

Revolutionizing photothermal CO₂ hydrogenation with ceria-based catalysts

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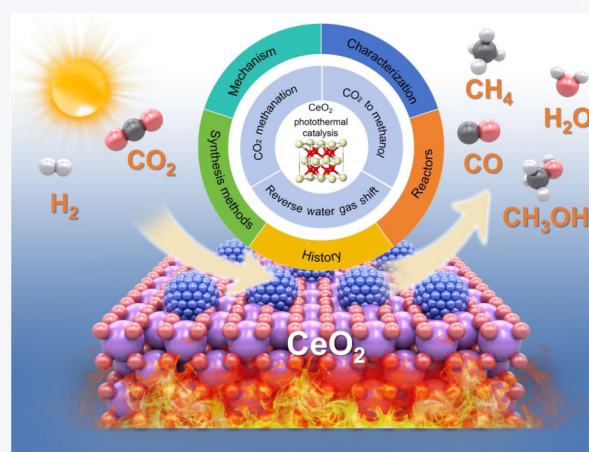
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ABSTRACT: In the context of achieving carbon neutrality, CO₂ catalytic conversion technologies are effective in reducing atmospheric CO₂ concentrations while simultaneously producing renewable products. This approach is seen as a viable method for constructing a new carbon cycle, thereby effectively addressing the issue of global warming. Photothermal CO₂ conversion has recently emerged as a promising research focus due to its high energy utilization efficiency, superior CO₂ conversion, excellent product selectivity, mild operating conditions, low energy consumption and minimal operating costs. Cerium oxide (CeO₂) has been widely used in photothermal catalysis due to its unique chemical properties, particularly when used as a support material with supported metals, creating distinctive interfacial sites for catalytic reactions. As an emerging star support in photothermal CO₂ conversion, its contributions are equally significant and should not be overlooked. However, to our knowledge, there has been no comprehensive review of CeO₂ applications in catalytic hydrogenation of CO₂. In this paper, we summarize and discuss CeO₂-based materials for photothermal CO₂ conversion to value-added products. This research particularly focuses on the synthesis methods of CeO₂-supported catalysts, the history of CeO₂ in photothermal catalysis, types of photothermal catalytic reactors, unique characterization methods for the photothermal catalysts and the photothermal CO₂ hydrogenation reactions by CeO₂-based catalysts. Perspectives related to further challenges and future directions for photothermal CO₂ hydrogenation are also provided.

KEYWORDS: CO₂ neutrality, hydrogenation, photothermal catalysis, ceria, C1 chemistry



1 Introduction

The greenhouse effect and consequent global environmental challenges stem from the rising atmospheric carbon dioxide (CO₂) emissions resulting from fossil fuel combustion [1–8]. The as-emitted CO₂ contributes to global warming, climate anomalies, ocean storms and desertification. Therefore, addressing CO₂

emissions and their rational utilization have become central to solving environmental issues [9]. The Emissions Gap Report 2023: Broken Record—Temperatures (*T*) hit new highs, yet world fails to cut emissions (again) indicates that current climate pledges put the earth on a trajectory to warm by 2.5–2.9 °C this century, far exceeding the goals set in the Paris Agreement [10]. To limit global warming to below 1.5 °C by 2030, greenhouse gas emissions must decrease by 42%. In light of global warming, numerous countries have collaboratively set carbon neutrality objectives. Carbon capture, utilization and storage (CCUS) is an innovative technology with the potential to combat the challenge significantly [11–16]. CO₂ can be captured from emission sources, such as power plants and industries, as well as from the atmosphere and utilized as a feedstock for chemical synthesis or permanent storage by injecting

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it into deep subsurface formations [17–19]. The most crucial step in CCUS is the transformation of CO_2 into renewable energy, also recognized as an effective approach to attain carbon neutrality amid the era of global carbon neutrality [20–22]. However, CO_2 represents the most oxidized form of carbon, characterized by high thermodynamic stability and kinetic inertness [23–25]. Consequently, chemical conversion of CO_2 necessitates highly reactive substrates with abundant energy, or the formation of highly stable products, often requiring more challenging reaction conditions. Therefore, conventional thermal catalytic reaction for CO_2 reduction usually operates under harsh conditions, such as high temperature and pressure [26]. Thermal catalysis involves the acceleration of chemical reactions by using a catalyst and applying heat. The catalyst provides an alternative reaction pathway with a lower activation energy, making the reaction proceed faster [27]. In the context of a low-carbon energy economy, renewable energy-driven CO_2 conversion methods, such as electrochemical and photochemical conversion, have rapidly attracted much attentions [28–32]. In photocatalysis, when the catalyst absorbs photons, electrons are excited from the valence band (VB) to the conduction band (CB), creating photogenerated electrons in the CB and leaving holes in the VB. These charge carriers drive the photocatalytic reaction. The positions of the VB and CB are critical in determining the redox potential of the photogenerated electrons and holes. A more negative CB position enhances the reducing power of the electrons, while a more positive VB position increases the oxidizing power of the holes. For CO_2 hydrogenation, the CB must be

sufficiently negative to reduce CO_2 (e.g., to CO or CH_4). The energy band positions of some catalysts are shown in Fig. 1.

However, limitations related to mass transfer, catalyst degradation, adsorption of impurities and other factors have hindered the industrial application of electrochemical and photochemical CO_2 conversion [37, 38]. Although CO_2 transformation by thermal catalysis requires relatively harsh conditions, it still holds more promise than electrochemical and photochemical conversion [39, 40]. Consequently, electrothermal catalysis, photothermal catalysis and plasma-thermal catalysis have rapidly emerged in recent years [41–46]. These externally driven thermal catalysis processes can overcome the stringent conditions of traditional thermal catalysis. These driven thermal catalysis processes offer a smaller device size, facilitate easier and faster temperature management and significantly enhance CO_2 conversion efficiency, potentially surpassing the equilibrium conversion rates of traditional thermal catalysis [47–49]. Photothermal catalysis is the catalysis with the participation of both thermal and photo energies [50], heat addresses the bottleneck issues of low catalytic efficiency and limited energy-mass transfer in photocatalysis, providing the required energy to overcome the activation energy barrier. This synergy breaks through kinetic limitations, significantly enhancing catalytic activity [51, 52]. Therefore, the photothermal catalytic CO_2 reduction holds a promising research potential and application value [53–55].

Cerium dioxide (CeO_2) is widely used in heterogeneous catalysis, especially in automobile exhaust purification and catalytic CO_2 reduction, due to its excellent redox performance and oxygen

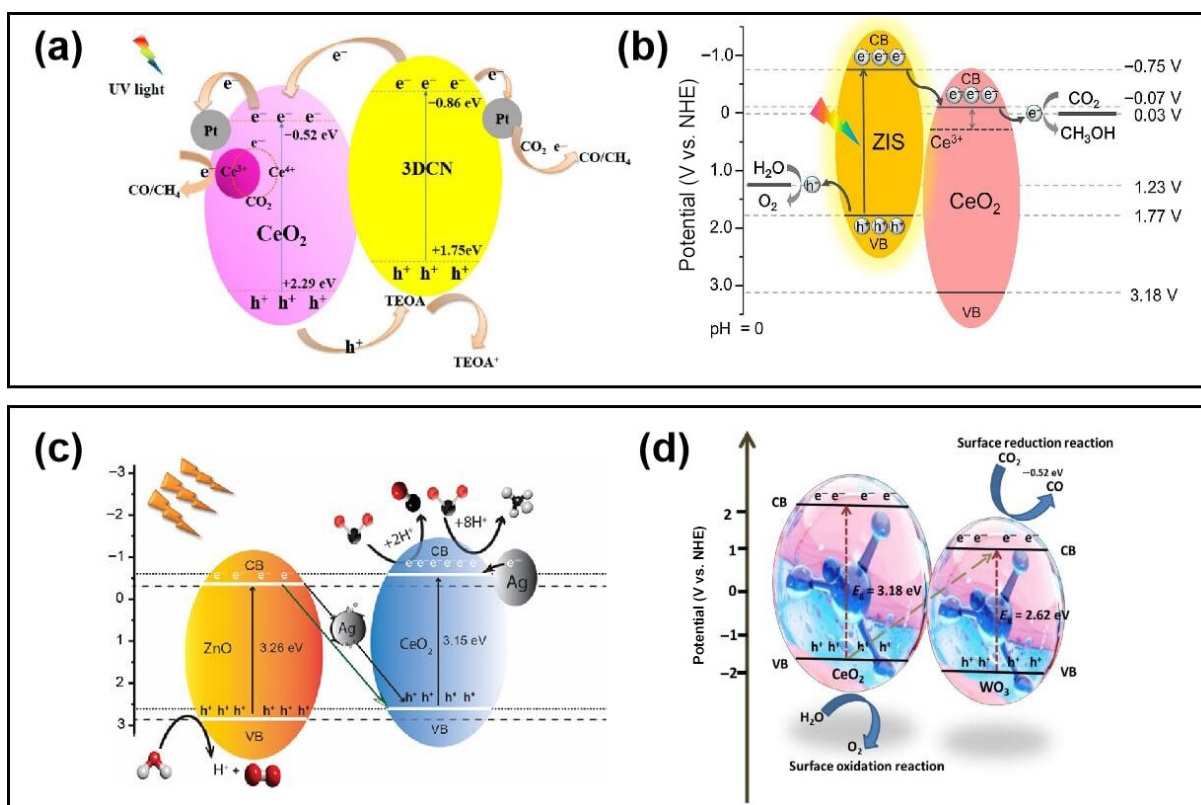


Figure 1 (a) Schematic illustration of $\text{Pt}@45\text{CeO}_2/\text{three-dimensional porous g-C}_3\text{N}_4$ (3DCN) for CO_2 photoconversion under UV-light irradiation. Reproduced with permission from Ref. [33], © Elsevier B.V. 2020. (b) Scheme illustrating the photocatalytic CO_2 reduction mechanism over the $\text{CeO}_2/\text{ZnIn}_2\text{S}_4$ composite. Reproduced with permission from Ref. [34], © Elsevier B.V. 2018. (c) Photocatalytic schematic mechanism of Z-scheme 3AgCZ and the probable charge separation. Reproduced with permission from Ref. [35], © American Chemical Society 2021. (d) Schematic representation of reaction mechanism for Z-scheme heterojunction. Reproduced with permission from Ref. [36], © Elsevier B.V. 2023.

storage capacity [56–67]. Additionally, its ultraviolet (UV) absorption ability, high refractive index and other optical properties have garnered significant attention for applications in photothermal CO_2 conversion [68–70].

Ce^{4+} within CeO_2 can readily convert into stable Ce^{3+} and undergo reversible switching in the oxidation-reduction cycle. The resulting Ce^{3+} species can directly activate CO_2 , extract oxygen from it and generate CO or carbon-containing intermediates. Additionally, when supporting metals, cerium oxide facilitates the

generation of highly dispersed metal particles, increasing the interfaces between metals and cerium oxide, enhance CO_2 hydrogenation catalytic activities.

Over the past decade, there has been a burgeoning interest in photothermal catalysis [23, 29, 53, 71–75]. The field of “photothermal catalysis” has seen over 1000 publications from 2008 to 2023, reflecting a steady increase in interest over the years (Fig. 2(a)). Since 2015, the application of CeO_2 -based catalysts in photothermal catalysis has also increased each year (Fig. 2(b)).

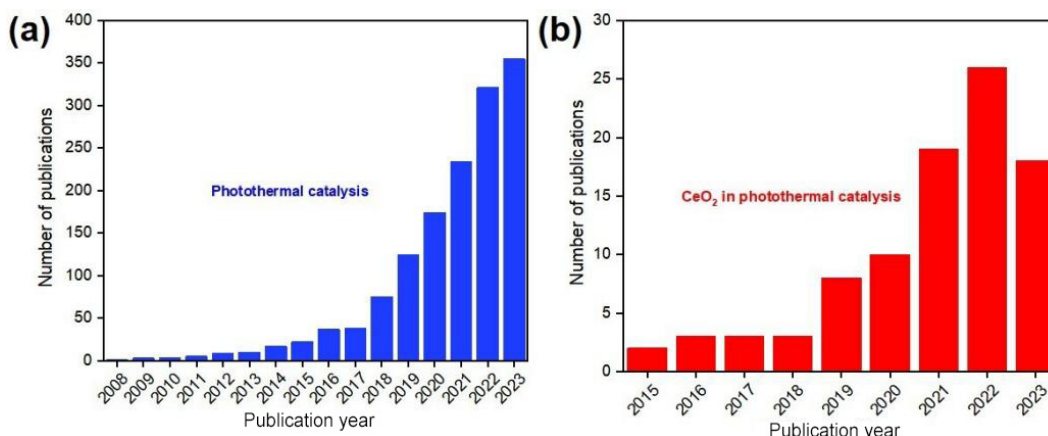


Figure 2 Number of published papers searched using (a) “photothermal catalysis” and (b) “photothermal catalysis” and “ CeO_2 ” as keywords, from 2008 to 2023 and 2015 to 2023, respectively.

Although CeO_2 has begun to emerge in photothermal catalysis, to the best of our knowledge, a systematic overview of CeO_2 for photothermal CO_2 reactions has not yet been reported and the understanding of its mechanisms remains superficial. In this brief review, we systematically summarize the progress of CeO_2 -based catalysts in photothermal CO_2 conversion. We also discuss the synthesis methods of CeO_2 -supported catalysts and the characterization techniques used in mechanistic studies. Moreover, a perspective is presented on the future development of CeO_2 in this field, as illustrated in Fig. 3.

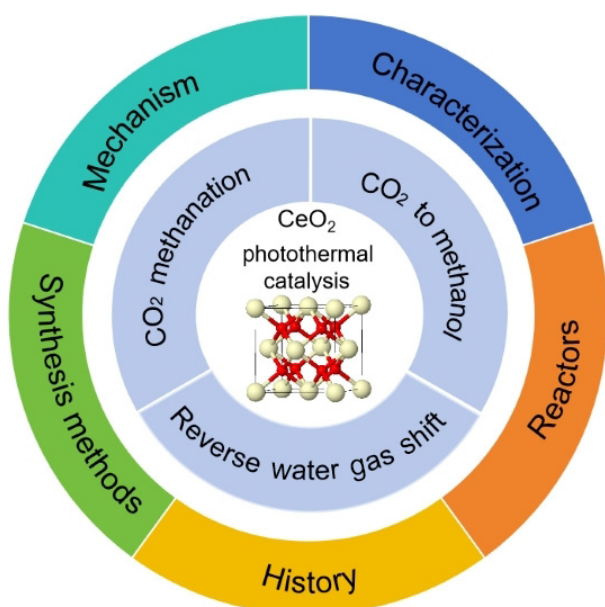


Figure 3 Schematic illustration of CeO_2 applications as a support for photothermal CO_2 hydrogenation reactions.

2 The history of photothermal catalysis

As early as 1911, Eibner observed that illuminating ZnO resulted in the bleaching of Prussian blue pigment, marking the emergence of a novel form of heterogeneous catalysis driven by photon energy—photocatalysis [76]. Subsequently, in 1972, Fujishima and Honda demonstrated that UV light irradiating a cell comprising a TiO_2 photoanode and a Pt counter electrode could generate hydrogen from water [77]. These groundbreaking studies paved the way for extensive research in thermal and photocatalysis, facilitating the production of value-added chemicals. The timeline of ceria-based materials in photothermal catalysis is summarized in Fig. 4. In 1991, J. Melsheimer and others proposed the photothermal photocatalysis concept to increase the reaction temperature and enhance catalytic efficiency during the investigation of Ru/titania catalyzed carbon dioxide methanation [78]. The concept of photo-assisted thermocatalysis was introduced by V. N. Parmon in 1997, in the paper entitled “Photocatalysis as a phenomenon: Aspects of terminology” [79]. Linic and his colleagues introduced the innovative concept of plasmonic catalysis in 2011, by investigating catalytic reactions on silver plasmonic nanostructures under high-temperature illumination [80]. Plasmonic catalysis hinges on the localized surface plasmon resonance (LSPR) effect, propelled by hot charge carriers and thermal energy [81]. However, accurately quantifying their contributions remains a challenge.

Photothermal catalysis using CeO_2 -based materials originated two decades ago. Alessandro Trovarelli published a review in 1996, comprehensively describing the catalytic properties of CeO_2 and its potential applications in various catalytic processes [82]. It was the first mention of the photothermal catalysis of CeO_2 -containing materials. About a decade ago, there was a surge in the field of photothermal catalysis involving CeO_2 -supported metal (M/CeO_2) catalysts. Various M/CeO_2 demonstrated excellent catalytic performance in photothermal catalytic reactions, such as Pd/CeO_2

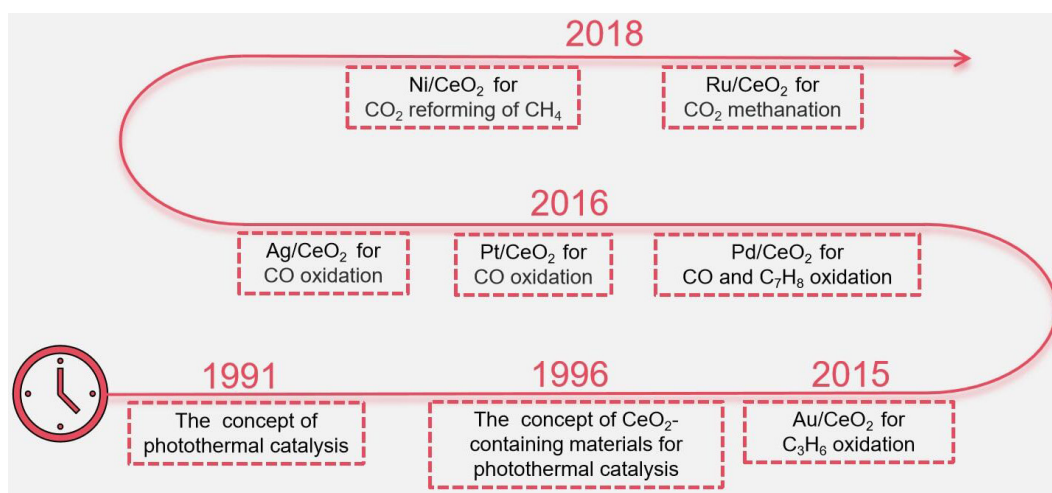


Figure 4 Historical timeline of CeO₂-based materials in photothermal catalysis: 1991, the concept of photothermal catalysis from Ref. [78]; 1996, the concept of CeO₂-containing materials for photothermal catalysis from Ref. [82]; 2015, Au/CeO₂ from Ref. [83]; 2016, Pd/CeO₂ from Ref. [84], Pt/CeO₂ from Ref. [85], Ag/CeO₂ from Ref. [86]; 2018, Ni/CeO₂ from Ref. [87], Ru/CeO₂ from Ref. [88].

[83], Pt/CeO₂ [84], Ag/CeO₂ [85], Au/CeO₂ [86], Ni/CeO₂ [87], Ru/CeO₂ [88] and others. The improved catalytic performance was attributed to the interplay between CeO₂ and metal carrier, instigating various structural modifications such as electronic interactions, active interface site formation and geometric alterations of metal sites, all of which profoundly impact catalytic performance [89]. According to previous reports, the interfacial sites between CeO₂ support and metal sites play an important role in photothermal reactions, the mechanisms involved in these interactions warrant further investigation. Oxygen vacancies in CeO₂ enhance the activity and stability of supported metal nanoparticles (NP). Additionally, Ce³⁺ species, acting as a Lewis base, facilitate the adsorption and conversion of CO₂. For instance, they effectively promote the disproportionation of CO₂ and stabilize CO-containing intermediates. However, the detailed roles of CeO₂-based materials in specific reactions are typically very complex and require thorough investigation to advance the development of novel catalysts.

Recently, a rapid and exciting development has been observed in photothermal catalysis, with a focus on catalyst design to enhance the catalytic performance [90–92]. Photothermal catalysis, as a synergistic integration of thermal and photocatalysis, exhibits superior catalytic performance. This method offers several advantages, including enhanced activity, selectivity and stability, along with mild reaction conditions and reduced costs. It has been widely applied in various chemical processes, demonstrating its effectiveness and versatility [93–95].

3 Synthesis methods for CeO₂-supported catalysts

CeO₂-supported catalysts, particularly those supporting atomic dispersed metals such as single-atom catalysts and highly dispersed nanocluster catalysts, have garnered considerable attention in heterogeneous catalysis owing to their outstanding catalytic performance [58, 99, 100].

Atomic dispersed metal catalysts maximize metal atom utilization, enhancing efficiency and reducing costs [101–125]. Common synthesis methods for CeO₂ include sol-gel, hydrothermal, precipitation and calcination methods, as shown in

Fig. 5, each with distinct advantages and limitations affecting particle size, surface area and crystallinity [96, 98].

Advancements in the synthesis and stabilization of CeO₂-supported atomically dispersed metal catalysts have opened new avenues for enhancing the catalytic performance of various processes. Achieving and maintaining atomic dispersion allows the maximum utilization of metal atoms, thus improving the catalytic efficiency and reducing costs [126–129]. This makes these catalysts indispensable in industries where high efficiency and durability are critical, such as automotive catalytic converters, fuel cells and environmental remediation [130–132].

CeO₂ is typically used as a support to load transition or noble metals [135–139]. Achieving atomic dispersion of active metal species on CeO₂ involves careful consideration of the synthetic atmosphere, support material properties and deposition techniques [133, 140–142] (Fig. 6). In contrast, calcination in the air often creates a saturated O-coordinated environment around metal atoms, diminishing catalytic activity due to inadequate activation of reactants [143, 144]. Conversely, H₂ reduction leads to the aggregation of noble-metal single atoms into nanoclusters [141, 143, 144].

Strong interactions between metal atoms and support surfaces are essential for enhanced stability of the catalyst [145]. Modifications like doping or creating defect sites on support materials can further improve dispersion. Doping CeO₂ with Zr or La elements can create oxygen vacancies and alter the electronic properties, stabilizing dispersed metal atoms on the support by acting as traps and preventing aggregation, thereby enhancing catalytic performance [146–148]. Creating defect sites through thermal treatment or plasma exposure also provides additional anchoring points for metal atoms. Deposition methods such as atomic layer deposition (ALD) and photo deposition allow precise control over the placement of metal atoms, ensuring uniform coverage and high catalytic activity [149, 150].

Furthermore, stabilization techniques such as encapsulation within the support material and ligand protection prevent metal atom aggregation, maintaining their dispersion and subsequent catalytic efficiency (Fig. 5(b)) [151]. Encapsulation traps metal atoms within the pores or channels of the support material, protecting them from sintering at high temperatures and ensuring

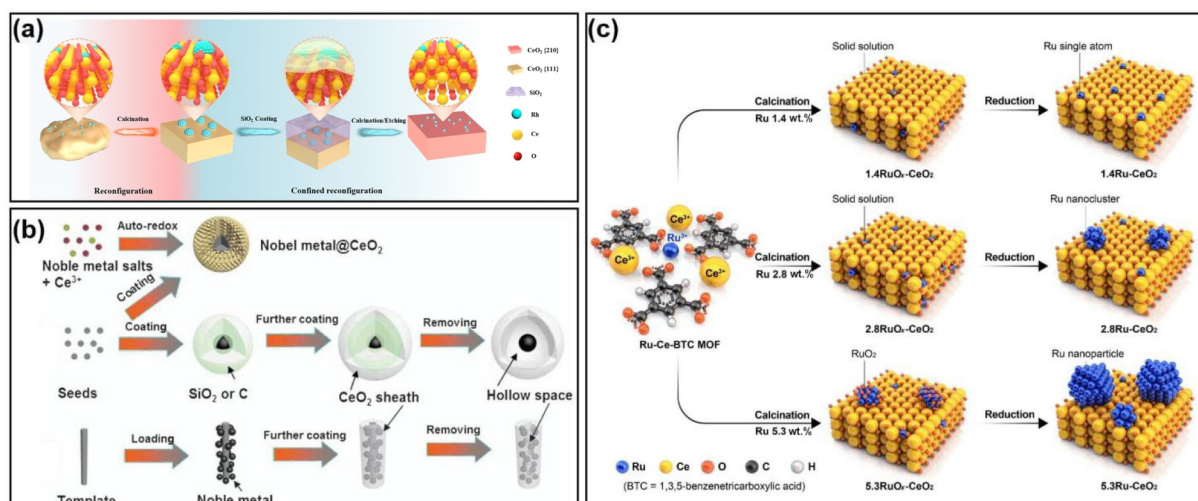


Figure 5 (a) Schematic illustration of “wrap-bake-peel” synthetic strategy. Reproduced with permission from Ref. [96], © Wiley-VCH GmbH 2023. (b) Schematic illustration showing the encapsulation of CeO₂ through various approaches. Reproduced with permission from Ref. [97], © Song, S. et al. 2015. (c) Synthesis of Ru-CeO₂ catalysts. Ru-Ce-BTC (BTC: 1,3,5-benzenetricarboxylic acid), RuO_x-CeO₂ and Ru-CeO₂ represent the raw, calcined and reduced forms, respectively. Reproduced with permission from Ref. [98], © Sivan, S. E. et al. 2022.

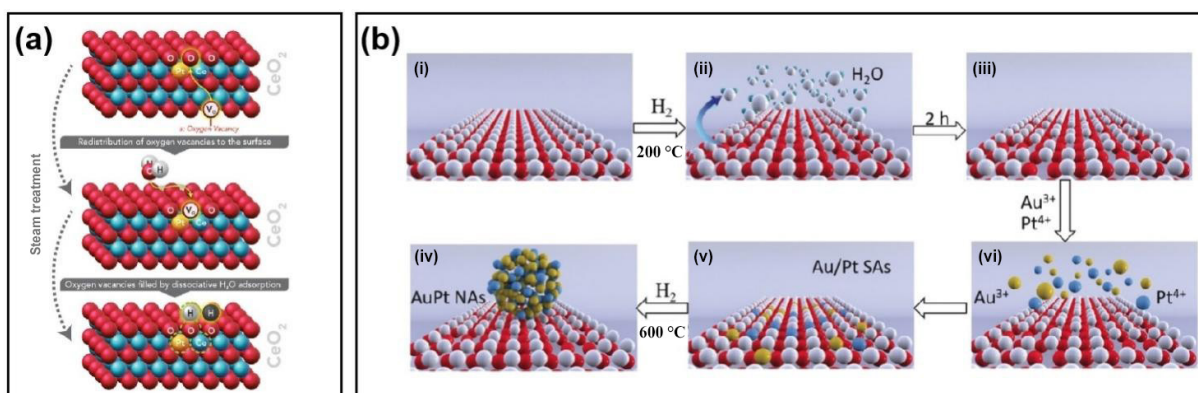


Figure 6 (a) Steam-treatment effects on atomically dispersed Pt/CeO₂ catalyst. Reproduced with permission from Ref. [133], © Nie, L. et al. 2017. (b) Schematic illustration of the catalysts prepared by the solid solvent method. Reproduced with permission from Ref. [134], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2020. NA refers nanoalloys and SA refers single-atom.

high stability during catalytic reactions [152, 153]. Ligand protection employs organic ligands to stabilize metal atoms during synthesis, preventing their aggregation and enhancing dispersion. These ligands can be removed by activation, leaving behind highly dispersed metal atoms. These advancements in synthesis and stabilization are pushing the boundaries of catalyst performance, promising even greater benefits in the future.

4 Reactors for photothermal catalytic reaction

The design and construction of appropriate photothermal reactors are crucial to achieving satisfactory catalytic performance [154, 155]. So far, various photothermal reactors have been constructed and used to match the optimal reaction conditions for the target catalyst [156, 157]. This part will categorize photothermal reactors into two main branches: reactor types and operation mode, as shown in Fig. 7(a). Fixed-bed and structured reactors will be comprehensively discussed based on their applications in photothermal CO₂ hydrogenation to carbon monoxide (CO), methane (CH₄), methanol (CH₃OH) and olefins [158]. These reactors operate either flow-through or in closed mode, with differences in product analysis methods [159, 160].

Flow-through reactors are characterized by continuously passing the reactant gases over the catalyst, allowing steady-state operation and suitability for continuous industrial processes [164]. These reactors are designed to handle a constant gas flow, which is advantageous for maintaining uniform reaction conditions and integrating with other process units. Conversely, batch reactors operate in a closed environment where a fixed number of reactants are charged and the reaction occurs cyclically (Fig. 7(b)) [165]. Reactions are carried out under controlled conditions (temperature and pressure) in this mode, which may be challenging in a flow-through system. Batch reactors, due to their closed operation, also facilitate the investigation of reaction kinetics and mechanisms, allowing precise monitoring of reactant consumption and product formation [166]. In summary, flow-through reactors are preferred for continuous operations and scalability, while batch reactors are suitable for detailed catalytic reactions and applications requiring precise control over reaction conditions. Flow-through reactors can be further divided into fixed-bed and structured reactors. The choice of reactor type is crucial in the efficiency and effectiveness of the photothermal conversion process, with each design offering unique benefits. Structured photothermal reactors, also known as monolithic reactors, are efficient for CO₂ hydrogenation (Fig. 7(d))

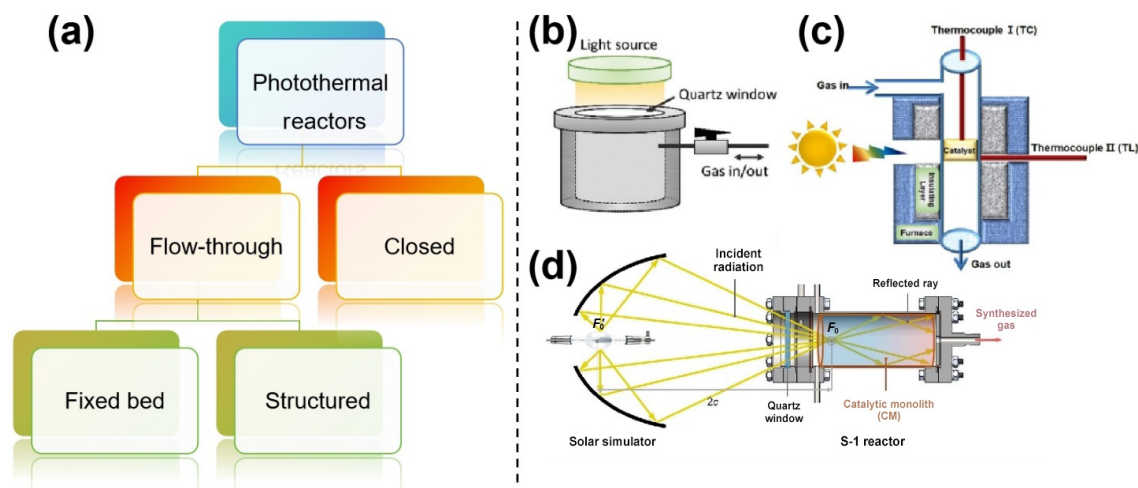


Figure 7 (a) Classification of photothermal reactors. (b) Photothermal closed reactor. Reproduced with permission from Ref. [161], © The Royal Society of Chemistry 2022. (c) Fixed bed photothermal reactors. Reproduced with permission from Ref. [162], © Elsevier B.V. 2022. (d) Structured photothermal reactors. Reproduced with permission from Ref. [163], © Elsevier Ltd. 2018.

[167]. These reactors contain numerous channels, resulting in a higher surface area (100 times) than other support systems [168]. The channel walls are coated with catalysts to enhance contact between reactants and catalysts, facilitating efficient light harvesting as well [169].

Fixed-bed reactors are widely utilized in the photothermal transformation of CO_2 into valuable products due to their high catalytic efficiency, scalability and the ability to maintain a stable reaction environment (Fig. 7(c)) [170, 171]. In this setup, the catalyst is evenly distributed at the bottom of the reactor or supported by materials like quartz [172] or glass [173] fiber filters. This arrangement not only safeguards the catalyst from degradation caused by particle wear but also ensures optimal light exposure. The fixed-bed design also facilitates unhindered light penetration, ensuring that the active surface of the catalyst is fully accessible to photons, which is essential for enhanced photocatalytic activity. This feature is particularly beneficial to maximizing the interaction between the catalyst and light, improving the reaction rates and overall process efficiency. By leveraging the effective light utilization capacity of fixed-bed reactors and their protective environment for the catalyst, these reactors are expected to be an optimal choice for photothermal CO_2 conversion to valuable hydrocarbon fuels [174].

5 Characterization methods for photothermal reaction

Characterizing photothermal catalysts is essential for comprehending their catalytic mechanisms and designing efficient catalysts. Many characterization techniques used in traditional thermal and photocatalysis are also applicable to photothermal catalysis [175]. However, the photothermal effect arises from both photochemical and thermochemical contributions. These two mechanisms coexist simultaneously in photothermal reactions; thus, understanding the in-depth reaction mechanism is challenging. Therefore, we summarize specific characterization methods for photothermal catalysis, which may help us gain a deeper understanding of photothermal catalysis.

To investigate the photothermal catalytic mechanism, characterizing the light absorption and photothermal conversion ability is crucial. Qin et al. employed *in situ* ultrafast infrared (IR)

spectroscopy to detect short-lived transient species by various catalysts and differentiate their photocatalytic behaviors under photon excitation. This approach delineated the distinctions between photocatalysis and photothermal catalysis [176]. Additionally, *in situ* ultrafast visible (Vis) pump/IR probe spectroscopy was utilized to monitor photon-induced electron excitation and transfer. Jiang et al. used electromagnetic simulations to demonstrate that the local electromagnetic field at the Au/CeO_2 interface was intensified more than 100-fold under 615 nm light irradiation [177]. The hot electrons are within the gold nanoparticles, which are then injected into the CeO_2 catalyst.

Another approach to understanding photothermal reactions involves direct temperature measurement at surface active sites. Thermorefectance and optical interferometry techniques utilize light reflection for thermal measurements. Thermorefectance relies on the relationship between the material's refractive index and temperature, generating temperature profiles at micrometer/submicrometer scale with high thermal and temporal resolutions, typically around 0.01 K and 0.1 μs , respectively [180]. Due to its extensive use in microelectronics for monitoring electrical self-heating, Wang et al. employed various thermorefectance techniques to evaluate the thermal enhancement in $\text{Au}/\text{Al}_2\text{O}_3$ plasmonic structures, achieving remarkable spatial and temporal resolutions of approximately 100 nm and several nanoseconds, respectively [181]. Sabastine et al. introduced near-field scanning thermorefectance imaging (NeSTRI) a novel non-contact technique that combines a modulated pump laser with a continuous-wave probe laser and near-field optical microscopy (SNOM) to map the thermal properties of thin films at nanoscale. They employed multilayer graphene films as a case study, demonstrating the capability for high-resolution imaging and quantification for thermal conductivity and specific heat (Fig. 8(a)) [178]. Besides, IR thermography is also suitable for thermal measurements. The estimation of a body's temperature profile based on the Planck blackbody emission principle involves analyzing its emitted energy [182]. Thermal mapping through IR cameras combined with bulk thermocouple measurements facilitates the determination of local and global temperatures. Liu et al. used an IR camera to measure the catalyst temperature (TC) and local temperature (TL) of a Pd/C catalyst [162].

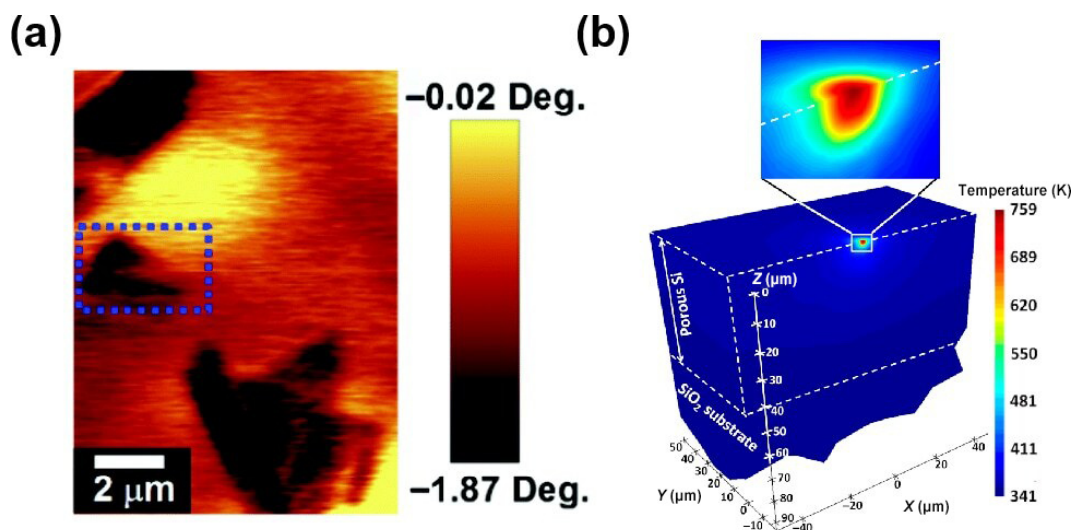


Figure 8 (a) NeSTRI phase images at 75 Hz pump beam modulation frequency in non-contact from the test sample. Reproduced with permission from Ref. [178], © The Royal Society of Chemistry 2017. (b) In-depth T distribution of porous Si NP films deposited on 1 mm thick SiO_2 glass substrate. Reproduced with permission from Ref. [179], © Kurbanova, B. A. et al. 2021.

The significant temperature difference confirmed the applicability of this photothermal material, achieving high temperatures at specific positions while maintaining lower temperatures in the surrounding environment. Bayan et al. investigated the photothermal effects and heat conduction in nanogranular silicon films, revealing a cubic-to-hexagonal phase transition induced by laser heating and demonstrating the control over thermal conductivity of these films by adjusting the film thickness, nanoparticle size and porosity (Fig. 8(b)) [179].

In recent years, an increasing number of emerging characterization methods have been applied to the field of photothermal catalysis. These methods can monitor changes in properties and investigate catalytic mechanisms. A correlation has been established between characterization results and catalyst efficacy, revealing new phenomena that highlight the precision and applicability of these techniques [175].

6 Photothermal catalytic transformation of CO_2

The solar-powered reduction of CO_2 , known as “artificial photosynthesis”, has the potential to decrease CO_2 emissions and

mitigate global warming [183–185]. The CO_2 reduction products can be categorized into C1 compounds (CO , CH_4 , CH_3OH) and C_{2+} compounds (multi-carbon alkanes and olefins) [186, 187]. C1 compounds are essential raw materials for manufacturing plastics, fuels and fertilizers, attracting significant global interest. These products are manufactured through reverse water gas shift reaction (RWGS), CO_2 methanation, methanol synthesis and other reactions. In the past decade, there has been exponential growth in photothermal catalysis to accelerate these reactions. The optimal temperatures and performance metrics of catalysts used for photothermal CO_2 conversion are summarized in Fig. 9.

6.1 Reverse water gas shift reaction

The RWGS is widely recognized as the primary reaction in CO_2 hydrogenation to produce CO and H_2O , serving as the initial step in CO_2 conversion processes, such as methanol synthesis and hydroformylation using CO_2 [188]. CeO_2 , as a metal oxide catalyst, demonstrates promising catalytic performance in the RWGS due to its unique redox properties in heterogeneous catalysis, distinguishing it from other conventional oxides such as Al_2O_3 and SiO_2 [189–191]. Two reaction pathways, the redox pathway and the

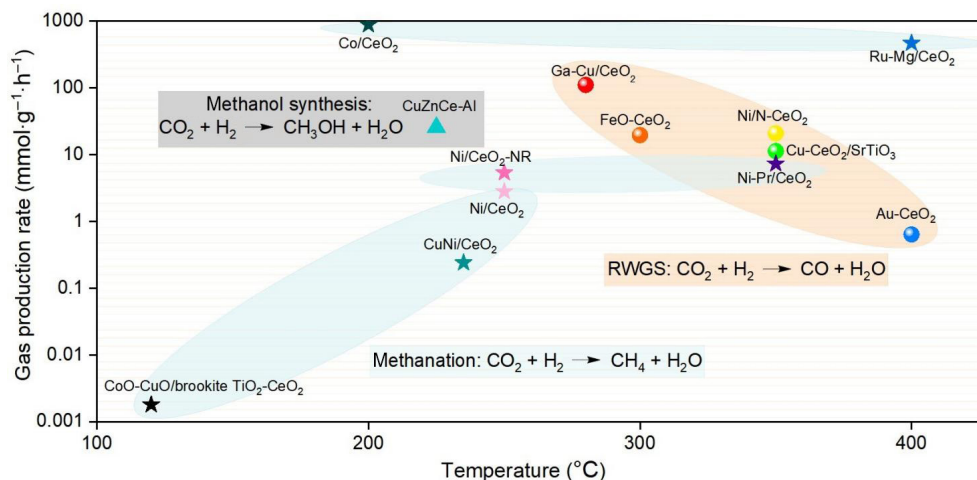


Figure 9 Summary chart of catalytic performance of CeO_2 -based catalysts.

associative pathway, can coexist over this type of catalysis [9]. CeO_2 in M/CeO_2 catalysts plays an essential role by mutual tuning effects with metals. The catalytic performance of representative CeO_2 -based catalysts is compared in Table 1.

Light-responsive supported metals (e.g., Cu, Fe and Au) are promising catalysts for photothermal RWGS [189, 198]. Ye et al. reported a Ga-Cu/ CeO_2 catalyst that achieved a CO production rate of $111.2 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with nearly 100% selectivity under full solar spectrum irradiation (Fig. 10(a)) [193]. Combining photothermal heating and light irradiation significantly increased the CO production efficiency. Incorporating Ga promoted the production of formate species, which are key intermediates in CO_2 hydrogenation. Moreover, light irradiation facilitated the conversion of the formate species to carbonyl compounds, further boosting CO production (Fig. 10(b)). Lu et al. synthesized an Au/ CeO_2 catalyst and the photothermal RWGS achieved a high conversion rate and CO selectivity [195]. The photothermal reaction rate was significantly 10 times higher than that of thermal-only conditions (Fig. 10(c)). The unique role of light promoted the hydrogen-splitting step. Under photothermal conditions, hydrogen molecules were efficiently dissociated, leading to the formation of Au-H species (Fig. 10(d)).

The LSPR and intraband/interband transitions are essential to shaping the optical properties of nanometals [74]. Chemical reactions can be initiated when nanometals are exposed to light with sufficient energy, resulting in the generation of energetic hot

carriers and localized thermal energy. Zhang et al. synthesized the Cu/ CeO_2 catalyst, demonstrating excellent RWGS catalytic activity and CO selectivity, with significantly increased CO production (30%) at 250°C under light irradiation (Fig. 10(e)) [196]. The LSPR generated by Cu nanoparticles stimulates the hot electrons transfer under visible light irradiation, which attacks bidentate formates and linear CO intermediates, accelerating their decomposition and desorption to CO while inhibiting further CO reduction (Fig. 10(f)). Zhu et al. synthesized a three-phase Cu- CeO_2 - $\text{SrTiO}_{3-\delta}$ catalyst [197]. This catalyst, featuring a unique multiphase heterojunction that demonstrated excellent performance, achieving a CO yield of $11.32 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with a high CO selectivity of 99.95%, 9 times greater than that of pure SrTiO_3 (Fig. 10(g)). The enhanced activity is primarily attributed to the synergistic effects of incorporating three phases: Cu nanoparticles, CeO_2 and $\text{SrTiO}_{3-\delta}$ interfaces. Similar to Cu/ CeO_2 , the LSPR effect of Cu nanoparticles significantly promoted the catalytic performance of RWGS (Fig. 10(h)).

Zhao et al. synthesized FeO- CeO_2 nanocomposite catalysts that demonstrated remarkable photothermal CO_2 reduction efficiency [192]. Notably, the FeCe-300 catalyst, with an optimal Fe to Ce molar ratio of 2:1, achieved a high CO_2 conversion rate (43.63%) and an outstanding CO selectivity (99.87%) under Xe lamp irradiation (Fig. 11(a)). The enhanced performance was attributed to FeO and CeO_2 nanoparticles, which promoted the photothermal RWGS reaction. Characterization results provided insights into the

Table 1 Summary of catalytic performance of CeO_2 -based catalysts in the RWGS

Catalyst	Catalyst amount (mg)	Product yield ($\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Selectivity (%)	Temperature ($^\circ\text{C}$)	References
FeO- CeO_2	50	19.61	99.87	300	[192]
Ga-Cu/ CeO_2	10	111.2	100	280	[193]
Ni/N- CeO_2	50	20.9	100	350	[194]
Au/ CeO_2	50	0.64	100	400	[195]
Cu/ CeO_2	240	—	100	250	[196]
Cu- CeO_2 /SrTiO ₃	150	11.32	99.95	350	[197]

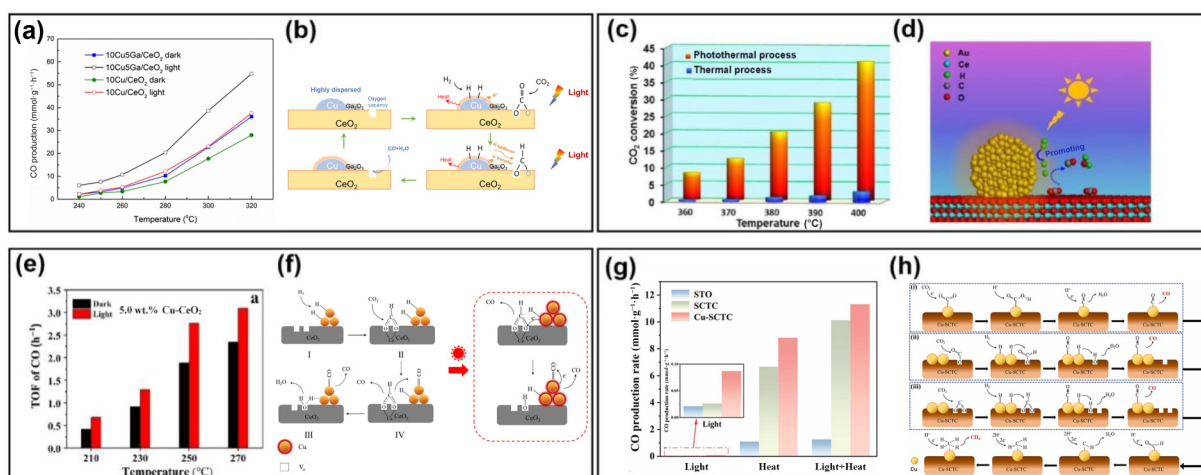


Figure 10 (a) CO production using 10Cu/ CeO_2 and 10Cu₅Ga/ CeO_2 catalysts as a function of temperature under dark and light conditions. (b) Proposed reaction mechanism for photothermal RWGS over Ga-Cu/ CeO_2 . Reproduced with permission from Ref. [193], © Elsevier B.V. 2021. (c) CO_2 conversion by the Au/ CeO_2 in the photothermal or thermal process. (d) Schematic diagram of enhanced CO_2 conversion in photothermal process using Au/ CeO_2 . Reproduced with permission from Ref. [195], © Elsevier B.V. 2019. (e) Catalytic performance of 5.0 wt.% Cu/ CeO_2 . (f) Proposed reaction mechanism for photothermal RWGS using Cu/ CeO_2 . Reproduced with permission from Ref. [196], © Elsevier Ltd. 2022. (g) CO production rates of SrTiO_3 (STO), desired crystalline Cu²⁺-doped, CeO_2 -loaded $\text{SrTiO}_{3-\delta}$ perovskite oxide (denoted as SCTC) and Cu-SCTC catalysts under dark, light and photothermal conditions. (h) Possible reaction pathways for the CO_2 reduction to CO using Cu- CeO_2 - $\text{SrTiO}_{3-\delta}$. Reproduced with permission from Ref. [197], © Zhu, Z. H. et al. 2024.

structure and key reaction intermediates, including formate, bicarbonate and methanol (Fig. 11(b)). The experimental findings highlighted the potential of FeO-CeO₂ nanocomposites for highly selective and stable solar-driven CO₂ conversion to CO, offering significant economic and environmental benefits. Jia et al. synthesized Ni nanoparticle-loaded N-doped CeO₂ (Ni/N-CeO₂) composite through a three-step method, which demonstrated exceptional photothermal CO₂ reduction performance [194]. The optimal Ni/N_{5.0}-CeO₂ achieved a CO yield of 20.9 mmol·g⁻¹·h⁻¹ and nearly 100% CO selectivity (Fig. 11(c)). This superior catalytic activity was due to the strong light absorption facilitated by Ni nanoparticles and an enhanced CO₂ adsorption/activation due to additional oxygen vacancies from N-doping, promoting the CO₂ reduction to CO while suppressing the methanation process (Fig. 11(d)).

6.2 CO₂ methanation

CO₂ methanation, also known as the Sabatier reaction, is another

common reaction in CO₂ hydrogenation [199, 200]. This reaction has been extensively explored to convert electrical energy into fuel, especially in regions lacking fossil energy but with abundant, low-cost electrical power available for H₂ production [201]. Transition metal sites are essential in CO₂ methanation catalysts since the reaction consumes more hydrogen atoms compared to the RWGS [202].

Table 2 indicates that most of the studies have focused on Ni, Ru and other group VIII metal catalysts for CO₂ methanation. Various transitional or noble metals have been intensively applied for CO₂ methanation [211–215]. Golovanova et al. synthesized a Ni/CeO₂ catalyst with a high CO₂ conversion efficiency (80%) and an impressive CH₄ selectivity (95%) [209]. Notably, the reaction rate under sunlight irradiation was 2.4 times higher than in the dark (Fig. 12(a)). Two key factors contributed to this enhancement: the LSPR effect of Ni nanoparticles under light generates heat, increasing the catalyst surface temperature and boosting reaction efficiency and CeO₂ support possesses photocatalytic activity, with light-excited carriers promoting the formic acid species

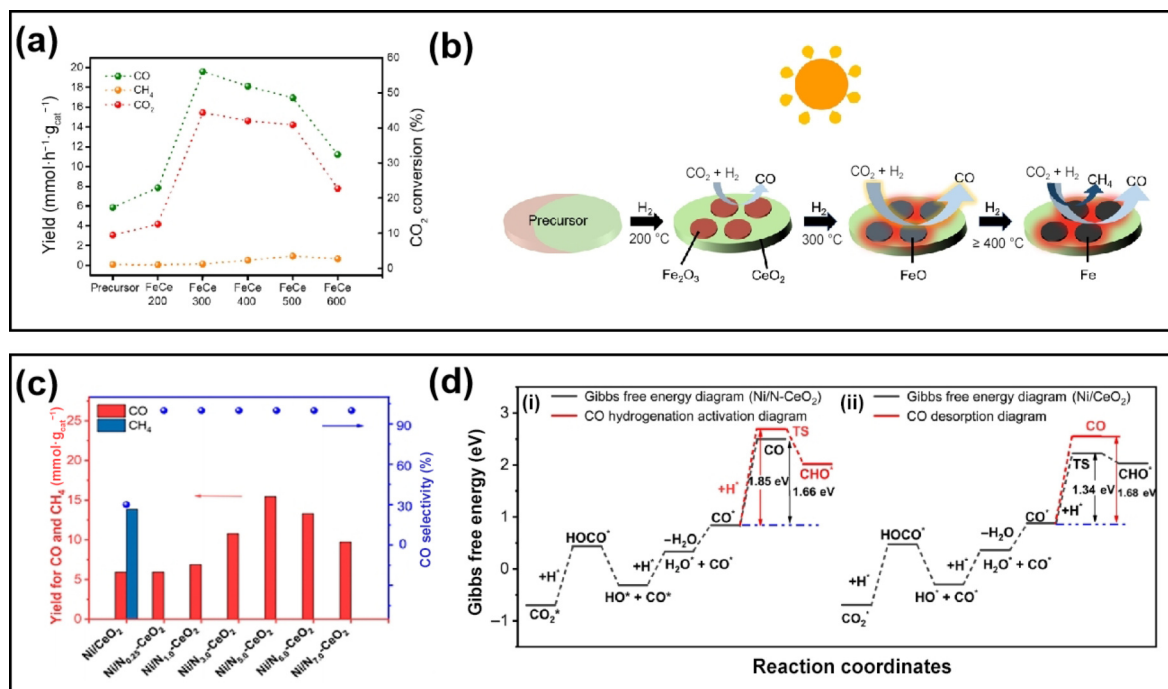


Figure 11 (a) CO₂ conversion and product yields of CH₄ and CO by FeCe-x hydroxide precursor and FeCe-x catalysts (a series of FeO-CeO₂ nanocomposite catalysts were successfully prepared by H₂ reduction of Fe(OH)₃-Ce(OH)₃ precursors at temperatures (x) ranging from 200 to 600 °C (the obtained catalysts are denoted as FeCe-x)). (b) Fabrication of FeCe-x catalysts by reduction of Fe(OH)₃-Ce(OH)₃ precursors at 200–600 °C. Reproduced with permission from Ref. [192], © Zhao, J. Q. 2020. (c) Photothermal CO₂ reductions by Ni/CeO₂ and Ni/N_x-CeO₂. (d) Gibbs free energy diagrams of Ni/N-CeO₂ for CO₂ reduction to CO and CHO*. Reproduced with permission from Ref. [194], © American Chemical Society 2021.

Table 2 Summary of catalytic performance of CeO₂-based catalysts in CO₂ methanation

Catalyst	Catalyst amount (mg)	Product yield (mmol·g ⁻¹ ·h ⁻¹)	Selectivity (%)	Temperature (°C)	References
Ni/CeO ₂	75	9.12	99.3	250	[203]
Co/CeO ₂	100	885.27	97.34	200	[204]
CoO-CuO/TiO ₂ -CeO ₂	200	0.0018	—	120	[205]
CuNi/CeO ₂	300	0.24	—	235	[206]
Ni/CeO ₂ -NR	50	5.36	100	250	[207]
Ni/Pr-CeO ₂	200	7.3	100	350	[208]
Ni/CeO ₂	—	2.8	95	250	[209]
Ru/Mg-CeO ₂	30	469	93.1	400	[210]

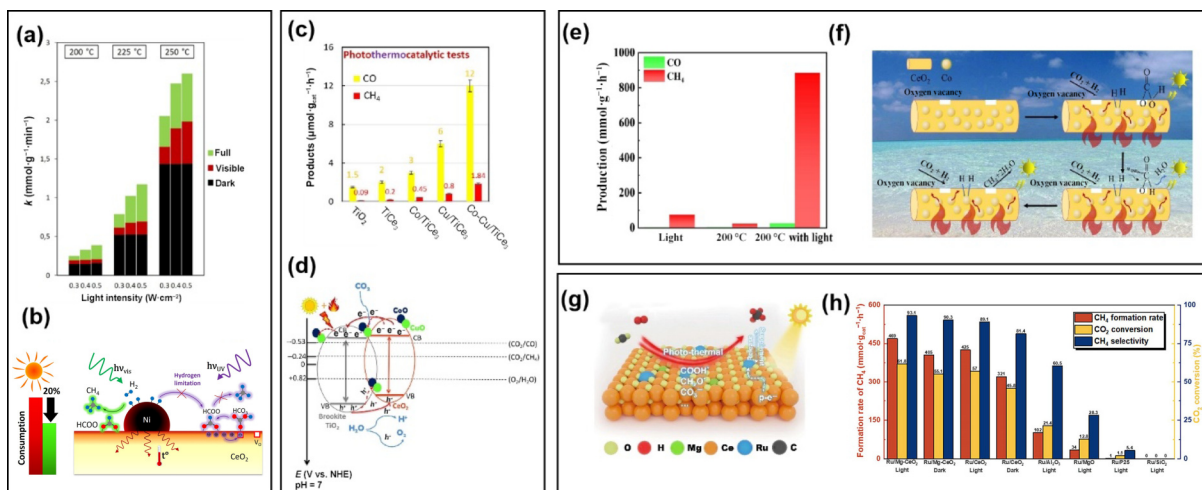


Figure 12 (a) The catalytic activity of Ni/CeO₂ catalyst under visible light and solar illumination of 3 to 5 suns at three different starting temperatures. (b) Proposed mechanism of CO₂ methanation under solar irradiation. Reproduced with permission from Ref. [209], © Golovanova, V. et al. 2021. (c) Photothermocatalytic tests at $T = 120$ °C on TiO₂-based samples. (d) Proposed photothermocatalytic mechanism of Co-Cu/TiO₂ catalyst. Reproduced with permission from Ref. [205], © Elsevier B.V. 2021. (e) CO₂ reduction activity of CC-1:1 comparison test under light and at 200 °C. (f) Photothermal catalytic CO₂ reduction mechanism for Co/CeO₂. Reproduced with permission from Ref. [204], © Elsevier B.V. 2023. (g) CH₄ formation rate, CO₂ conversion and CH₄ selectivity for different catalysts. (h) Proposed mechanism of CO₂ methanation by Ru/Mg-CeO₂. Reproduced with permission from Ref. [210], © Elsevier Inc. 2024.

formation, altering the reaction pathway and enhancing methane selectivity (Fig. 12(b)). Fiorenza et al. investigated the solar photothermocatalytic conversion of CO₂ using CoO-CuO/brookite TiO₂-CeO₂ catalysts [205]. The bimetallic oxide-based catalyst demonstrated superior photocatalytic performance, achieving higher CO and CH₄ formation rates than pure brookite (Fig. 12(c)). Furthermore, the photothermal approach with the CoO-CuO/TiO₂-CeO₂ catalyst substantially enhanced CO₂ conversion, highlighting the strong interaction between CO₂ and catalyst surface sites (Fig. 12(d)).

Pan et al. developed a highly efficient Co/CeO₂ catalyst, which demonstrated a notable CH₄ yield of 885.27 mmol·g⁻¹·h⁻¹ and a CO yield of 24.5 mmol·g⁻¹·h⁻¹ (Fig. 12(e)) [204]. Examining the reaction mechanism under photothermal catalysis revealed that the efficient CH₄ and H₂O production from formate hydrogenation was facilitated by hot carriers (Fig. 12(f)). Additionally, Zhang et al.

developed a Ru/Mg-CeO₂ single-atom catalyst for efficient photothermal CO₂ methanation, achieving a high CH₄ formation rate of 469 mmol g⁻¹ h⁻¹ with excellent stability at 400 °C (Fig. 12(g)) [210]. The catalyst achieved superior performance due to the synergistic effects of single-atom Ru, Ru-O-Ce structure and Mg doping (Fig. 12(h)).

Yue et al. reported that the CuNi/CeO₂ catalyst demonstrated distinct product selectivity in photothermal CO₂ reduction reactions under dark and visible light conditions [206]. Visible light promoted further hydrogenation to CH₄, revealing that the electrons transfer between Cu and Ni altered the thermal reduction and enhanced CO₂ trapping via increased surface hydroxyl and oxygen vacancies (Fig. 13(a)). This study presented insights into the non-thermal effects of photothermal catalysis (Fig. 13(b)). Bian et al. investigated the morphology dependence of Ni/CeO₂ catalysts,

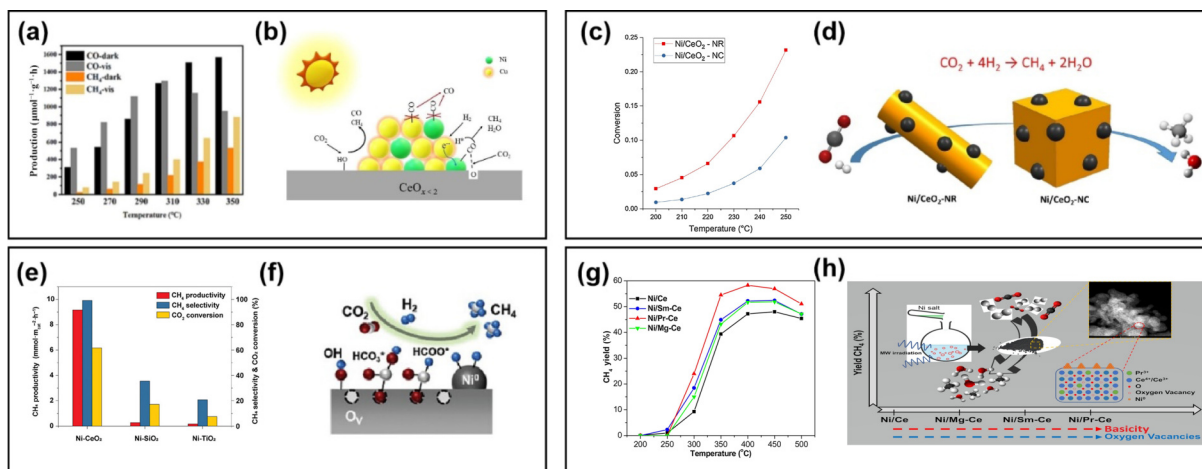


Figure 13 (a) The catalytic activity of Cu₅Ni₃/CeO₂ at different temperatures. (b) Schematic diagram of the photothermal catalytic mechanism of Cu₅Ni₃/CeO₂. Reproduced with permission from Ref. [206], © Elsevier B.V. 2023. (c) Catalytic conversion test of Ni/CeO₂. (d) Proposed mechanism of CO₂ methanation by Ni/CeO₂. Reproduced with permission from Ref. [207], © Elsevier B.V. 2018. (e) Comparison of photothermal methanation performance of Ni/CeO₂, Ni/TiO₂ and Ni/SiO₂. (f) Schematic illustration of photothermal CO₂ methanation reaction mechanism using Ni/CeO₂ catalysts. Reproduced with permission from Ref. [203], © Wiley-VCH GmbH 2023. (g) Catalytic performance of Ni/Ce, Ni/Sm-Ce, Ni/Pr-Ce and Ni/Mg-Ce as a function of reaction temperature. (h) Proposed CO₂ methanation mechanism by Ni/CeO₂. Reproduced with permission from Ref. [208], © Elsevier B.V. 2020.

suggesting that Ni/CeO₂ nanorods (NR) exhibited higher methanation activity and selectivity compared to nanocubes (NC) at low temperatures (Fig. 13(c)) [207]. Characterization techniques indicated that Ni/CeO₂-NR exhibited a higher proportion of Ce³⁺. The presence of more oxygen vacancies served as active sites for formate production in the methanation mechanism (Fig. 13(d)). This research provides a novel strategy to prepare efficient catalysts and conduct fundamental kinetic and mechanistic studies in heterogeneous catalysis.

Zhang et al. developed a hydrothermal growth strategy that selectively targets CO₂ to synthesize CeO₂ octahedral nanocrystals, exhibiting strong physicochemical interactions with CO₂ molecules, significantly enhancing photothermal CO₂ hydrogenation to methane [203]. The Ni-loaded CeO₂ catalyst demonstrated superior performance with a CH₄ production yield of over 9 mmol·h⁻¹·m_{cat}⁻² and a selectivity higher than 99%, possibly due to the abundant oxygen vacancies and hydroxyl species on the CeO₂ surface that created numerous active sites and the strong metal-support interaction that enhanced H₂ dissociation and CO₂ hydrogenation (Figs. 13(e) and 13(f)). This approach presented a novel pathway for developing catalysts with targeted properties for specific chemical reactions. Siakavelas et al. comprehensively investigated CO₂ methanation reaction over Ni catalysts supported on CeO₂, Sm₂O₃-CeO₂, Pr₂O₃-CeO₂ and MgO-CeO₂ binary oxides [208].

The catalysts were synthesized by a microwave-assisted sol-gel method and characterized by various techniques. Adding Sm³⁺ or Pr³⁺ to CeO₂ generated oxygen vacancies and restricted nickel agglomeration, thus improving low-temperature hydrogenation and enhancing CO₂ methanation activity.

Particularly, the Ni/Pr-Ce catalyst demonstrated the highest CO₂ conversion and CH₄ yield of 54.5% each, along with 100% selectivity at 350 °C (Fig. 13(g)). The Mg²⁺ addition created strong

metal-support interactions, enhancing the catalyst's resistance to sintering and providing a crucial understanding of the role of non-thermal effects in photothermal catalysis (Fig. 13(h)).

6.3 CO₂ conversion to methanol

Compared to CO and CH₄ production, the CO₂ reduction to methanol holds greater economic appeal [216, 217]. Methanol, a pivotal platform chemical, can be further converted to olefins, aromatics and dimethyl ethers through well-established processes [218, 219]. Global methanol production currently stands at 106 million metric tons per year [220]. Methanol-to-olefin conversions represent 31.5% of global methanol consumption, marking a significant growth over the past decade [221]. Another substantial application of methanol is in the transport sector, where it constitutes 27% of methanol consumption [222]. In this sector, methanol is utilized either directly as a fuel or blended with gasoline, providing a cleaner-burning alternative to pure gasoline. Methanol, as a liquid fuel, boasts relative ease of transportation, storage and distribution [223]. Consequently, methanol production from CO₂ reduction has become an increasingly attractive area for researchers worldwide [225, 226]. While a variety of catalysts can catalyze the RWGS reaction, methanol production relies heavily on a select group of transition metal catalysts, such as Cu, Ag, Au and Pd [227, 228]. Among these, Cu-based catalysts are the most extensively used due to their cost-effectiveness for large-scale applications [229]. Numerous oxides have been explored as supports in methanol synthesis, such as ZnO, Al₂O₃, TiO₂, ZrO₂, SiO₂, Cr₂O₃ and CeO₂ [230]. CeO₂-based materials have attracted growing attention in methanol synthesis reactions due to their distinctive catalytic properties. Xie et al. fabricated a ceria-modified Cu/ZnO/Al₂O₃ catalyst (CuZnCe-Al) that significantly enhanced

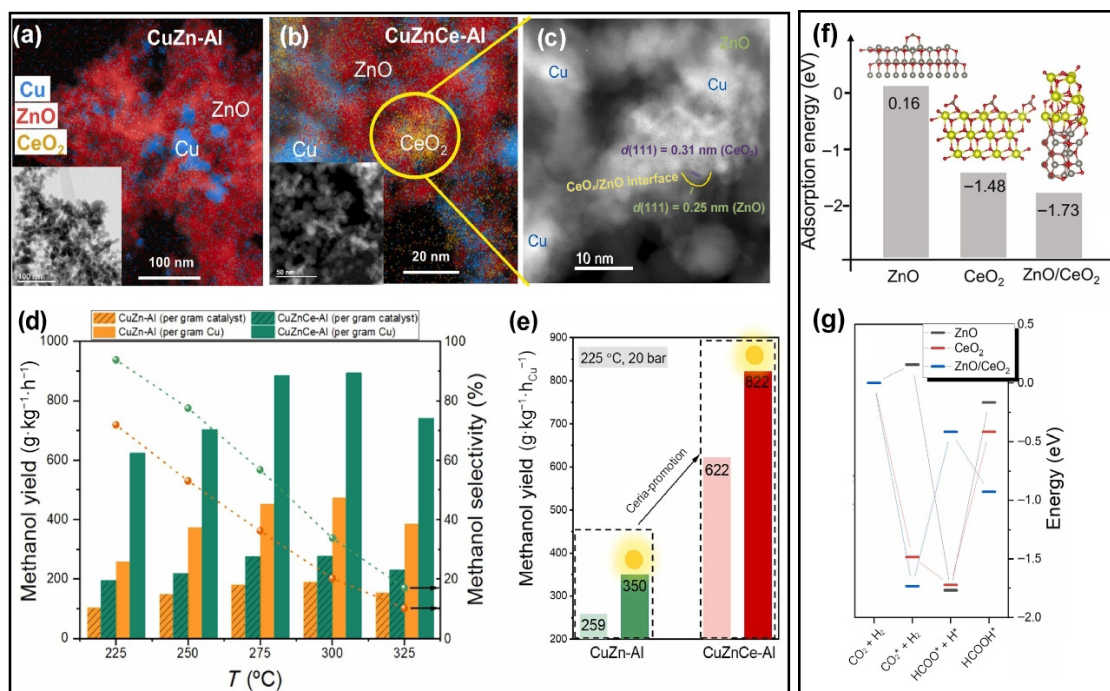


Figure 14 Morphology and catalytic performance of reduced CuZn-Al and CuZnCe-Al catalysts. Energy dispersive spectroscopy (EDS) mapping of (a) CuZn-Al and (b) CuZnCe-Al. The inset shows the corresponding TEM image of each sample. (c) HRTEM image of CuZnCe-Al microstructure. (d) Methanol selectivity and space-time yield under dark conditions when normalized to the mass of the catalyst and the mass of Cu. (e) Catalytic activity at 225 °C under dark and light conditions. (f) Adsorption energies of CO₂ on constructed ZnO, CeO₂ and ZnO/CeO₂ model structures. (g) Energy profiles of elementary steps for formate production and hydrogenation over ZnO, CeO₂ and ZnO/CeO₂ interface. Reproduced with permission from Ref. [224], © Elsevier B.V. 2022.

low-temperature methanol production from CO₂ hydrogenation under light irradiation.

Figures 14(a)–14(c) displays the high-resolution transmission electron microscopy (HRTEM) images and elemental mapping of Cu-ZnO-Al₂O₃ (CuZn-Al) and ceria-modified (CuZnCe-Al) catalysts. Figure 14(d) illustrates the catalytic activity and selectivity of both materials at 21 bar. The catalysts demonstrated a yield of 822 g·kg⁻¹·h_{Cu}⁻¹ and a selectivity of 94% at 225 °C and 20 bar (Fig. 14(e)). The results reveal that an optimal CeO₂ content promotes CO₂ chemisorption and the formate pathway, beneficial for methanol synthesis. The findings underscore the potential of CeO₂-promotion and photo-activation strategies to improve the CO₂ conversion efficiency to methanol, offering a sustainable approach to utilizing CO₂ as a chemical feedstock (Figs. 14(f) and 14(g)).

The robust interaction between metal particles and the CeO₂ support inhibits the metal particles sintering during catalyst preparation [231, 232], creating smaller metal particles and a narrower size distribution than other oxide supports like ZrO₂ and Al₂O₃ [233]. The high metal dispersion can enhance the hydrogen dissociation, thereby increasing the concentration of surface H atoms and facilitating the oxygen vacancies generation through surface reduction. Moreover, the highly dispersed metal particles elevate metal-support interface sites, playing a crucial role in CO₂ activation and methanol production [234].

6.4 Reaction mechanism

So far, two main reaction mechanisms have been proposed in the literature for the photothermal reaction over CeO₂-based materials [9]. One is the redox mechanism, where Ce⁴⁺-O-Ce⁴⁺ species on the surface of CeO₂ are reduced by H₂ to produce H₂O and □ (oxygen vacancy) adjacent to Ce³⁺ species (Ce³⁺-□-Ce³⁺ species). Ce³⁺-□-Ce³⁺ species are then reoxidized by CO₂ to yield CO and Ce⁴⁺-O-Ce⁴⁺ species [235, 236]. The other is the associative mechanism, which

involves the formation and conversion of intermediates, such as formate or carboxyl groups. In this pathway, CO₂ is adsorbed onto the catalyst surface and reacts with adsorbed hydrogen to form a key intermediate. The efficiency of this pathway relies on surface OH groups, which act as the primary active sites for CO₂ adsorption and activation, due to the absence of adsorbed O²⁻ sites [237, 238].

6.5 Stability

Heterogeneous catalysis often deals with processes of direct industrial relevance. In such cases, the ability to produce large product volumes is crucial, which translates into the need for long catalyst lifetimes-usually months-in order to reduce costs [239]. Catalyst stability, intended as the ability to retain catalytic function over time rather than structural stability, is routinely assessed through time-on-stream or recycling experiments. Figure 15 shows the stability of some photothermal catalysts. However, these tests are occasionally performed with reactions run at full conversion [240]. In these cases, the reactions are limited by the amount of available reagent and a potential activity decrease would not be revealed. Since those conditions do not reflect a kinetically controlled regime, any stability claim remains unsupported. Best practice, in this case, suggests performing experiments at low conversion or away from equilibrium conversion.

7 Conclusion and perspective

Reducing CO₂ emissions has become a critical objective in global ecological environmental protection efforts. Photothermal catalytic CO₂ hydrogenation holds significant promise in curbing atmospheric CO₂ levels and fostering a high-quality carbon cycle due to its inherent efficiency, environmental friendliness and sustainability. The main products of photothermal catalysis are CH₄, CO and CH₃OH, with high yield and selectivity. Of all the

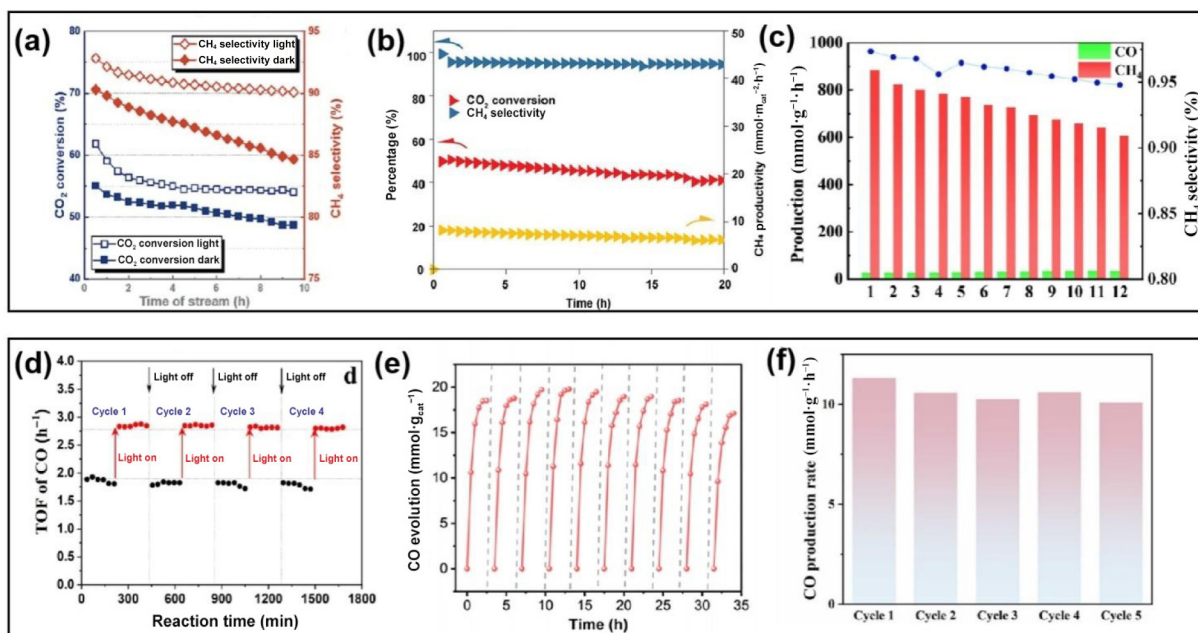


Figure 15 (a) Stability of Ru/Mg-CeO₂ for CO₂ methanation. Reproduced with permission from Ref. [210], © Elsevier Inc. 2024. (b) Stability of Ni/CeO₂-CO₂ in photothermal CO₂ methanation. Reproduced with permission from Ref. [203], © Wiley-VCH GmbH 2023. (c) 12 h stability test at 200 °C for CC-1:1. Reproduced with permission from Ref. [204], © Elsevier B.V. 2023. (d) The stability test of Cu-CeO₂ for RWGS reaction under visible light and dark conditions. Reproduced with permission from Ref. [196], © Elsevier Ltd. 2022. (e) 10 cycles of reaction over Ni/N₅₀-CeO₂. Reproduced with permission from Ref. [194], © American Chemical Society 2021. (f) Photothermal stability cycling experiments of Cu-SCTC catalysts. Reproduced with permission from Ref. [197], © Zhu, Z. H. et al. 2024.

reported catalysts in RWGS, the Ga-Cu/CeO₂ catalyst synthesized by Ye et al. achieved the best performance, with a CO yield of 111.2 mmol·g⁻¹·h⁻¹ [193]. For CO₂ methanation, the Co/CeO₂ catalyst prepared by Pan et al. demonstrated an impressive yield of 885.27 mmol·g⁻¹·h⁻¹ [204]. However, very few photothermal cerium-based catalysts have been developed for methanol synthesis. For example, the CuZnCe-Al catalyst reported by Xie et al. achieved a performance of 822 g·kg⁻¹·h_{Cu}⁻¹ [224]. The extensive efforts dedicated to utilizing Ce-based photothermal catalysts yielded extremely promising prospects in CO₂ hydrogenation to value-added products. Nevertheless, several aspects of photothermal CO₂ hydrogenation still need attention and warrant future investigation, as detailed below;

(1) Advanced photothermal catalysts development. In current studies, the primary products of photothermal CO₂ reduction are CO and CH₄. At the same time, some studies have reported producing other high-value products such as methanol, ethanol, or C₂₊ hydrocarbons in photothermal CO₂ reduction systems. However, there remains a substantial gap between current progress and meeting the actual demand. Researchers are focusing on developing novel photothermal catalysts with enhanced light absorption and heat management capabilities, including bimetallic nanoparticles and hybrid materials. Furthermore, developing photothermal catalysts that maintain activity over extended periods and resist deactivation is crucial for practical applications. Fine-tuning reaction conditions to control product selectivity remains a key challenge. Advanced materials and reaction engineering are essential to achieve the desired outcomes.

(2) Recognition of photothermal catalytic reaction mechanism. The mechanism of photothermal CO₂ reduction systems under solar energy remains to be fully explored. To advance the study of photothermal catalytic processes, it is crucial to develop *operando* methods rather than *in situ* methods to establish correlations between spectral changes and product formation, enabling direct identification of reaction intermediates and thereby deducing reaction mechanisms. Without this, some spectral changes might only be artifacts rather than reflecting the dynamic changes on the catalyst surface. For instance, *in situ* IR has previously focused primarily on spectral changes of adsorbed species [236, 241]. These changes could merely be the result of side reactions, rather than representing intermediates in the reaction process. Therefore, *operando* characterization methods should be developed to investigate the real reaction intermediates.

(3) Aggregation and dispersion behavior of active metals under photothermal conditions. The interaction between the CeO₂ surface and active metal sites varies with temperature and different reaction atmospheres. It will be necessary in the future to conduct comprehensive studies on the aggregation and dispersion behavior of active metals on CeO₂ surfaces under photo-thermal conditions. Based on the experience in pervious atomic dispersion [99], it is essential to develop *in situ* observation techniques to study the dynamic of active sites under photo, thermal and photo-thermal conditions. This will provide a clear understanding of the influence of light-induced electron-hole pairs on metal dispersion, facilitating the development of high-performance CeO₂-based catalysts.

(4) Integration with carbon capture. Combining photothermal catalysis for CO₂ conversion with carbon capture could transform CO₂ under mild conditions, contributing to establishing a new carbon cycle. Therefore, developing continuously operable photothermal catalytic systems for CO₂ capture and conversion, along with related high-performance catalysts, is a significant future research area.

Data availability

Not applicable.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Z. R. Z.: Investigation, writing – original draft. X. H.: Writing – review & editing. J. H. Z.: Supervision, writing – review & editing. Y. Y. D.: Writing – review & editing. J. S. Z.: Supervision, funding acquisition, writing – review & editing. Q. X.: Writing – review & editing. N. Q. Z.: Conceptualization, supervision, funding acquisition, writing – review & editing. All the authors have approved the final manuscript.

Use of AI statement

None.

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