

MAXIMIZING LIGHT UTILIZATION IN PHOTOTHERMOCATALYSIS VIA BALANCED THERMAL AND NON-THERMAL CONTRIBUTIONS

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Keywords: PHOTOTHERMOCATALYSIS, AMMONIA DECOMPOSITION, THERMAL CONTRIBUTION, NON-THERMAL CONTRIBUTION

Abstract

Solar-driven chemical reactions stand as a pivotal technological pathway for developing and utilizing renewable energy within the global energy transition. Among various strategies, solar photothermocatalysis stands out as a novel green technology. It combines the synergistic benefits of photocatalysis and thermocatalysis to efficiently drive reactions under relatively mild conditions, thus enabling comprehensive utilization of solar energy. However, light irradiance and temperature are critical factors influencing the performance of photothermocatalytic reactions, and their matching relationship directly governs the efficiency of photothermal synergy. Existing studies have yet to clearly identify the optimal regulation ranges for these two parameters. Therefore, the present work systematically elucidates the coupling mechanism between thermal and non-thermal contributions in photothermocatalysis, aiming to maximize light utilization efficiency. It reveals that an optimal matching window exists between light irradiance and temperature. By constructing a dimensionless analytical model to quantify their synergistic effects, the optimal conditions for achieving efficient photothermal synergy and catalytic performance are ultimately established. This study provides a new approach for the performance optimization of photothermocatalytic reactions.

1 Introduction

Against the global backdrop of addressing climate change and promoting energy transition, solar-driven chemical reactions are recognized as a key technology for utilizing renewable energy and advancing sustainable development. Solar photothermocatalysis is an emerging green technology that differs from traditional photocatalysis and thermocatalysis in that it harnesses both light and heat for reactions simultaneously^[1]. This photothermocatalytic approach has been widely validated in various chemical reactions^[2, 3], whose advantages lie in enabling highly efficient reactions by synergistically reducing the activation energy barrier and prolonging the lifetime of photogenerated charge carriers^[4, 5]. However, the lack of clear evaluation criteria has led to continued debate over the roles of thermal and non-thermal contributions in photothermocatalysis.

The mechanism by which hot carriers and thermal effects enhance plasmon-mediated reactions was reported by Yu et al.^[6]. Their results demonstrated that the hot carriers and thermal effects exhibit distinct dependencies on the excitation light irradiance. Additionally, the non-thermal energy transfer from hot carriers to intermediates adsorbed on active sites could induce electronic or vibrational excitation, thereby altering the reaction pathway^{[7][8]}. Recently, the non-thermal effect from the overall light response has successfully decoupled by Geng et al.^[9]. Systematic experiments further revealed that the non-thermal effect depends on light irradiance and temperature, whereas the thermal effect is governed collectively by light irradiance, temperature, and catalyst thickness.

After reviewing previous studies on non-thermal contribution, it is found that the indices proposed by numerous scholars are all quantities with units, which are not applicable to various reaction systems and conditions. Therefore, in this study, taking photothermocatalytic ammonia decomposition as an example, we define the non-thermal contribution and thermal contribution, aiming to propose a dimensionless quantity. This dimensionless quantity is independent of the mass of the catalyst involved in the reaction and the reaction system, thus possessing certain extensibility and universality.

2. Experimental

2.1 Preparation of catalysts

CeO₂ was synthesized via a hydrothermal method. Typically, 24 g of NaOH was dissolved in 90 mL of ultrapure water. Separately, 2.17 g of Ce(NO₃)₃·6H₂O was dissolved in 20 mL of ultrapure water, and this solution was slowly added to the NaOH solution under continuous stirring for 30 minutes. The resulting mixture was transferred to a 100 mL PTFE-lined stainless-steel autoclave and heated at 100 °C for 12 h. The product was collected by centrifugation, washed repeatedly with ultrapure water and anhydrous ethanol, and dried at 60 °C for 12 h. Finally, the obtained powder was calcined in air at 400 °C for 4 h with a heating rate of 5 °C/min.

Ru/CeO₂ was prepared by a photodeposition method. In a typical procedure, 0.2 g of the synthesized CeO₂ and a calculated amount of RuCl₃·3H₂O precursor were dispersed in 35 mL of ultrapure water. The suspension was then irradiated for 1 h using a 300 W Xe lamp (MC-PF300-UV). The

suspension was then filtered and dried in a drying oven for 12 hours. Finally, it was ground uniformly using a mortar and pestle.

2.2 Catalyst characterization

X-ray diffraction (XRD) analysis was performed using a Shimadzu X-ray diffractometer to conduct qualitative and quantitative analysis of the crystal structure, crystallographic plane characteristics, and lattice parameters of the catalytic materials. Transmission electron microscopy (TEM) was utilized with a Talos F200X instrument for in-depth examination of the microstructure of the catalysts, including their morphology and chemical composition. The chemical valence states and electronic structures of species were determined using X-ray photoelectron spectroscopy (XPS) from USA Thermo Fisher Scientific. Binding energy values were calibrated by referencing the C 1s peak at 284.8 eV. Data processing was performed with the Advantage software.

2.3 Catalysis experiment

Photothermocatalytic experiments were performed in an ambient-pressure reactor equipped with automatic temperature control. Product analysis was conducted using an online gas chromatograph (GC) fitted with a thermal conductivity detector (TCD). The reactor features dual temperature measurement points: a thermocouple inserted inside the quartz tube monitors the actual catalyst bed temperature, while an external sensor tracks the furnace temperature.

The detailed experimental procedure was as follows: 50 mg of the Ru/CeO₂ catalyst was physically mixed with 0.5 g of quartz sand and loaded into a quartz reactor tube. Prior to the reaction, the catalyst was activated at 550 °C under a 20% NH₃ atmosphere for 1 hour. Subsequently, the system was purged with high-purity argon for 1 hour to remove residual gases. Upon stabilization of the reactor at the target temperature, the reactant gas was introduced to initiate the reaction. Catalytic performance was then evaluated by systematically adjusting the light irradiance and reaction temperature.

2.4 Quantification of performance and contributions

The formula for the hydrogen production rate(*R*) from ammonia decomposition is as follows:

$$R = \frac{\frac{F_{\text{NH}_3, \text{in}}}{22.4} \times X_{\text{NH}_3} \times 1.5}{m_{\text{cat}}} \quad (1)$$

where $F_{\text{NH}_3, \text{in}}$ is the flow rate of inlet gas, ml/min, X_{NH_3} is ammonia conversion, and m_{cat} is the catalyst mass.

In this work, an analytical framework is established to deconvolute the photothermal performance. First, the overall ammonia decomposition performance under photothermal conditions is defined as the total performance index (*R*). The hydrogen production rate measured at the same temperature without light irradiation is subsequently designated as the thermal contribution (R_{TC}). Consequently, the performance

enhancement attributable solely to light introduction, excluding R_{TC} , is obtained and defined as the non-thermal contribution (R_{NTC}). The corresponding formula for R_{NTC} is thereby derived.

$$R_{\text{NTC}} = R - R_{\text{TC}} \quad (2)$$

With the decoupling of thermal contribution and non-thermal contribution, a new dimensionless quantity is proposed as an evaluation index for photo-thermal catalysis to better assess its performance.

$$\xi = (R_{\text{NTC}} - R_{\text{TC}}) / R \quad (3)$$

This indicator is improved based on previous research by eliminating the physical units of multivariate factors, allowing for a clearer assessment of whether nonthermal and thermal contributions are the main drivers of total performance. This strategy not only facilitates the optimization of photothermal catalysis but also aids in identifying the most efficient approaches for solar energy utilization.

3 Results

3.1 Structure of catalysts

The micro-morphology and structure of Ru/CeO₂ are characterized (Fig. 1). All samples exist in the form of nanorods. From Fig. 1(b), the lattice fringes of CeO₂ can be clearly observed, and defect structures are present. Furthermore, from Fig. 1(c) and Figs. 1(d-f), it can be seen that the Ru element cannot be detected throughout the nanorod. These results confirm that the Ru element is introduced into the catalyst in the form of single atoms or nanoclusters. The phase structure changes under different conditions are analyzed using XRD technology. Fig. 2 presents the XRD patterns of the activated Ru/CeO₂ samples and those obtained after the reaction. The XRD pattern of the sample subjected to high-temperature activation retains the characteristic peaks of CeO₂, while no characteristic peaks of Ru are observed. Furthermore, the XRD pattern of the catalyst remains stable following the photothermal reaction, with no significant changes detected, which suggests that the catalyst possesses good structural stability.

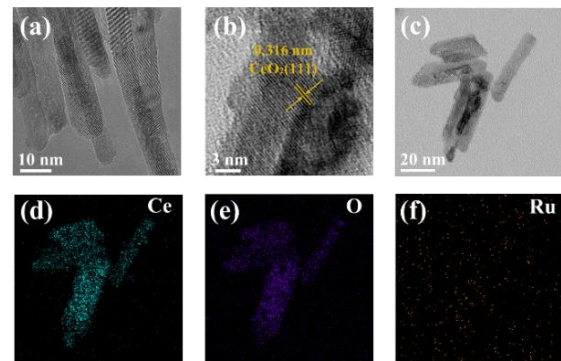


Fig. 1 TEM images of Ru/CeO₂ nanorods and the corresponding elemental distribution maps

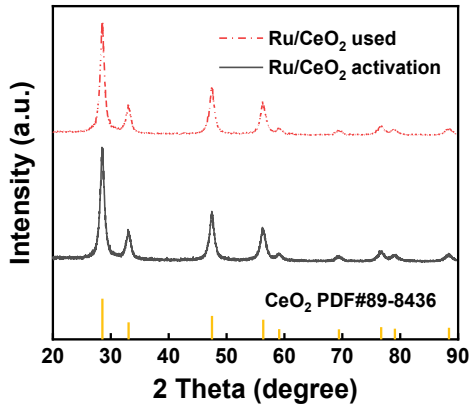


Fig. 2 XRD patterns of Ru/CeO₂

To elucidate the non-thermal contribution, the apparent activation energy (E_a) and the surface chemical state of Ru are investigated. As shown in Fig. 3, under light irradiation, the E_a decreased from 54.39 kJ/mol to 29.21 kJ/mol. This reduced energy barrier suggests that photogenerated carriers participate in the catalysis. The chemical origin of this lowered E_a was probed by XPS (Fig. 4). Compared to the sample under 0 kW/m², the Ru species under 35 kW/m² exhibited a shift toward lower binding energy. This indicates that photo-generated electrons are injected into the CeO₂ support, enriching the electron density of the Ru active sites. These electron-rich Ru sites facilitate the coupling and desorption of N, thereby promoting the ammonia decomposition process.

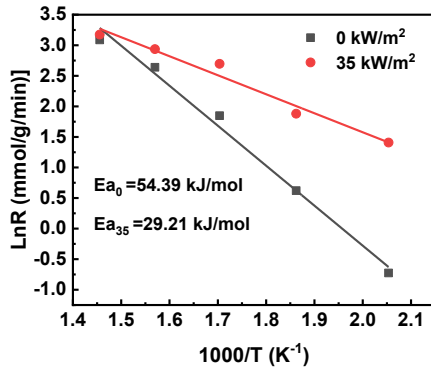


Fig. 3 Arrhenius plots for ammonia decomposition over the Ru/CeO₂ catalyst.

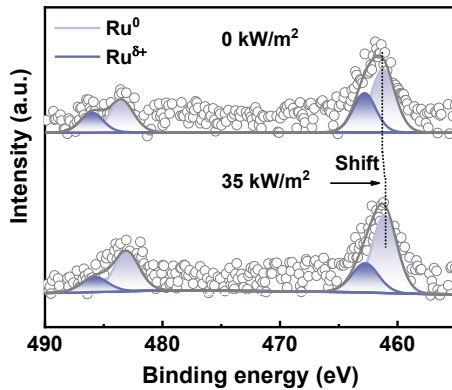


Fig. 4 XPS of Ru 3p for Ru/CeO₂

3.2 Thermal contribution and non-thermal contribution

The relationship between thermal and non-thermal contributions at different temperatures is clearly illustrated in Fig. 5, where the non-thermal contribution is observed to increase initially and then decrease with rising temperature. The proportional relationship between thermal and non-thermal contributions to photothermal performance at an irradiance of 35 kW m⁻² is clearly evaluated in Fig. 5. At this specific light irradiance, the thermal contribution is observed to increase continuously to a peak value as the temperature rises. In contrast, the non-thermal contribution does not remain constant, although the light irradiance is fixed, but instead exhibits a trend where it increases initially and then decreases. Furthermore, an opposite trend is presented by the proportions of thermal and non-thermal contributions, which indicates that the performance generated by the non-thermal contribution is dominant at low temperatures, whereas the thermal contribution dominates at high temperatures. This temperature-dependent behavior implies that an optimal temperature range may exist for photothermal catalysis.

The variation of the non-thermal contribution with light irradiance is further elucidated in Fig. 6; under the experimental conditions, a positive correlation is exhibited between the non-thermal contribution and light irradiance. The proportional relationship between thermal and non-thermal contributions to photothermal performance at a constant temperature of 350 °C is illustrated in Fig. 6. At this temperature, the value of the thermal contribution remains stable, while the non-thermal contribution increases continuously with the enhancement of light irradiance. As the light irradiance increases, the proportion of the thermal contribution decreases constantly until it eventually approaches a state where it maintains a ratio of approximately 0.5 relative to the non-thermal contribution. This evolution process demonstrates that, at a fixed temperature, the enhancement of light irradiance can effectively excite and strengthen the non-thermal contribution, which enables it to gradually become the dominant factor for the improvement of hydrogen production performance.

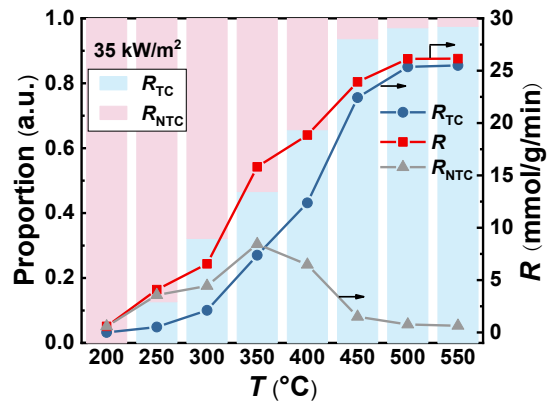


Fig. 5 Proportions and hydrogen production rates of thermal and non-thermal contributions at 35 kW m⁻²

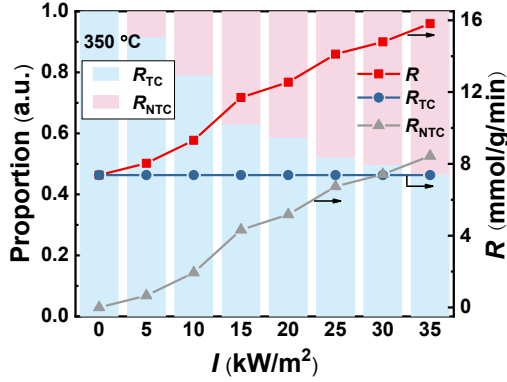


Fig. 6 Proportions and hydrogen production rates of thermal and non-thermal contributions at 350 °C

To validate the reliability of the quantified thermal and non-thermal contributions, a series of control experiments in which temperature and light irradiance are systematically modulated is conducted, as depicted in Figs. 7 and 8. The hydrogen production rate of photothermocatalytic ammonia decomposition increases rapidly with rising temperature and reaches a maximum value at 500 °C (Fig. 7). At the same temperature, the photothermocatalytic performance is observed to exhibit an upward trend as light irradiance increases, where the increase is particularly significant at 350 °C and 400 °C (Fig. 8). However, when the temperature is elevated to 450 °C, the photothermal hydrogen production performance becomes largely insensitive to variations in light irradiance, implying that thermal contribution becomes the dominant factor at sufficiently high temperatures.

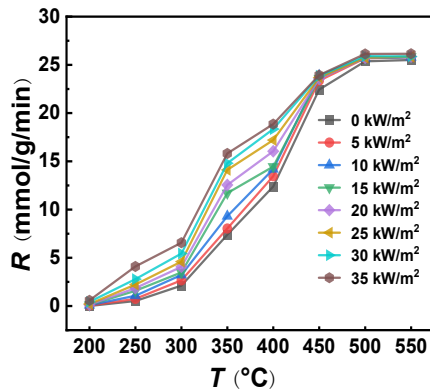


Fig. 7 Hydrogen production rates of photothermocatalytic ammonia decomposition under different light intensities

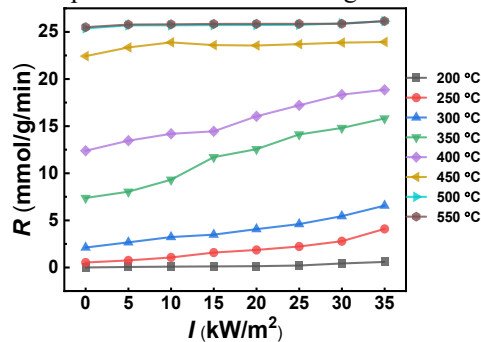


Fig. 8 Hydrogen production rates of photothermocatalytic ammonia decomposition under different temperatures

3.3 Maximizing light utilization

To investigate the thermal and non-thermal contributions, a 3D surface plot of the non-thermal contribution is constructed to systematically observe the influence of temperature and light irradiance, as illustrated in Fig. 9. From this figure, the conditions under which the optimal non-thermal contribution is achieved are identified as 35 kW/m², within a temperature range of 350–400 °C. Strikingly, the hydrogen production rates and non-thermal contributions at different light intensities and temperatures exhibit a high degree of consistency with the trends observed in Figs. 5 and 6, displaying a strong regularity. At various light intensities, the non-thermal contribution increases rapidly and then decreases, where the temperature range of 350–400 °C consistently emerges as the optimal regime for light utilization in photothermocatalytic ammonia decomposition. Interestingly, when the reaction temperature is below 400 °C, both the hydrogen production rate and the non-thermal contribution are in an upward trend. In the data obtained at 450 °C, the hydrogen production rate remains stable as light irradiance increases; this stability occurs because the high temperature is sufficient to drive the reaction across the energy barrier of the rate-determining step, rendering the reaction performance independent of further increases in light irradiance. This result not only confirms the synergistic effect of light and heat in the photothermocatalytic process but also indicates that the contribution distribution can be regulated from heat-dominant to photothermal-balanced at the same temperature by adjusting the light irradiance.

The distributions of the dimensionless quantity ξ as a function of temperature and light irradiance are presented in Figs. 10 and 11, respectively. Photothermocatalysis is dominated by non-thermal contributions when $\xi > 0$, whereas it is dominated by thermal contributions when $\xi < 0$. As observed in Fig. 10, the non-thermal contribution is dominant in the high-light-irradiance region at low temperatures (200–350 °C), whereas the thermal contribution is dominant in other regions (the low-light-irradiance region at low temperatures and the high-temperature region). This confirms that the introduction of light does not necessarily promote thermal catalysis at arbitrary temperatures. In Fig. 11, photothermocatalysis is dominated by non-thermal contributions at temperatures of 200 °C and 250 °C, whereas thermal contributions dominate when the temperature exceeds 400 °C. When $\xi = 0$, the light-energy input is made such that the nonthermal and purely thermal contributions are brought into balance. When deviation occurs from that point, the chemical-energy output per unit light energy is reduced. One is when an excess nonthermal contribution causes light-energy saturation and waste. The other is when a dominant thermal contribution causes light energy to be ineffectively converted into nonthermal chemical energy. When the thermal and nonthermal contributions are held in balance, the most efficient synergy between photogenerated carriers and thermally excited processes is achieved. Therefore, from the perspective of efficient light utilization, $\xi = 0$ is identified as corresponding to optimal light-utilization efficiency.

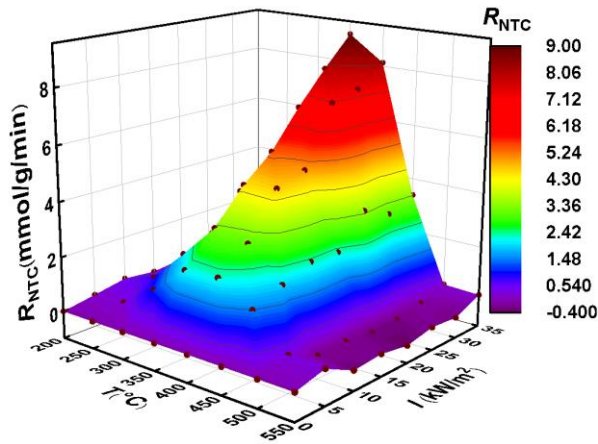


Fig. 9 3D plot of non-thermal contributions in photothermal catalysis under different light intensities and temperatures

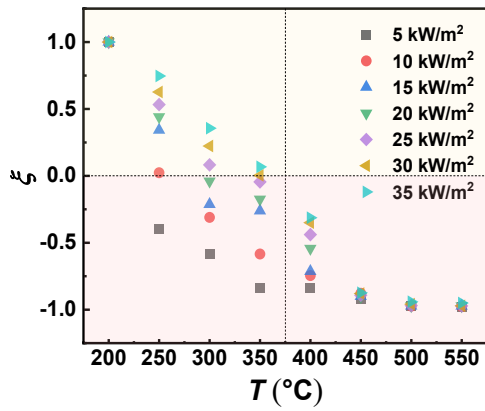


Fig. 10 Dimensionless quantity ξ under different light intensities

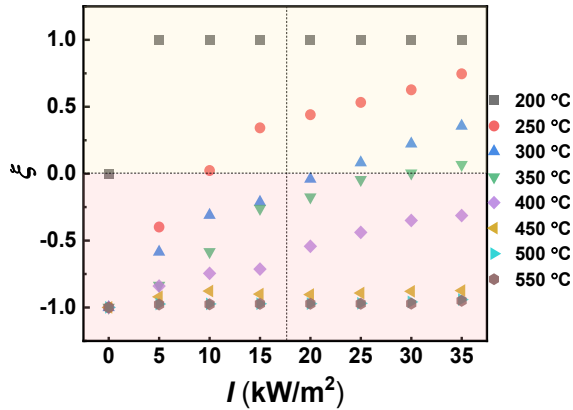


Fig. 11 Dimensionless quantity ξ under different light temperatures

To verify the applicability of ξ , different systems are selected for analysis^[10-12](Fig. 12). It is found in the literature that when $\xi > 0$ the photothermal catalytic behavior is dominated by the nonthermal contribution, whereas when $\xi < 0$ it is dominated by the thermal contribution, which is consistent with the previous analysis. Because ξ possesses normalized and bounded properties, it is suitable for comparisons across different experimental conditions and different catalytic systems.

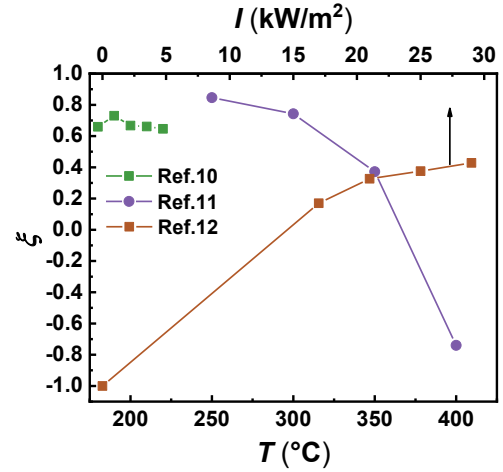


Fig. 12 ξ of different systems

4 Conclusion

In this study, an important dimensionless photothermocatalytic performance index ξ is proposed to evaluate the overall effect of photothermocatalytic reaction systems. A facile and universal method is demonstrated, which enables the extraction of non-thermal contribution from the overall photothermal performance and clarifies the complex relationship between thermal and non-thermal contributions. The research findings confirm that, in the ammonia decomposition reaction for hydrogen production over Ru/CeO₂, the non-thermal contribution exhibits a strong correlation with light irradiance and temperature. Therefore, for photothermocatalytic reactions, there always exist optimal experimental conditions where an optimal combination of thermal and non-thermal contributions can be achieved to maximize light utilization efficiency. In future photothermocatalysis research, thermal and non-thermal contributions should be carefully considered, and the structure-activity relationship describing the evolution of thermal and non-thermal contributions should be established through catalyst optimization and in-situ characterization techniques.

5 Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (52176202).

6 References

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