Achieving Maximum Overall Light Enhancement in Plasmonic Catalysis by Combining Thermal and Nonthermal Effects

Zhiija Geng[1*], Yifan Yu[1*], Joey Offen[1], Jie Liu[1†]

[1] Department of Chemistry, Duke University, Durham, North Carolina, United States.

[†] Corresponding author, email: j.liu@duke.edu

[*] Both authors contributed equally to this work.

Abstract

Plasmonic photocatalysis presents a promising method for light-to-matter conversion. However, most current studies focused on understanding the relative importance of thermal and nonthermal effects while their synergistic effects remained less studied. Here, we propose an index, termed Overall Light Effectiveness (OLE), to capture the combined impact of these light effects on reactions. By systematically varying the thickness of catalyst layers, we isolated thermal and nonthermal contributions and optimized them to achieve maximum light enhancement. We demonstrate the approach using carbon dioxide hydrogenation reaction on titania-supported rhodium nanoparticles as a model reaction system. It shows a generalizable potential in designing catalyst systems with optimum combinations of heating and light illumination, especially with broadband light illumination such as sunlight, for achieving the most economical light-to-matter conversion in plasmonic catalysis.

Introduction

Photocatalysis has been an active research field since the discovery of photocatalytic water splitting in the 1970s.[1] However, certain fundamental limitations have prevented the wide applications of photocatalysis in industry.[2,3] One of such limitation is that standard photocatalysis relies on semiconductors such as TiO_2, and ZnO to absorb light and generate electron-hole pairs with high enough energy to drive half-reactions. Only photons with energy higher than the band gaps of these semiconductors can be absorbed. This will waste a significant amount of energy from sunlight and reduce the total efficiency of the process. Another limitation is that the reaction efficiency is negatively related to the intensity of light and temperature.[4] Electron-hole pairs tend to have a shorter lifetime at high temperatures and high-intensity light illumination, thus reducing the overall photo-efficiency. These two limitations, together with the shallow penetration depth of light,[5] created challenging problems for large-scale photocatalytic processes, since industry prefers to use small-size reactors and high temperatures to accelerate reaction kinetics while current photocatalysis needs to use large-scale 2D reactors at room temperature and under low light intensity.[6] Luckily, an emerging photocatalysis method has the potential to solve these problems: plasmonic catalysis, where plasmonic metal nanoparticles can absorb light and generate hot carriers to accelerate chemical reactions.[7,8] Compared to traditional photocatalysis that is based on semiconductors, plasmonic catalysis is more efficient at high temperatures and high light intensities. This type of catalyst, in principle, can overcome the limitations that are intrinsic in photocatalysis and enable the design and realization of high-intensity, broad-spectrum, high-temperature photocatalysis that will be more attractive to industry for large-scale production of solar fuels and other chemicals.[7,9-17]

However, the research field of plasmonic catalysis still has its own challenges and debates. One of the most active debates currently is on the relative importance of thermal and non-thermal effects.[5,18-23] Being able to separate the thermal and non-thermal effects in plasmonic catalysis is a major step in understanding the reaction mechanism. Previous research clearly showed that for some reactions, the photothermal effect can dominate[24] while in other reaction systems, the non-thermal effect is more important.[5,19,25] Nevertheless, a standard evaluation criterion of the overall light effectiveness that describes both thermal and nonthermal effects appropriately is lacking, leading to conclusions that cannot be compared between different reactions and reactor systems. Moreover, only a few studies have exploited the synergic relationship between thermal and nonthermal effects.[26-28]

In this work, an index, the overall light effectiveness (OLE), is proposed to evaluate the overall light effectiveness, including thermal and nonthermal effects. The underlying working principle is revealed with the assistance of a method that can extract nonthermal effect from the overall light effect. The work is demonstrated based on the CO_2 hydrogenation reaction with Rh/TiO_2 as the plasmonic photocatalyst. However, the general approach can be adapted to other reactions and reactor systems. The main conclusion is that in order to achieve the highest OLE, both contributions from thermal and non-thermal effects need to be optimized. These two effects respond to temperature and light intensity as well as the thickness of catalyst layers differently. The most effective use of energy from light will be achieved when both the thermal and non-thermal effects are optimized. Consequently, it is possible to design plasmonic catalysts that can utilize energy from the full spectrum of sunlight for efficient enhancement of important chemical reactions, overcoming the limitation of traditional photocatalysis.

Introduction of overall light effectiveness

In plasmonic photocatalysis, one of the primary objectives is to maximize the products output per unit light energy input, whether through thermal or nonthermal approaches. The current research has focused on untangling these two effects to gain a deeper understanding of the fundamental mechanisms involved.[5,21,25,29] By combining thermal and nonthermal effects in a synergistic manner, it may be possible to achieve a greater level of control over the catalytic process and to enhance the overall light effectiveness. Therefore, it is essential to investigate and understand the mechanisms underlying the individual thermal and nonthermal effects in plasmonic photocatalysis and to explore ways to combine them effectively.

However, catalytic reactions are intricate systems that are highly dependent on many factors, such as temperature, light wavelength, and intensity, which have been investigated a lot individually.[29,30] These parameters do not affect the reaction separately, and the light enhancement is the combined result of these factors. To determine the most economical approach for utilizing light irradiation, a standard measurement index is required to evaluate the overall light efficiency. In earlier publications, apparent quantum efficiency (AQE) was introduced to estimate light efficiency in plasmonic catalysis.[7,8] However, AQE itself is not sufficient to describe the overall enhancement from light in such a complicated process where both photothermal and nonthermal effects exist and it is difficult to show the photothermal effect using quantum efficiency. Herein, we propose an index to characterize the total effect of light in plasmonic catalysis: overall light effectiveness (OLE), defined as the amount of additional products produced under direct illumination compared to dark conditions, per second per unit power of light, regardless of catalyst mass (Eq. 1). Unlike previous approaches where the mass of the catalyst was taken as a factor, this metric considers the ratio between the product generated by light and the power input per unit area to accommodate the 2D nature of light illumination.

$$\text{Overall light effectiveness } (\mu\text{mol}\cdot\text{s}^{-1}/\text{W}\cdot\text{cm}^{-2}) = \frac{\text{Total production rate enhanced by light } (\mu\text{mol}\cdot\text{s}^{-1})}{\text{Light intensity } (\text{W}\cdot\text{cm}^{-2})} \quad (1)$$

Based on this definition, we performed a series of experiments by systematically varying the set temperature (T3) and light intensity using a Harrick reactor with several thermal couples (**Fig 1a)**. The TEM and SEM characterizations of the catalyst, Rh/TiO_2, showed Rh NPs having an average particle size of 5 ± 1 nm (**Supplementary Figure 1**). By adding the Rh NPs onto the supporting TiO_2, it shows an enhanced visible light absorption, while UV light absorption remains the same (**Supplementary Figure 2**). Similar to the previous studies, the reaction of CO_2 reduction using H_2 on Rh/TiO_2, with fully reduced Rh NP (**Supplementary Figure 3**), will only generate CH_4 under both dark and mild heating conditions. [5,19,30]

By measuring the distinct thermocatalytic and photocatalytic activities of Rh/TiO_2 under identical temperature conditions, the total production rate enhanced by light can be extracted. **Supplementary Figure 4** shows the total production rate of 20 mg Rh/TiO_2 under different conditions. The red line represents the pure thermocatalytic performance at 0 $W\cdot cm^{-2}$ light intensity. As the light intensity is increased from 0 to 1.41 $W\cdot cm^{-2}$, pure photocatalysis is observed when the set temperature is held at 25 °C, indicating no external heating input. Meanwhile, the photocatalytic effects can be observed at any given set temperature, and a reversal pattern is evident. Therefore, OLE under diverse light intensities and set temperatures can be calculated. Surprisingly, the measured OLE displays systematic nonlinearity and non-monotonicity depending on the light intensity, set temperature, and the thickness or the amount of catalyst. The optimum conditions varied by different amounts of catalyst. In our reaction system, 20 mg of catalyst is the amount needed for achieving the maximum OLE under low light intensity (**Fig. 1b**). Moreover, there is always an optimum light intensity for 20 mg catalyst to reach the maximum OLE, and the optimum light intensity for the highest OLE is a function of the set temperature (**Fig. 1c**). The lower the set temperature, the higher the light intensity needed to achieve the best OLE. Similarly, we could analyze the OLE as a function of set temperature (**Fig. 1d**). Under dark conditions, the OLE is always 0 since there is no light effect. However, under light irradiation, there exists an optimum set temperature to achieve the highest OLE under a given light intensity. The highest OLE is achieved when the set temperature is at 325 °C and under 0.67 $W\cdot cm^{-2}$ UV light irradiation. These conclusions are based on setting T3 as the reference temperature to minimize temperature fluctuation.

Since the surface temperature (T1) is the result of both external heating and light irradiation, the analysis based on surface temperature is more complex. We also studied the relationship between the catalytic performance and surface temperature. At a constant setting temperature, the total reaction rate increases with higher surface temperatures (**Supplementary Figure 5a**). However, when the surface temperature is higher than 450 °C, the total reaction rate begins to decrease. The total rate enhanced by light exhibits a clear trend, with 375 °C being the optimal surface temperature for achieving the highest light enhancement (**Supplementary Figure 5b**). Nevertheless, even though the total rate enhanced by light reaches its maximum when T3 is 250 °C and T1 is 375 °C, this reaction condition is not the most efficient one for light enhancement, as the corresponding light intensity is the highest. Therefore, we conclude the OLE for a more reliable evaluation than the total reaction rate. Overall, these trends align with the conclusions when setting T3 as the reference temperature. It is observed that the optimal surface temperature is 375 °C, and OLE reaches its maximum when T3 is between 325-350 °C, with the related light intensity around 0.67-0.76 $W \cdot cm^{-2}$, as shown in **Supplementary Figure 5c**. In short, these results showed that in order to achieve the best OLE, both temperature and light intensity should be optimized. The previously well-accepted and simpler concept of plasmonic catalysis, where the reaction rate increases super-linearly as a function of light intensity, needs to be modified to include a better understanding of both the thermal and nonthermal effects.[31-34]

Extraction of nonthermal effects

Although the optimum reaction conditions for achieving the highest OLE have been discovered, the underlying working principle responsible for the observed nonlinearity and non-monotonicity is of particular interest. To comprehend the synergistic interplay between thermal and nonthermal effects leading to this outcome, further investigation is required. In our experimental setup, only the surface layer of the catalyst within the penetration depth of light can undergo both nonthermal and thermal effects, while the remaining catalyst inside the reactor can only contribute to the overall reaction through photothermal and external heating effects (**Fig. 2a**). Therefore, we propose that the photothermal effects penetrate the catalyst bed in a systematic manner. Consequently, there should be a well-behaved dependence between the thickness of the catalyst inside the reactor and the thermal effects. According to this mass-dependent property of thermal effects, we designed an innovative method to extract the nonthermal rate from the total rate enhanced by light in addition to the two methods developed from previous works.[19,25] As shown in **Fig. 2b**, we added pure TiO_2 powder, which is the same material used as catalyst support, under the Rh/TiO_2 catalyst layer. The addition of TiO_2 ensured that the thickness of all powders in the reactor and the distance between the catalyst surface and the light sources remained constant, resulting in an approximately constant temperature profile within the reactor when the set temperature and light intensity were the same. The catalytic activity of TiO_2 study can be found in **Supplementary Figure 6.** Under 400 °C, TiO_2 at 25 mg was found to provide a production rate of 0.2 $\mu mol \cdot s^{-1}$. However, the introduction of light irradiation on TiO_2 surface showed minimal rate enhancement. When considering the overall light effect, the focus lies on the difference between light irradiation and dark conditions. Therefore, the thermocatalytic activity of TiO_2 can be ignored.

Since light only penetrates about 0.1 μm into the catalyst bed according to earlier experiments and literature, the nonthermal effect from light is only limited to the surface layer, while the thermal effect penetrates much deeper into the catalyst powder.[5,35-37] As the thickness of the catalyst layer increases when more catalyst is used, the thermal effect increases while the nonthermal effect remains the same. Experimentally, we found that the total rate enhanced by light has an exponential relationship with the catalyst thickness when the catalyst weight is lower than 10 mg and reaches a steady stage after 10 mg (**Fig. 2c**). By increasing the amount of catalyst inside the reactor, the contribution from photothermal effect to the total light-enhanced rate will continue increasing until it reaches a plateau, when the photothermal contribution maximized and would not increase further with the thickness of the catalyst bed. We then plotted the total light-enhanced reaction rate as a function of catalyst mass and extended it mathematically to zero mass. The intercept of the curve to the y-axis should be the estimated nonthermal contribution. Consequently, the photothermal contribution can be obtained by subtracting the nonthermal contribution from the overall production rate. As expected, the nonthermal contribution stays constant under the same reaction condition while the photothermal one is a function of the amount of catalyst. Compared to other experimental approaches developed by our group and others[25,29], this method is simpler and more straightforward with no need to modify the reactor design. More importantly, this method relies on the global reaction rate data instead of the local temperature values, while accurately measuring the local temperature of plasmonic nanoparticles is still a challenge, making the results measured by the mass-dependence test more reliable than other ones. [5,19,25]

By conducting the mass-dependence test under different light intensities, we could extract the nonthermal rate at different light intensities (**Fig. 2d**). The dots are experimental data, an the dash lines are exponential simulation curves. Then, the nonthermal rates as a function of light intensity can be obtained (**Fig. 2e**). From earlier studies in the field, the nonthermal rates are supposed to have a linear or superliner relationship with light intensity.[38,39] However, in our reaction system, the extracted nonthermal rates displayed a sublinear behavior at high light intensity. The main finding is that even though the nonthermal rates increased from nearly 0 to 0.6 $\mu mol \cdot s^{-1}$ when the light intensity changed from 0.11 $W \cdot cm^{-2}$ to 1.41 $W \cdot cm^{-2}$ at a set temperature of 325 °C, the nonthermal rate would reach to a plateau if the light intensities keep increasing. The extracted nonthermal rate at 250°C is provided in **Supplementary Figure 7.** Similar trends were also observed, although the plateau started at higher light intensity. Interestingly, we observed that the nonthermal contribution is a function of set temperature, despite being referred to as nonthermal, as we had discovered before.[25] We justify such temperature dependence as the following: the localized surface plasmon resonance is a fast quantum mechanical process with nearly no relationship with temperature.[16,40,41] However, the bond forming and breaking during the chemical reaction process are affected by temperature, making the nonthermal rate a function of temperature. The observed sublinear behavior of the nonthermal rate is a rare occurrence. This is likely attributed to the suppressed plasmonic effect at high temperatures.[42-44] Higher light intensities bring higher surface temperatures, which cause plasmons to decay faster due to an increased number of thermalized electrons, increasing the likelihood of hot electrons being scattered back to lower energy states. Therefore, the overall hot electron generation rate is controlled by two competing factors: higher photon flux increases the generation of hot electrons, while higher temperatures cause their decay.

Consequently, the nonthermal effect is suppressed under high light intensity due to an increase in the surface temperature.

Maximizing OLE by combining thermal and nonthermal effects

By effectively differentiating between the nonthermal and photothermal effects, we were able to evaluate their respective contributions to the OLE as a function of light intensity for a 20 mg catalyst at 325 °C (**Fig. 3a**). Our results reveal that the peak position of the OLE differs from that of either nonthermal or photothermal light effectiveness. This suggests that a singular focus on manipulating one effect is inadequate to attain the most efficient utilization of light. The contribution of the thermal effect is as crucial as that of the nonthermal effect. Based on the normalized contribution factors, it is evident that the photothermal effect dominates under low light intensities, while under higher light intensities, the nonthermal effect becomes dominant as more photons provide additional hot electrons to facilitate the reaction (**Fig. 3b**). However, a continuous increase in light intensity does not lead to stronger nonthermal contributions. Therefore, there exists an optimum experimental condition that yields the optimal combination of thermal and nonthermal effects to achieve the highest OLE.

Optimization of OLE in other catalytic systems

For our specific reactor and specific reaction system, after the systematic analysis of all the data above, we found that, under the light intensity of 0.67 $W\cdot cm^{-2}$ at the set temperature of 325 °C, we can achieve the highest OLE with 20 mg of catalysts in our reactor. These values are unique to our system, but the OLE and the observed trend should be generalizable to other reaction systems involving plasmonic catalysis. We have measured CO_2 reduction on Rh/TiO_2 under broadband white light in addition to UV light for comparison. The OLE calculation results display a similar trend to that observed under UV light; however, the OLE is lower at high light intensities (**Fig. 4**). This is due to the weaker plasmonic effect of Rh NP under white light, while the nonthermal effect is expected to dominate at high light intensities. This result pointed to a possibility that the OLE can also be applied to broadband plasmonic catalysts. We have recently demonstrated that by the addition of solar thermal absorber materials into a plasmonic catalyst, the overall light effectiveness can be improved over pure catalysts.[45]

Conclusions

Overall, this work proposes an important index, the overall light effectiveness (OLE), to evaluate the overall light effect in plasmonic photocatalysis. We demonstrate a facile and universal method to extract the nonthermal effect from the overall light effect and untangle the complex relationship between thermal and nonthermal effects. Our findings confirm that, in CO_2 hydrogenation on Rh/TiO_2, the nonthermal effect is a function of light intensity and temperature, while the thermal effect is more complicated as a function of light intensity, temperature, and catalyst thickness. Thus, there is always an optimum combination of heating and light illumination for achieving the highest overall light efficiency. Future research should take both thermal and nonthermal effects into careful consideration when designing the catalysts and the reactors to have the most economical path to use light to enhance chemical reactions, especially when broadband light sources such as sunlight are used.

Methods

Photocatalyst preparation

The catalyst synthesis process can be found in our previous publication.[25] In general, rhodium nanoparticles are synthesized by a modified polyol method. Polyvinylpyrrolidone (50 mg, PVP, Mw = 55,000, Aldrich) was dissolved in ethylene glycol (11.2 mL, EG, J. T. Baker) in a 50 mL round bottom flask, and stirred in an oil bath with constant heating at 160 °C for 30 min. Rhodium (III) chloride hydrate (25 mg, $RhCl_3 \cdot H_2O$, 40% Rh, Pressure Chemical) was first dissolved in 0.8 mL EG in a separate viral and quickly injected into the hot solution. The reaction mixture was kept stirring for another 30 min, and then cooled to room temperature. The brownish solution of Rh nanospheres was washed with 20 mL acetone three times to remove the spectator ions. The residue was mixed with 3 mL of deionized water and 30 mL ethanol under sonication till fully dissolved. The oxide support, titanium dioxide (~190 mg, TiO_2, Degussa, P25, specific surface area 35-65 $m^2 \cdot g^{-1}$), was activated in air at 500 °C for 5 h before impregnation. The pre-heated TiO_2 was added to the nanoparticle solution and stirred vigorously overnight. The mixture was then dried on the hotplate till all the solvent evaporated. The remaining solid was ground into a fine powder and calcined in air at 400 °C for 2h. The collected powder was stored in the oven at 70 °C for further measurement.

Catalysts characterization

Transmission electron microscopy (TEM) images were collected by an FEI Tecnai G2 Twin operating at 200 kV. The TEM samples were prepared by dispersing the Rh nanospheres and Rh photocatalysts in ethanol with sonication, then depositing on a copper grid coated with a carbon film (Ted Pella, 01813). Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) images were collected by a ThermoFisher Scientific Apreo 2 SEM. Diffuse reflectance UV–vis extinction spectra were obtained on an Agilent Cary 5000 equipped with an external diffuse reflectance accessory (DRA-2500). The composition of the photocatalysts was measured by a Kratos Analytical Axis Ultra X-ray photoelectron spectrometer (XPS).

Catalytic experiment

All data shown in this work is obtained using a system consisting of a gas delivery system, a fixed-bed reactor equipped with a quartz window, LED/laser light sources (Prizmatix, UHP-F, 365 nm), an online mass spectrometer, and a multi-thermocouple setup with a programmable temperature controller. The catalysts are placed inside the Harrick reactor, and thermocouples (TCs) are used for temperature measurements (Fig. 2a). There is a total of 3 TCs that have been placed inside the reactor, and any one of the TC can be selected to maintain the set temperature and monitored by a PID temperature controller kit (Harrick, ATK-024-3). The surface TC (TC1) is the one that being placed nearest to the top surface of the catalyst layer. The collected temperature is expected to be the real surface temperature. The bottom TC (TC2) measures the temperature at the lower part of the catalyst. The heater TC (TC3) is placed right above the heating cable and is supposed to record the temperature from the cable heater. TC3 is selected as the reference TC for controlling the PID output of the external heating, since it is buried deep inside the reactor and will endure the least amount of light influences. Therefore, the external heating is constant under the same set temperature. The other two TCs are connected with a handheld temperature data logger (Omega, RDXL6SD-USB) and used to record the real-time temperatures from two positions in the reaction chamber.

For each experiment, approximately 25 mg of the prepared Rh photocatalyst was loaded in the reactor to fill a 6-mm diameter, 3-mm height catalyst cup (stainless steel, 500 mesh, 0.0010”) to ensure the complete absorption of light for the catalytic measurement. The Rh/TiO_2 photocatalysts were first reduced under 60 standard cubic centimeters per minute (sccm) H_2 and 40 sccm Ar at 350 °C for 2 h to remove any Rh oxidation, and then the gas flow was switched to a mixture of CO_2, H_2, and Ar with the desired ratio and a total flow rate of 60 sccm. The gaseous product was monitored by an inline quadrupole mass spectrometer (Hiden, HPR-20) equipped with a Faraday cup and secondary electron multiplier (SEM) detector at $m/z = 2$ (H_2), 15 (CH_4), 18 (H_2O), 28 (CO), 40 (Ar) and 44 (CO_2) in real-time with filament settings of 70 V and 250 μA. The detection limit of the mass spectrometer was ~ 0.001% conversion of CO_2. For each temperature and light intensity condition, at least 30 min elapsed before ten sequential measurements were made to ascertain the steady-state concentration of each gas and the associated reaction rates and uncertainties. All reactions were operated under atmospheric pressure.

Mass spectrometer signals were calibrated using calibration gases (Gasco, Inc., 1 vol% CH_4/Ar) over a range of flow rates and with argon gas as an internal standard. For example, the CH_4 reaction rate was calculated according to **Eq. (2)**.

$$R_{CH_4}(\mu mol \cdot g^{-1} \cdot s^{-1}) = \frac{\left(flow\ \frac{CH_4}{Ar} ratio\right)(fAr, sccm)(10^6, \mu mol \cdot mol^{-1})}{(60, \mathrm{s} \cdot \mathrm{min}^{-1})(22{,}400, \mathrm{mL} \cdot \mathrm{mol}^{-1})\left(\mathrm{m_{catalyst}}, \mathrm{g}\right)} \quad (2)$$

Mass-dependence experiments

For the mass-dependence study, the experiments were carried out by changing the amounts of catalysts from 2.5 to 25 mg. To maintain the same thickness and the level of the catalyst surface, the corresponding amounts of TiO_2 were placed underneath to achieve a total of 25 mg of solid inside the catalyst holder. The same chemical treatment was performed on TiO_2 as Rh/TiO_2 to obtain the solid with a similar physical character.

Data Availability

All data supporting this work are available with source data.

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Author Contributions

J.L. conceived and supervised the research project. Z.G. and Y.Y. designed the experiments and carried out the photocatalytic tests. Y.Y. fabricated the photocatalysts and carried out the SEM and XPS characterization. Z.G. performed the TEM characterization. J.O. contributed to the conceptual discussion and performed some of the initial experiments. Z.G. and Y.Y. analyzed the results and wrote and revised the paper with input from the other authors.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary material is available in the online version of this article.

Figure Legends/ Captions:

Fig. 1 | The reactor setup and the calculated overall light effectiveness (OLE). a-d, (**a**) Schematic diagram of reactor setup, where thermocouples measure temperatures at different positions. (TC1: surface catalyst temperature, TC2: bottom catalyst temperature, TC3: heating temperature). The calculated OLE as a function of light intensity (b) with different amounts of catalyst; (c) at different set temperatures, and (d) as a function of set temperatures with 20mg catalyst under different light intensities of UV light. All OLE data is obtained by taking an average and standard deviation of 20 data points under the same conditions.

Fig. 2 | The separation of thermal or nonthermal contributions. a-e, (**a**) Schematic diagram of catalyst bed under direct light illumination, NP is nanoparticles. (**b**) Schematic illustration of mass-dependence test. **(c)** The calculated light-enhanced rate, the nonthermal rate and the calculated photothermal rates under 325 °C, 0.85, and **(d)** 0.11- 1.41 W·cm^{-2} UV light with different amounts of catalysts in the reactor. Each data point of the total rate enhanced by light is obtained by taking the average and standard deviation of multiple identical experiments. **(e)** The extracted nonthermal rate as a function of light intensity with 20 mg catalyst at 325 °C under UV light.

Fig. 3 | Contributions from nonthermal and photothermal effects to the total OLE. (a) The relationship between different light effectiveness, including overall, nonthermal and photothermal ones, and light intensity, and **(b)** the contributing factors from nonthermal and photothermal effects to the OLE with 20 mg catalyst at 325 °C under UV light.

Fig. 4 | The OLE under broadband white light illumination. The calculated overall light effectiveness as a function of light intensities at different set temperatures with 20mg catalysts under white light. All data is obtained by taking an average and standard deviation of 20 data points under the same conditions

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