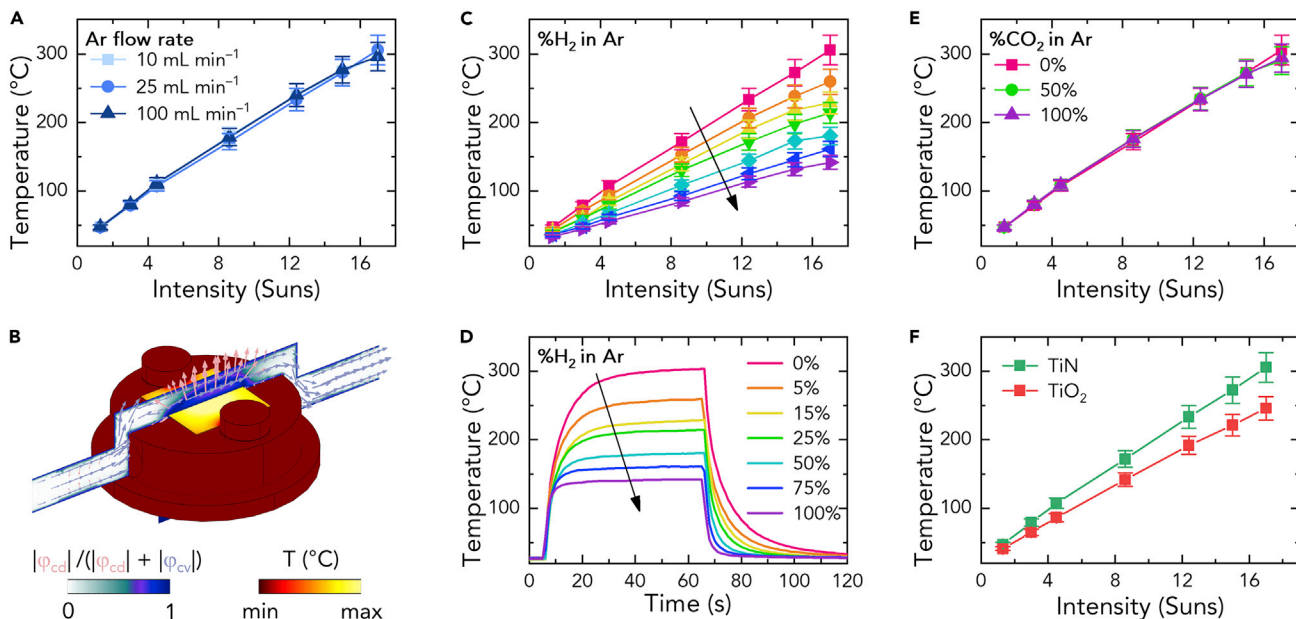


Figure 2. Effect of gas flux and gas composition

(A) Temperature of TiN nanotubes under 1.3–17 suns irradiation by increasing a pure Ar gas flow from 10 to 100 mL min⁻¹. In all graphs, each temperature value was assigned an error bar of $\pm 7\%$, as discussed in the main text and in [Note S1](#).

(B) Numerical simulations of the spatial temperature distribution and the conductive heat flux magnitude ($|\phi_{cd}|$) normalized to the total heat flux (conductive and convective, $|\phi_{cd}| + |\phi_{cv}|$) in the system for the highest gas flow and illumination conditions (100 mL min⁻¹, 17 suns). Conductive (ϕ_{cd}) and convective (ϕ_{cv}) heat fluxes are also shown within the input and output pipes and close to the sample. The latter was computed as the product $\rho u H$, with ρ the fluid density, u its velocity, and H its enthalpy.

(C and D) Temperature of TiN nanotubes in the presence of Ar/H₂ gas mixtures at the steady-state under 1.3–17 suns illumination (C) and time-dependent plots under 17 suns irradiation (D).

(E) Steady-state temperatures of TiN nanotubes under 1.3–17 suns irradiation in the presence of Ar/CO₂ gas mixtures.

(F) Steady-state temperatures of TiN and TiO₂ nanotubes under 1.3–17 suns irradiation in the presence of pure Ar gas.

photothermal materials based on ordered arrays of nanostructures can offer the possibility of engineering the optical properties to achieve broadband light absorption within a sub-mm thickness and substantial heating under light irradiation. For example, TiN nanocavities have been recently considered for photothermal catalysis upon decoration with Rh NPs.⁹ We introduce a modified setup for photothermal catalysis experiments featuring a sample holder with a through-hole to allow imaging the back-surface of the sample by IR temperature measurements through a back viewport ([Figure 1C](#)). By employing thin conductive Ti (~ 100 μm) substrates, thermal gradients persist along the radial coordinate ([Figure 1D](#)) but are negligible along the z-direction in the sample ([Figure S1](#)), validating the temperature measurement from the back surface.

Effects of gas flux and gas composition

The modified setup introduced above was employed to systematically measure the temperature of TiN and TiO₂ nanotubes grown on a Ti plate by varying the gas flux and the gas mixture composition under solar-simulated light, thus mimicking the realistic conditions for photothermal catalysis experiments (see [Figures S2](#) and [S3](#) for the morphological and optical characterization, respectively, and [Note S1](#) for the details on sample preparation). For each experiment, a commercial IR sensor measured the temperature from the sample back surface under 1.3–17 suns illumination (see [Note S1](#) for further details and [Figure S4](#)). First, the effect of the gas flow rate on the sample surface temperature (steady-state value under irradiation) was investigated in a typical experimental in-

terval, i.e., 10–100 mL min⁻¹, with pure Ar gas ([Figures 2A](#) and [S5](#)). In the case of pure H₂ atmosphere, lower temperatures were measured due to the larger thermal conductivity of H₂ compared to Ar, as explained below ([Figure S6](#)). In any case, the temperature linearly increased with the light intensity without a significant effect on the gas flow rate. Therefore, in typical laboratory reaction chambers, the flow rate can be freely chosen to find the optimal conditions for the experiment to maximize the conversion efficiency. Numerical simulations were performed to provide more insights on this effect ([Note S2](#)). A thermo-fluidic model of the whole experimental setup under stationary conditions revealed a negligible contribution of convective motion of the gas close to the sample surface, while the thermal transfer was essentially due to

conduction (Figure 2B). The impact of convective heat transfer would be relevant at gas flow rates much larger than those employed in typical experimental conditions. As a result, the simulated temperature versus light intensity successfully replicated the experimental results (Figure S7). For mixed gases, the total flux was set at 25 mL min^{-1} and the sample temperature in contact with several Ar/H₂ gas mixtures was measured under each light intensity, showing a monotonic decrease from the pure Ar case to the pure H₂ one (Figures 2C and S8). In particular, under 17 suns, i.e., the highest light intensity, the temperature measured on TiN nanotubes decreased from $\sim 305^\circ\text{C}$ in pure Ar to $\sim 140^\circ\text{C}$ in pure H₂; the steady-state value was also reached with faster dynamics (Figure 2D). This effect can be easily understood by realizing that the main thermal transfer mechanism is based on conduction and that the thermal conductivity of H₂ ($k \sim 187 \text{ mW m}^{-1} \text{ K}^{-1}$ at room temperature) is one order of magnitude higher than that of Ar ($k \sim 18 \text{ mW m}^{-1} \text{ K}^{-1}$ at room temperature). Indeed, by performing the same experiments in Ar/CO₂ mixtures, no significant changes in the steady-state temperature values were found (Figures 2E and S9), which is likely related to the similar thermal conductivity values between Ar and CO₂ ($k \sim 17 \text{ mW m}^{-1} \text{ K}^{-1}$ at room temperature). Therefore, the catalyst temperature should be monitored in real-time during the catalytic process, and it may vary for reaction mechanisms that either produce or consume a substantial amount of H₂ gas. A recent experimental demonstration of this effect was reported for the CO₂ methanation reaction driven by Ni₂V₂O₇ photocatalyst decorated with Ru NPs, which is an exothermic process that consumes H₂ and, therefore, can lead to an increase in the catalyst bed temperature, further favoring the reaction itself.¹⁰ Concerning semiconducting photocatalysts, TiO₂ is considered a benchmark material, so TiO₂ nanotubes were tested in pure Ar under irradiation (Figure 2F) and in Ar/H₂ mixtures (Fig-

ure S10). The same qualitative results were found as in the case of TiN nanotubes, despite achieving overall lower temperatures due to the lower optical absorption than TiN (Figure S3). Nevertheless, the generated temperatures could still reach significant values for photothermal catalysis (i.e., $\sim 250^\circ\text{C}$ under 17 suns).

Measurement instrumentation and potential sources of error

TiN nanotubes were further illuminated under Ar atmosphere and in air to allow a comparison of the measured temperature by non-contact techniques, i.e., the sensor and the thermal camera, and a conventional type K thermocouple. Thermal camera images provide time- and spatially resolved information on the sample temperature, as shown in the thermograms in Figures 3A and 3B, which allows visualizing and measuring thermal gradients in the radial direction from the sample center due to the light spot focusing with $r_{\text{light}} = 0.6 \text{ cm}$, as further shown in 2D thermal profiles (Figure 3C). Thus for each irradiation condition, we define T_{max} as the maximum steady-state temperature value in the thermogram and T_{avg} as the average steady-state temperature evaluated in the circle with radius $r_{\text{sensor}} = 0.25 \text{ cm}$, corresponding to the spot where the sensor collects the signal. The time-dependent temperature profiles acquired with the different instruments under 17 suns showed a discrepancy (Figure 3D). The same result was obtained under all irradiation conditions: the overall temperatures measured with the thermocouple were lower than those measured with the IR sensor and in turn lower than the T_{avg} values (Figures 3E and S11). In particular, the temperatures given by the thermocouple were also affected by the highest instrumental noise likely related to poor thermal contact between the thermocouple head and the sample back surface (Figure S12). Though a thinner thermocouple may give more reliable results in the case of powdered photocatalysts,⁸ the same strategy would not conclusively solve the

problem in this case due to the impossibility of physically inserting it into the thin film. The discrepancy between the temperatures measured by the sensor and T_{avg} may instead be due to technical limitations of the sensor, such as the impossibility of accounting for the window transmittance and a lower accuracy of light spot focusing. Therefore, the thermal camera likely provides more accurate results despite a higher cost. Furthermore, the data can be corrected without repeating the experiment by setting the emissivity value directly in the thermogram. For example, the TiN nanotubes considered in this study exhibited an ultra-broadband solar absorption; thus, the average emissivity evaluated for thermal camera experiments was $\epsilon = 0.98$ (Figure S3). By systematically decreasing ϵ by 5% intervals, it is possible to note an increase in the apparent measured temperature (Figure 3F). In particular, the steady-state values of T_{max} increased from $\sim 457^\circ\text{C}$ for $\epsilon = 0.98$ to $\sim 489^\circ\text{C}$ for $\epsilon = 0.80$, i.e., a $\sim 7\%$ temperature increase corresponding to a $\sim 20\%$ decrease in the emissivity value. Therefore, care should be taken in the emissivity measurement because it may lead to under- or over-estimation of the catalyst temperature. Temperature-dependent total normal emissivity should be, ideally, directly measured by radiometric measurements rather than by room-temperature reflectivity measurements.¹¹ However, such techniques are not easily available because they require a dedicated setup. Therefore, the measured temperature is inevitably affected by a systematic inaccuracy in the emissivity data retrieved by Fourier transform infrared spectroscopy at room temperature.

Based on the average values obtained by repeated experiments and errors associated with the emissivity estimation, we estimate at least a $\sim 7\%$ error in the measurement of the catalyst temperature (see also Note S3), which includes both the random and systematic components. The experimentally measured

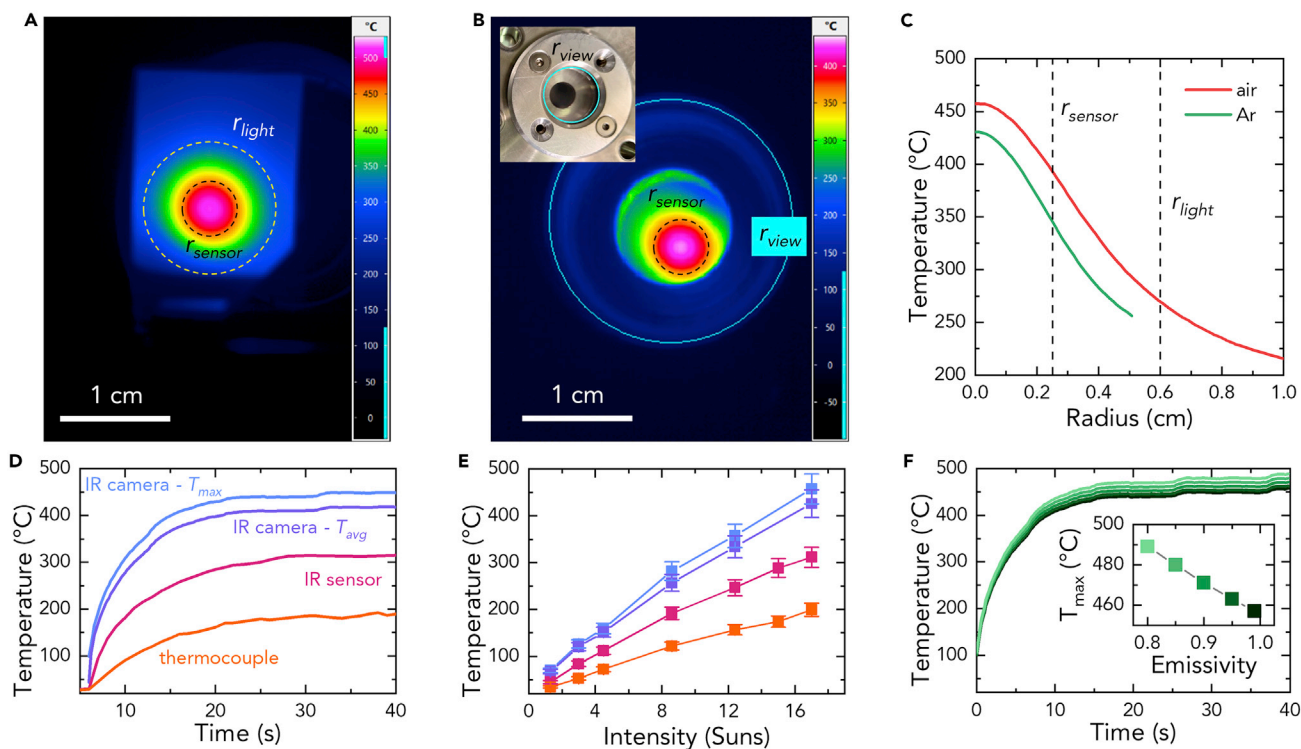


Figure 3. Temperature measurements on TiN nanotubes with different instrumentation

(A–C) Thermal camera images of TiN nanotubes under 17 suns irradiation in air (A) and inside the vacuum cell in Ar atmosphere (B) and corresponding radial temperature profiles (C). In (A–C), $r_{\text{sensor}} = 2.5$ mm is the radius of the target spot of the commercial IR sensor and $r_{\text{light}} = 6$ mm is the radius of the focused light spot. (B) and (C) show a limited portion of the sample back surface because of the sample holder morphology. The inset in (B) shows a digital picture of the vacuum chamber highlighting the back viewport with radius $r_{\text{view}} = 0.9$ cm.

(D and E) Time-dependent temperature of TiN nanotubes under 17 suns irradiation in air (D) and steady-state temperatures under 1–17 suns irradiation (E) measured by different instrumentation. T_{max} is the maximum temperature measured by the thermal camera, while T_{avg} is the average temperature measured by the same averaged in the area defined by r_{sensor} .

(F) Time-dependent temperature of TiN nanotubes under 17 suns irradiation in air measured by thermal camera by changing the emissivity value of 5% increments from the correct value (i.e., $\epsilon = 0.98$). The inset shows the steady-state temperatures for clarity.

temperature and reaction rate are typically used to estimate the activation rate for the reaction (E_{Δ}) by the Arrhenius equation. A reduction of E_{Δ} by plasmonic effects compared to a purely thermal mechanism has been claimed in several works, which has led to heated debates due to the uncertainties in the temperature values.^{7,12–14} The issue is even worsened by the presence of thermal gradients (Figure 3C), which arise in common experimental setups employing lenses to concentrate the solar radiation. In such cases, the reaction could proceed at a substantially slower rate in the “cold” regions of the sample for processes associated to a high activation energy (i.e., $E_{\text{A}} = 1.0$ eV, Figure S13A) or that already occur at moderate temperatures

(i.e., $T_{\text{max}} = 300^{\circ}\text{C}$, Figure S13B). This means that a control experiment in the dark should also be performed at T_{max} to prevent an underestimation of the reaction rate arising from solely thermal effects. As a consequence, despite the assistance provided by guidelines,¹⁵ the distinction between photothermal and electronic effects in photothermal catalysis by temperature measurements remains challenging.

Conclusions

Recent studies have fervently pursued a distinction between thermal and non-thermal effects in photothermal catalysis by controlling experiments in the dark by external heating or numerical simulations. Nevertheless, small errors in the

temperature estimation are hardly avoidable in experiments and may lead to significant deviations in the estimate of the activation energy by the exponential dependence of the Arrhenius law. Moreover, an exact replication of thermal gradients under irradiation by experiments in the dark is challenging. An alternative approach to isolate the purely thermal mechanism from the overall photothermal route may consist in modifying the photocatalyst with a catalytically inactive material. For example, a Ti_2O_3 photothermal layer was added on a Ru-Cs/MgO powdered photocatalyst to rule out non-thermal effects in photothermal NH_3 synthesis.⁸ In the case of thin-film photocatalysts, we suggest modifying this approach by including a thin

interlayer of wide-bandgap oxide, such as Al₂O₃ or MgO by atomic layer deposition, between the photothermal material and the supported catalytic NPs. This would be sufficient to block electronic transfer from the former to the latter without affecting the solar-to-heat generation of the overall photocatalyst. Further studies may also be conducted on the electric field effects produced by semiconductor metasurfaces, currently restricted to liquid-phase applications, which offer a highly tunable absorption spectrum.¹⁶ To conclude, we hope that our experimental findings and acknowledgment of the limitations in temperature measurements will inspire further work in photothermal catalysis. Additional knowledge on the synergy between thermal and non-thermal effects may be uncovered through material/reactor design strategies.

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AUTHOR CONTRIBUTIONS

Conceptualization, A.N. and P.F.; methodology, L.M., A.S., T.M., A.A., and A.N.; validation, L.M.; software, A.S. and A.A.; investigation, L.M. and A.S.; writing – original draft, L.M.; writing – review and editing, A.A., A.N., and P.F.; supervision, T.M., A.A., A.N., and P.F.; project administration, A.N. and P.F.; funding acquisition, A.N. and P.F.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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