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Photothermal catalytic C1 conversion on supported catalysts

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Photothermal catalysis has emerged as a robust approach for converting C1 feedstocks into valuable chemicals, providing a clean and sustainable alternative that reduces the carbon footprint and enables energy-efficient green synthesis. Supported metal materials are promising candidates for scaling up photothermal catalysis, as their photothermal properties can be precisely tailored to optimize energy conversion efficiency and product distribution for specific processes. In this review, we provide an in-depth examination of the application of supported catalysts in photothermal catalytic C1 chemistry, which begins with an introduction of the mechanism of photothermal catalysis and elucidation of the fundamental principles behind this process. An overview of the design strategies for supported catalysts follows, encompassing various techniques for tailoring their properties to meet specific catalytic requirements. Advancements made in utilizing supported catalysts for photothermal catalytic reactions in C1 chemistry are then highlighted. Finally, challenges in the fledgling field are summarized and valuable insights into the future development directions and focuses are provided. This comprehensive review is anticipated to offer a deeper understanding of the design, performance, and potential applications of supported catalysts in photothermal catalysis for C1 chemistry, transforming conventional chemical processes into 'green'.

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1. Introduction

The current chemical industry faces a critical challenge as it heavily relies on fossil fuels to produce commodity chemicals and energy sources. However, this dependence on non-renewable resources is not sustainable due to limited reserves and the release of harmful greenhouse gases into the atmosphere. To address these issues, the industry must find alternative ways to manufacture chemicals without solely relying on

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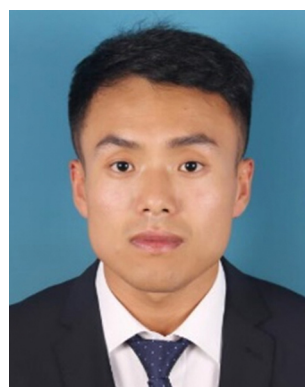
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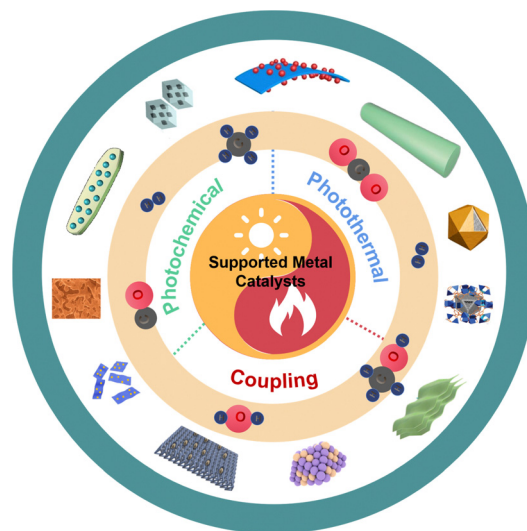


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In this comprehensive review, we delve into the fascinating world of photothermal catalysis and explore its intricate mechanisms. Our aim is to provide a detailed understanding of the photochemical and photothermal effects that underpin this cutting-edge technology, as well as their synergistic coupling.



Then, we explore the two important components (active and support components) in supported metal catalysts and conduct an in-depth exploration of their design strategies. Additionally, we comprehensively examine the recent advancements in supported metal catalysts for photothermal catalytic C1 chemistry. This includes the conversion of CO (such as Fischer–Tropsch synthesis and water-gas-shift reaction), CO₂ (reverse water-gas-shift reaction, methanation, methanol and higher hydrocarbon production), and methane (oxidation, non-oxidative coupling, steam and dry reforming) (Fig. 1). Finally, we provide a concise summary of the current research challenges and prospects within this field. This review contributes fundamental knowledge to the emerging field and holds the potential to revolutionize conventional chemical processes in a green and sustainable manner.

Photothermal catalysis represents an emerging technology that harnesses the synergy between photo and thermal energy to enhance catalytic activity and selectivity, enabling alternative reaction pathways. In the realm of C1 chemistry, the conversion of C1 molecules necessitates the cleavage of C–O/C=O/C–H bonds, demanding a significant driving force. Photothermal catalysis can be categorized into three modes, depending on the primary driving force: photo-assisted thermocatalysis, thermal-assisted photocatalysis, and photothermal synergistic catalysis.^{6,12} In order to facilitate the design and development of more resilient catalysts, we, in this section, present a comprehensive analysis of the mechanisms governing photothermal catalytic C1 chemistry, elucidating its intricate and multifaceted steps.

Photochemical processes involve the excitation of semiconductors, leading to the generation of charge carriers (photogenerated

electrons and holes) that migrate to the semiconductor surface and participate in chemical reactions with adsorbed molecules.¹³ Since the groundbreaking work of Fujijima and Honda in 1972, significant advancements have been made in the field of photocatalysis.¹⁴ However, most photocatalytic processes still suffer from low efficiency, primarily due to rapid carrier recombination and limited solar spectrum absorption and utilization by conventional wide-band gap semiconductors. This limitation has driven the rise of photothermal catalysis as a technology to improve photocatalytic activity.¹⁵

In addition, noble metal nanoparticles, such as Au, Ag, and Cu, can harness the wide solar spectrum (including visible and infrared light regions) through the strong localized surface plasmon resonance (LSPR) effect.¹⁶ These nanoparticles then undergo energy dissipation through three pathways: First, a significant portion of energy is absorbed within the metal nanoparticles, generating energetic hot charge carriers, primarily hot electrons, through non-radiative decay (Landau damping process).¹⁷ These energetic hot charge carriers further induce chemical reactions. Second, a small fraction of the non-radiative decay energy transfers to the metal lattice phonons, resulting in localized heating known as plasmonic-induced thermal effects (Section 2.2). The remaining minor amount of energy is re-emitted as photons through radiation decay, augmenting the optical near-field. It is worth noting that the first two pathways play crucial roles in photothermal catalysis.

2.2 Photothermal effect

The photothermal effect is a phenomenon frequently observed in photo-driven thermal catalysis. In this process, the catalyst utilizes incident light to generate thermal energy (heat) upon irradiation, thereby elevating the surface temperature to facilitate catalytic reactions. Photothermal catalysis stands out among other solar energy harnessing technologies due to its exceptional efficiency in energy conversion. The photothermal effect in the catalyst arises from various mechanisms, including non-radiative relaxation in semiconductors, plasmonic localized heating, and

thermal vibration of molecules.¹⁸ Fig. 2 demonstrates that different photothermal materials can convert light into heat through one or more pathways of photothermal conversion.

When light illuminates a semiconductor, photons with energy equal to or greater than the bandgap can excite the semiconductor, resulting in the generation of electron-hole pairs. These partial electrons and holes have the ability to migrate to the surface of a catalyst and participate in redox reactions. A significant portion of the electron-hole pairs releases energy through both radiative and non-radiative dissipation mechanisms. The non-radiative dissipation process induces phonons, which leads to heat energy generation through lattice vibration. This phenomenon, known as the photothermal effect in semiconductors, relies on the generation of charge carriers through photoexcitation. Similarly, the LSPR effect of plasmonic nanomaterials generates charge carriers, including high-energy hot electrons, that drive photochemical reactions. The non-radiative relaxation in plasmonic materials also contributes to local heating through electron-phonon scattering, thereby enhancing the activity of photothermal catalysis.

In addition to semiconductors and plasmas, photothermal effects can be observed in other materials with strong light absorption capacities, such as carbon-based materials (carbon nanotubes, graphene, amorphous carbon, *etc.*), metal-organic frameworks (MOFs), and mexenes.^{19–30} When these materials are excited by light, electrons undergo transitions from the highest occupied molecular orbital (HOMO) of the ground state to the lowest unoccupied molecular orbital (LUMO) of a higher energy state. Subsequently, through electron-vibrational relaxation processes, heat energy is generated. This photothermal conversion primarily occurs through thermal vibration in molecules.

2.3 Coupling of photochemical and photothermal effects

The photothermal catalytic process involves a complex interplay between the photochemical effect and photothermal effect,

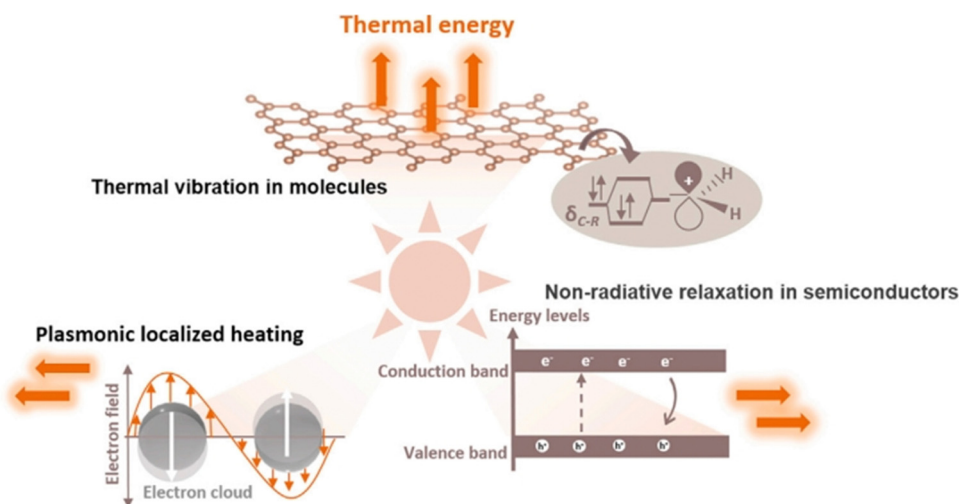


Fig. 2 Different mechanisms of photo-to-thermal process in various materials.¹⁸



as these two phenomena are intricately connected and jointly determine the overall outcome. In the photochemical process, carriers excited by semiconductor photocatalysts or plasmonic materials act as driving forces for chemical reactions. The hot carriers generated through light irradiation actively participate in catalytic reactions, constituting the photochemical effect. On the other hand, the thermocatalytic process in photothermal catalysis relies on the non-radiative relaxation of semiconductors, plasmonic localized heating, and thermal vibration in molecules. These factors play pivotal roles in converting light into heat. The photothermal effect enables efficient dissipation of absorbed photon energy as heat under light irradiation, facilitating carrier transfer and enhancing catalytic activity. Furthermore, photothermal catalysis has the advantage of reducing or eliminating the need for additional heat input and energy consumption. The process concentrates most of the heat on the catalyst's surface, leading to high energy utilization rates. In certain cases, photothermal catalysis effectively prevents catalyst deactivation and enhances the selectivity of desired products. Therefore, the reaction mechanism of heterogeneous photothermal catalysis typically involves the coupling of both photochemical and photothermal effects, representing the interplay between these phenomena.³¹

3. Design of supported metallic photothermal catalysts

Supported catalysts are materials where the active component is uniformly dispersed and supported on a carefully chosen substrate. Typically, supported catalysts consist of two main elements: the active component and the support component. In certain cases, the support component can also exhibit catalytic activity. These two components work together synergistically, resulting in a combined effect that exceeds the sum of their individual contributions. An effective photothermal catalyst should possess specific capabilities, including (1) strong light absorption, (2) high efficiency in photothermal conversion and heat retention, and (3) excellent catalytic activity, product selectivity, and stability. Therefore, the design and modification of catalysts primarily focus on enhancing light absorption across the solar spectrum, promoting efficient heat generation and transfer, and improving catalytic kinetics. In the following section, we will discuss the design strategies for the active and support components in supported catalysts separately, considering their respective roles and functionalities.

3.1 Design of active components

Metals possess exceptional properties which make them indispensable in various industries. Their efficient conductivity of electricity and heat makes them ideal for applications such as electrical wiring, power generation systems, and sustainable heating solutions. Additionally, metals exhibit efficient solar energy absorption and conversion capabilities, making them increasingly popular as a sustainable heat source for homes and buildings. By harnessing the power of the sun through

metal-based technologies like solar panels or thermal collectors, we can reduce our reliance on non-renewable energy sources such as fossil fuels and significantly decrease our carbon footprint. Therefore, metals are versatile and valuable resources that play an essential role in the functioning of modern society. Their unique combination of conductivity and solar absorption capabilities makes them vital components in numerous critical applications today while offering promising solutions for future renewable energy needs.

The LSPR effect plays a crucial role in determining the optical properties of metal nanomaterials. When nanometals are exposed to light with suitable energy, they induce the generation of energetic hot carriers and localized thermal energy, triggering chemical reactions. Previous research studies have demonstrated the remarkable responsiveness of plasmonic metal nanostructures to visible and near-infrared light.^{32,33} The LSPR effect involves three pathways (Section 2.1) which provide the necessary energy for catalytic reactions to occur on the surface of metal nanostructures. Enhancing the LSPR effect of plasmonic nanomaterials is an effective strategy for broadening the optical absorption spectrum, improving photothermal conversion rates, and enhancing catalytic performance.

In photothermal catalysis, metals in photothermal catalysts primarily include precious metals (Au,³⁴ Ag,³⁵ Ru,³⁶ Rh,^{37,38} Pd,^{39,40} Ir, and Pt⁴¹) and non-precious metals (Fe,⁴² Co,⁴³ Ni,⁴⁴ Cu,⁴⁵ Al,^{46,47} and Nb²⁸). By precisely controlling their sizes, shapes, and compositions, their photothermal catalytic performance can be tailored. In a recent study, Yang *et al.* achieved continuous size regulation of monodisperse Pd nanoparticles ranging from 2.8 to 8.1 nm (Fig. 3a). Through precise size control and manipulation of the surface electronic structure, the 6.3 nm Pd nanoparticles exhibited the highest catalytic activity in the photothermal catalytic hydrogenation of CO₂ to CO.³⁹ These findings illustrate that the catalytic activity of size-regulated nanoparticles is primarily influenced by the quantum size effect, metal-support interaction, and photothermal effect.

Single-atom catalysts (SACs) have emerged as promising candidates in catalysis due to their exceptional atomic utilization and unique electronic structures. Researchers have shown a growing interest in exploring the potential applications of SACs. In a study conducted by Guo *et al.*, they constructed Pd₁/TiO₂ SACs through the selective encapsulation of co-existing Pd nanoclusters/nanoparticles based on different conditions of SMSI occurrence (Fig. 3b).⁴⁰ By utilizing detailed characterization techniques and density functional theory (DFT) calculations, the team gained valuable insights into the behavior of these SACs. The results were intriguing, as photo-induced electrons transferred from TiO₂ to adjacent Pd atoms, facilitating acetylene activation and highlighting the potential of these SACs in various catalytic reactions.

However, the excessive surface free energy of single-atom metals makes them susceptible to agglomeration at high temperatures, resulting in a significant reduction in the exposed metal surface area, a phenomenon known as sintering. This process adversely affects catalytic reactivity and, in some cases, can render the catalyst inactive. Metal sintering occurs



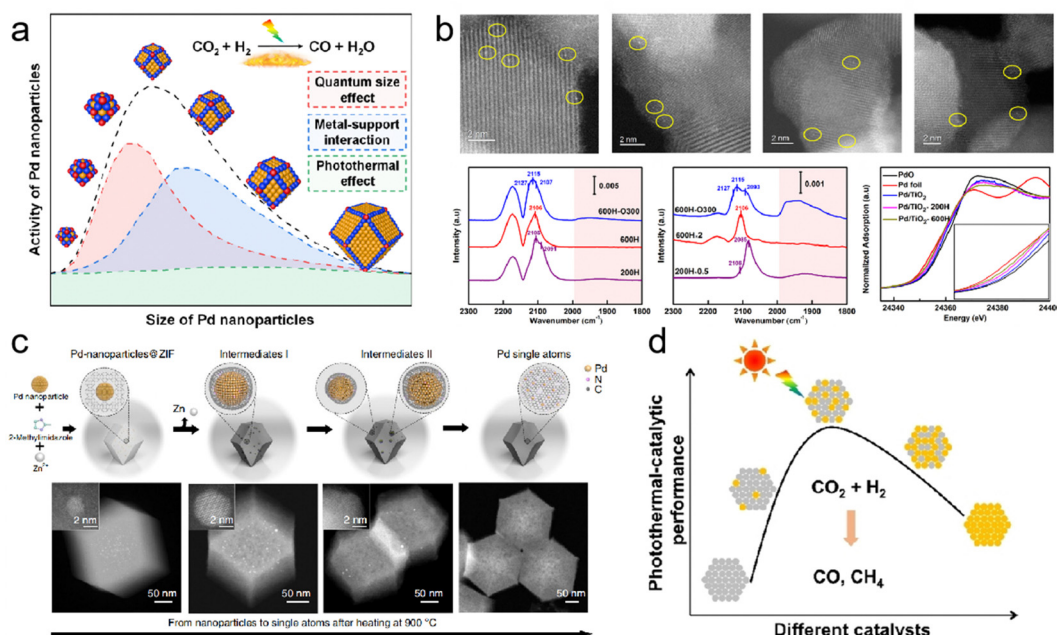


Fig. 3 (a) Monodispersed Pd nanoparticles with a narrow size distribution supported on TiO_2 .³⁹ (b) Structural characterization of Pd/ TiO_2 serial catalysts.⁴⁰ (c) Scheme of the transformation of nanoparticles to single atoms and structural characterization of Pd single atoms.⁵⁰ (d) The influence of the composition of bimetallic nanocrystals on photothermal catalytic performance.⁵¹

through two main pathways: migration between individual metal atomic nanoparticles or the coalescence of adjacent metal nanoparticles. It is worth noting that these pathways are not mutually exclusive and often occur simultaneously, particularly at elevated temperatures. To address this issue, researchers have explored strategies such as the introduction of SMSI or ligands to thermodynamically stabilize metal atoms. These approaches effectively reduce surface energy and limit the migration tendency of individual atoms. However, the use of certain ligands may have toxic effects, leading to deactivation of the catalyst. Alternatively, preventing collisions and coalescence kinetically can be achieved by confining metal nanoparticles within microporous solids such as zeolites and metal-organic frameworks.^{48,49} A groundbreaking study by Wei *et al.* achieved a significant breakthrough in the field of nanotechnology.⁵⁰ The researchers successfully reversed the sintering process of nanoparticles by utilizing nitrogen-doped carbon (CN) as an anchoring substrate to capture migrating metal atoms at high temperatures (Fig. 3c). They employed ZIF-8 as the framework and transformed noble metal nanoparticles into highly active single atoms, including Pd, Pt, and Au. The resulting thermally stable particles exhibited exceptional catalytic activity. During the process of recording films with *in situ* environmental transmission electron microscopy (ETEM), an intriguing observation was made. Despite exposure to high temperatures, sintering occurred, causing smaller particles to fuse and form larger ones. However, as the Pd nanoparticle collided with the substrate, it gradually shrank and transformed into a single atom. The resulting thermally stable Pd single atoms exhibited superior catalytic activity and selectivity for acetylene semi-hydrogenation compared to Pd nanoparticles. This study presents a user-friendly top-down

approach for obtaining single-atom catalysts from nanoparticles and even reactivating sintered industrial precious metal nanocatalysts by dispersing them into individual atomic sites. These findings provide valuable insights for the development of high-performance, heat-stable catalysts.

In addition to the aforementioned strategies, the preparation of dispersed supported bimetallic nanocrystalline catalysts represents another feasible solution to enhance the performance of single-component metal catalysts. Chen *et al.* reported on the photothermal hydrogenation of CO_2 using Al_2O_3 -supported CoFe alloy catalysts.⁴⁶ Their research demonstrated the effectiveness of these catalysts in the conversion process. Similarly, Zhu *et al.* developed a monodispersed Pd-Ni nanoalloys/ SiO_2 catalyst, where the inclusion of Ni improved the optical absorption and photothermal conversion properties, while the presence of Pd enhanced the selectivity of the catalyst in converting CO_2 to CO (Fig. 3d).⁵¹ These findings highlight the potential of dispersed supported bimetallic nanocrystalline catalysts in enhancing the performance and efficiency of catalytic processes.

However, the synthesis of these metal materials presents several challenges that need to be considered. Factors such as the wide range of metal materials available, the need for controllable morphology, environmental impact, high cost, and complex preparation processes should not be overlooked. Additionally, metal nanoparticles can undergo structural distortion when exposed to acids, bases, or salts, and they are susceptible to agglomeration under harsh conditions or contamination by trace impurities. Therefore, the careful selection of a suitable support material becomes crucial in ensuring the stability and functionality of the catalyst.



To address these challenges, specific design strategies have been employed in the investigation of inorganic semiconductors. One prevalent method involves doping and/or introducing defects or vacancies to broaden the light absorption range and accelerate the separation of photogenerated carriers.^{52,53} For example, treating molybdenum trioxide (m-WO₃) with pure hydrogen generates oxygen-deficient WO₃ (m-WO_{3-x}) catalysts,

Ren *et al.* developed a hierarchical graphene foam as a solar absorber (Fig. 5a), exhibiting high absorption across the solar spectrum (295–2500 nm) with minimal transmittance ($\approx 0\%$) and an exceptional photo-thermal conversion efficiency of up to 93.4%.⁶⁴ This innovative design maximizes the utilization of incoming sunlight for energy conversion. Similarly, Ito *et al.* designed a versatile porous graphene material with excellent heat localization and steam generation capabilities, achieving an impressive energy conversion rate of 80% through solar radiation (Fig. 5b).⁶⁵ These advancements highlight the potential of carbon-based materials in photothermal catalysis. However, one challenge associated with graphene sheets is the shading effect due to their light-blocking nature. This issue can be



Fig. 4 Illustration of the preparation processes and micrographs of (a–c) ZnSe–CdSe@NC frame-in-cage,⁵⁹ (d–f) Bi₂S₃@In₂S₃,⁶⁰ and (g–i) Cu_{2–x}S@ZnIn₂S₄ core–shell hollow nanoboxes.⁶¹

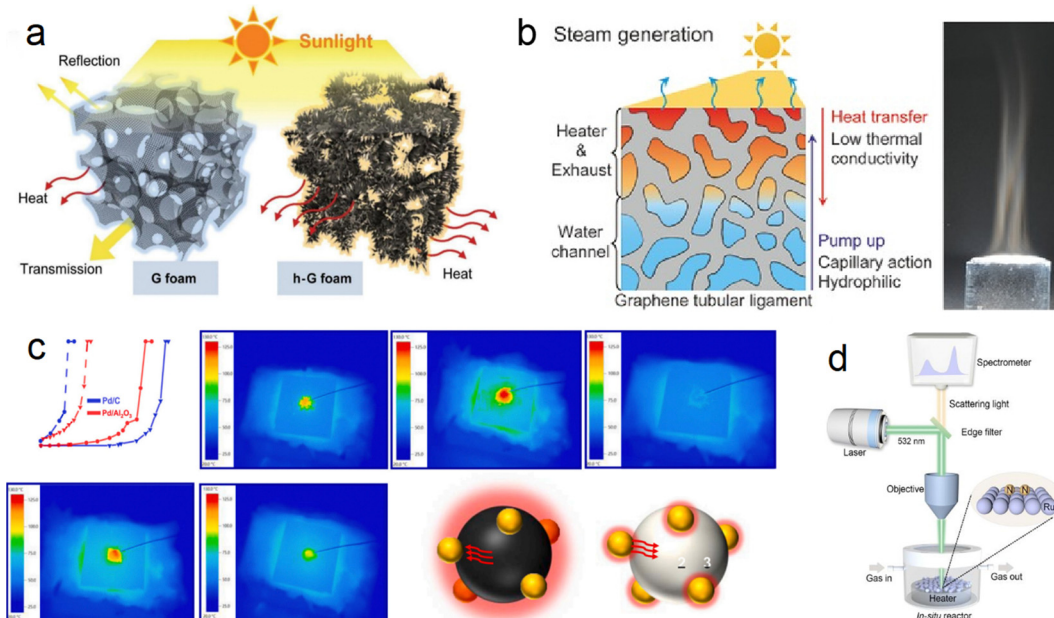


Fig. 5 (a) Difference in solar-thermal conversion processes between ordinary graphene foam and hierarchical graphene foam.⁶⁴ (b) Multifunctional nanoporous graphene converting solar illumination into high-energy steam.⁶⁵ (c) Heat transfer path in CO conversion proved by IR monitoring images (carbon support → Pd → Al₂O₃).⁶⁶ (d) Schematic illustration of the customized *in situ* Raman system.⁶⁷

mitigated by controlling the dosage of graphene sheets and utilizing small-pore semiconductors or in-plane pore materials for structural adjustments, allowing for improved light exposure and efficient catalytic performance.

Although significant advancements have been made in the field of graphene-based photothermal catalysis, it is important to acknowledge that these materials still lag behind noble metal/oxide catalysts due to their weaker interactions with

reactants. However, carbon emerges as a promising candidate for exploring photothermal catalysis when utilized as both a catalyst support and a photothermal material with full-spectrum light absorption capabilities. Liu *et al.* synthesized a Pd/C catalyst using commercial carbon (XC-72R) as a catalyst support through a reduction and impregnation method and applied it in the photothermal catalytic oxidation of CO reaction.⁶⁶ The Pd/C catalyst demonstrated excellent light absorption ability, exhibiting significantly better catalytic performance under light conditions compared to dark conditions. Under a light intensity of 900 mW cm⁻², the temperature for achieving 100% CO conversion (TF₁₀₀, furnace temperature) for the 1% Pd/C catalyst decreased from 146 to 30 °C, realizing complete CO conversion at room temperature (Fig. 5c). This exceptional catalytic performance is attributed to the ultra-high local temperature generated by the excellent photothermal conversion ability of carbon. Furthermore, infrared light was identified as the primary contributor to the improved catalytic performance. This work opens new possibilities for harnessing solar energy using carbon-based materials.

In a different study, Bian *et al.* measured the actual reaction temperature of photothermal synthesis of ammonia on carbon-supported Ru catalysts to quantify the contribution of thermal electrons, employing Le Chatelier's principle (Fig. 5d).⁶⁷ By excluding the local heating effect, they found that the activation energy of photothermal catalysis is significantly lower than that of thermal catalysis (54.9 kJ mol⁻¹ compared to 126.0 kJ mol⁻¹). This reduction in activation energy is attributed to the phenomenon of hot electron injection, which lowers the energy barrier for N₂ dissociation and intermediate product hydrogenation. Additionally, the injection of hot electrons suppressed the methanation reaction of carbon carriers, resulting in excellent operational stability of the catalyst over 1000 hours.

3.2.3 MXenes. MXenes, a group of 2D transition-metal carbides and nitrides, hold great promise in various photothermal

applications, including cancer treatment, solar water desalination, solar photothermal electrodes, and light-driven actuators. These materials exhibit exceptional photothermal conversion properties by efficiently absorbing electromagnetic waves and displaying LSPR effects.²⁸ The incorporation of metal nanoparticles into MXenes further enhances photocatalytic processes by facilitating the transfer of LSPR-excited hot charge carriers to both the metal nanoparticles and adsorbed reactants. Additionally, the strong binding between metals and MXene supports improves the dispersion of metal species on the MXene surface. By utilizing MXenes with excellent photothermal properties as catalyst supports, the sunlight absorption and photothermal conversion efficiency of supported metal catalysts can be significantly enhanced.

For example, Wu *et al.* utilized a chemical stripping method to obtain two-dimensional Mo₂TiC₂ nanosheets, which were then functionalized with Ru clusters (Ru/Mo₂TiC₂) (Fig. 6a).⁶⁸ These MXene-supported clusters exhibited remarkable photothermal conversion performance, with the surface temperature of Ru/Mo₂TiC₂ rapidly reaching 360 °C within 30 seconds under sunlight. After 5 minutes of illumination, the CO production rate reached 3.9 mol g_{Ru}⁻¹ h⁻¹, accompanied by a CO selectivity of 90% (Fig. 6b and c). This achievement positions Ru/Mo₂TiC₂ as one of the most effective photothermal catalysts reported for the reverse water-gas shift (RWGS) reaction. Another advantage of MXene materials lies in their tunable optical, electronic, thermal, and surface properties, which can be adjusted by modifying their compositions, structures, and terminations. This inherent versatility expands the range of available MXene-based materials. Notably, recent work by Wu *et al.* demonstrated that two representative MXene materials, Nb₂C and Ti₃C₂, enhance the photothermal effect, thereby boosting the photothermal catalytic activity of Ni nanoparticles (Fig. 6e and f).²⁸

3.2.4 MOFs. MOFs are three-dimensional networks constructed from metal ion nodes and organic ligands, exhibiting

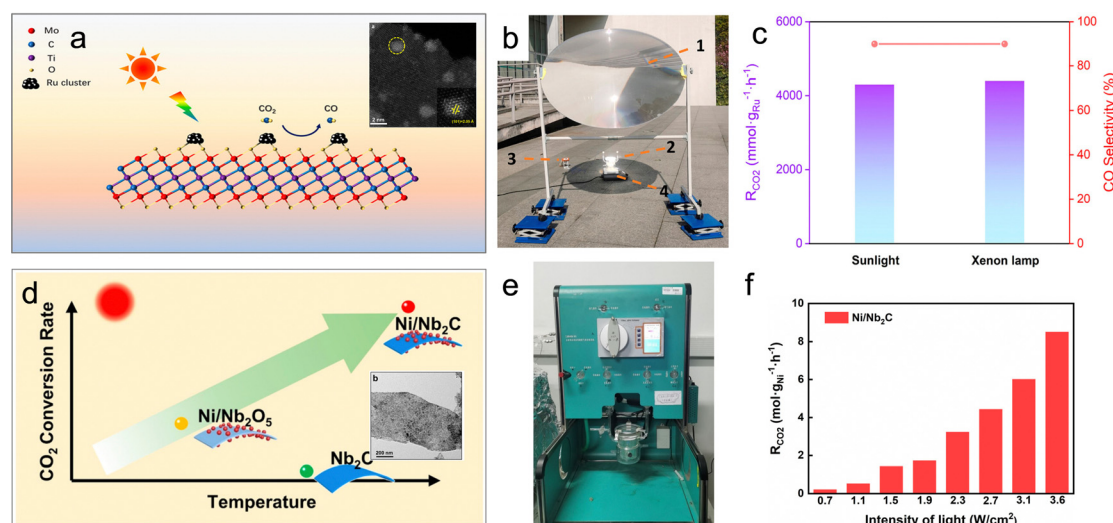


Fig. 6 (a) Schematic illustration and TEM image of the Ru/Mo₂TiC₂ photothermal catalyst. (b) Setup of the outdoor photothermal catalysis. (c) CO₂ conversion and product selectivity of Ru/Mo₂TiC₂ in photothermal catalytic RWGS.⁶⁸ (d) Schematic illustration and TEM image of the Ni/Nb₂C photothermal catalyst. (e) Photograph of the batch reactor. (f) Photothermal catalytic activity of Ni/Nb₂C in photothermal catalytic RWGS.²⁸



semiconductor-like behaviors. The regularity, adjustable pore size, diverse topological structures, and malleability of MOFs make them promising materials for various catalytic reactions. While pure MOFs have limited active sites for photothermal catalytic conversion, they are commonly used as supports for photothermal catalysts in photothermal catalysis. The synthesis of the Pd nanocube (NC)@ZIF-8 composite has opened new avenues in catalytic research (Fig. 7a).⁶⁹ This innovative approach involves encapsulating Pd nanocubes into ZIF-8, resulting in a highly efficient and selective catalyst for hydrogenation reactions. The plasmonic photothermal effects of Pd nanocube cores convert light into heat, driving catalytic reactions. The ZIF-8 shell protects the Pd cores from oxidation and deactivation while also promoting catalytic hydrogenation through H₂ enrichment (Fig. 7b). The composite offers superior performance, including high selectivity and efficiency under irradiation conditions. Moreover, ZIF-8 functions as an ‘insulator’ for thermal management, reducing heat loss and enhancing catalyst performance. For instance, Zhang *et al.* developed a hybrid structure of Pt nanocubes and Au nanocages encapsulated in ZIF-8 (Au&Pt@ZIF).⁷⁰ Pt nanocubes act as catalysts, Au nanocages with strong extinction serve as solar conversion nanocrystals, and ZIF-8 functions as a ‘heat insulator’, preventing heat dissipation and forming a localized high-temperature area that significantly enhances the catalytic activity of Pt nanocubes under light irradiation (Fig. 7c). Recently, Chen *et al.* successfully fabricated a layered tubular structure of MOF-74 (Cu) by assembling nanosheet arrays, exhibiting remarkable photothermal catalytic properties for carbon dioxide conversion at room temperature under sunlight irradiation (Fig. 7d).⁷¹ The MOF-74-HT material possesses abundant optical traps on its outer surface, nano-sized building blocks, and large accessible contact surface

areas, synergistically enhancing photothermal effects and catalytic activity. The creation of such superstructures has the potential to revolutionize the field of pure MOFs, paving the way for innovative and multifunctional materials.

Overall, although semiconductor-based supports are widely used in photothermal catalyst applications, ongoing research aims to explore new materials and approaches to further advance this field.^{36,72,73} In these approaches, heat energy is harnessed to drive catalytic reactions instead of being dissipated to the surrounding environment through convection and conduction. Through structural control, interface engineering, multifunctional assembly and nanoscale effects for meticulous selection and optimization of both the active component and support structure, researchers can develop highly efficient systems capable of catalyzing complex chemical transformations with exceptional precision and control. This continuous exploration and refinement of materials and strategies hold great promise for pushing the boundaries of photothermal catalysis and unlocking new possibilities in diverse areas of chemistry and beyond.

4. Photothermal catalytic C1 conversion using supported metal catalysts

When it comes to harnessing the power of solar energy, photothermal catalytic C1 chemistry has emerged as a highly promising alternative to traditional thermocatalysis. This innovative approach capitalizes on abundant and clean energy sources, and it has made remarkable progress in recent years. Over the past decade, significant advancements have been achieved in



Fig. 7 (a) Self-assembly of Pd NCs@ZIF-8 and plasmon-driven selective catalysis of hydrogenation of olefins. (b) The hydrogenation performance of Pd NCs@ZIF-8.⁶⁹ (c) Schematic illustration of the formation of Au&Pt@ZIF and temperature variation under light irradiation.⁷⁰ (d) Phase transformation from the MOF precursor to MOF-74-HT.⁷¹

Table 1 Representative supported metal catalysts and their performances in photothermal catalytic C1 conversion

| Catalysts | Reactant | Conversion/% | Products | Selectivity or mass specific activity | Ref. |
|---|-----------------|---|--|---|------|
| Fe ₅ C ₂ /NC600 | CO | 22.3 | C ₂₋₄ = | 55.3% | 75 |
| Ni/MnO | CO | 14.9 | Light olefins | 33% | 76 |
| Fe-500/ZnO-Al ₂ O ₃ | CO | 20.9 | Light olefins | 42.4% | 77 |
| Co-Co ₃ O ₄ /ZnO-Al ₂ O ₃ | CO | 15.4 | Light olefins | 36% | 78 |
| TiO ₂ -supported Ni ₂ P/Ni | CO | 20.7 | C ₂₊ | 70.7% | 79 |
| Ru ₁ Co-SAA | CO | 58.6 | C ₅₊ | 75.8% | 80 |
| Pt/ α -MoC | CO | 22 | H ₂ | | 83 |
| CuO _x /Al ₂ O ₃ | CO | > 95 | H ₂ | | 86 |
| CeO ₂ /Cu _{1.5} Mn _{1.5} O ₄ | CO | 96.6 | H ₂ | | 87 |
| Ni ₁₂ P ₅ /SiO ₂ | CO ₂ | 960 \pm 12 (mmol g _{cat} ⁻¹ h ⁻¹) | H ₂ | Near 100% | 100 |
| K ⁺ -Co-C | CO ₂ | 758 (mmol g _{cat} ⁻¹ h ⁻¹) | CO | 99.8% | 105 |
| Ru-Al ₂ O ₃ | CO ₂ | 95.75 | CH ₄ | 99.22% | 38 |
| Rh-Al ₂ O ₃ | | | | | |
| Ni-Al ₂ O ₃ | | | | | |
| Fe ₃ O ₄ | CO ₂ | 11.3 (mmol g _{cat} ⁻¹ h ⁻¹) | CO | 100% | 42 |
| Fe ₃ C | | | CH ₄ | 97% | |
| Pd-loaded WN-WO ₃ | CO ₂ | 40.6 \pm 0.7 (mmol g _{cat} ⁻¹ h ⁻¹) | CH ₄ | 100% | 107 |
| Ru-Al ₂ O _{3-x} -L | CO ₂ | 87.68 | CH ₄ | Near 100% | 108 |
| SA Ni/Y ₂ O ₃ | CO ₂ | 80 | CH ₄ | 7.5 L m ⁻² h ⁻¹ | 110 |
| Au-Ru/TiO ₂ | CO ₂ | | CH ₄ | 99% | 116 |
| Fe/FeO _x supported on MgO-Al ₂ O ₃ | CO ₂ | 50.1 | C ₂₊ | 52.9% | 117 |
| AuCu-ZnO | CH ₄ | | CH ₃ OH, CH ₃ OOH and HCHO | 100% | 120 |
| Pd-def-In ₂ O ₃ | CH ₄ | | CH ₃ OH and CH ₃ OOH | 82.5% | 121 |
| Au/In ₂ O ₃ | CH ₄ | | CH ₃ OH | 97.62% | 122 |
| | | | HCHO | 89.42% | |
| Pt@BT-O | CH ₄ | 8.2 | propane | 65% | 123 |
| Au/ZnO | CH ₄ | | C ₂ H ₆ | | 124 |
| TiO ₂ -supported Rh NPs | CH ₄ | | CO ₂ , H ₂ | | 125 |
| TiO ₂ -supported Pt | CH ₄ | | H ₂ | 185 (mmol g ⁻¹ h ⁻¹) | 126 |
| Single-layer Ni cluster stabilized by Al ₂ O ₃ | CH ₄ | | CO | 9614.26 (mmol g _{Ni} ⁻¹ min ⁻¹) | 128 |
| | | | H ₂ | 8572.96 (mmol g _{Ni} ⁻¹ min ⁻¹) | |
| Ni/Ga ₂ O ₃ | CH ₄ | | CO ₂ , H ₂ | | 129 |
| Cu-Ru/MgO-Al ₂ O ₃ | CH ₄ | | H ₂ | 34 (mol mol _{Ru} ⁻¹ s ⁻¹) | 130 |
| Pt/CeO ₂ | CH ₄ | | CO | 22.7 (mmol g _{cat} ⁻¹ h ⁻¹) | 131 |
| Rh/Ce _x WO ₃ | CH ₄ | | H ₂ | 88.5 (mmol g _{Rh} ⁻¹ h ⁻¹) | 3 |
| | | | CO | 152.3 (mmol g _{Rh} ⁻¹ h ⁻¹) | |

the field of photothermal catalytic C1 conversion. From improving photothermal catalytic CO conversion to groundbreaking developments in CO₂ hydrogenation, and conversions of methane and methanol, researchers are continuously pushing the boundaries of what can be accomplished with this transformative technology. The performance of supported catalysts for photothermal catalytic reactions in C1 chemistry has been summarized in Table 1. By harnessing the unique properties of light and heat, photothermal catalysis offers a more efficient and sustainable method for converting raw materials into valuable products. This exciting field holds immense potential for revolutionizing the energy landscape and enabling a more sustainable and greener future.

4.1 CO conversion

4.1.1 Fischer-Tropsch synthesis. Fischer-Tropsch synthesis (FTS) is a well-established method for converting syngas into fuels and chemicals, which has gained significant attention in light of declining oil resources and mounting environmental concerns.⁷⁴ In addition to its application in fuel synthesis, FTS can also be employed to produce light olefins (C₂₋₄=) from syngas, a process known as Fischer-Tropsch to olefins (FTO). Typically, harsh conditions (200–400 °C and 2–5 MPa) are

required to lower the energy barrier for CO molecule activation and the C–C coupling process in the FTO process. However, solar-driven FTS has emerged as a promising alternative to conventional thermocatalytic FTS, as it enables operation under milder reaction conditions with lower energy requirements.

Recent studies have shown that Fe-based supported catalysts exhibit high selectivity for C₂₋₄= products and demonstrate excellent reaction activity in the FTO process. For instance, Ou's group synthesized a Fe₅C₂-loaded N-doped carbon microsphere catalyst (Fe₅C₂/NC600) using a wet chemistry method.⁷⁵ This catalyst exhibited broad sunlight absorption ability, exceptional C₂₋₄= selectivity of 55.3% (CO₂-free) at 22.3% CO conversion, and superior catalytic activity, which was 3.5 times higher than that of pristine Fe₅C₂ in the photothermal catalytic FTO process. Characterization techniques such as XPS, XAFS, CO-TPD, and CO pulse reaction revealed that pyrrolic N in the N-doped carbon support acted as an electron donor, transferring electrons to the surface of the active Fe₅C₂ phase and modifying its electronic structure. This electron transfer process created electron-rich active sites, enhancing the CO adsorption and dissociation ability of the Fe₅C₂-based catalyst, thereby increasing the CO conversion rate (Fig. 8a). The author further



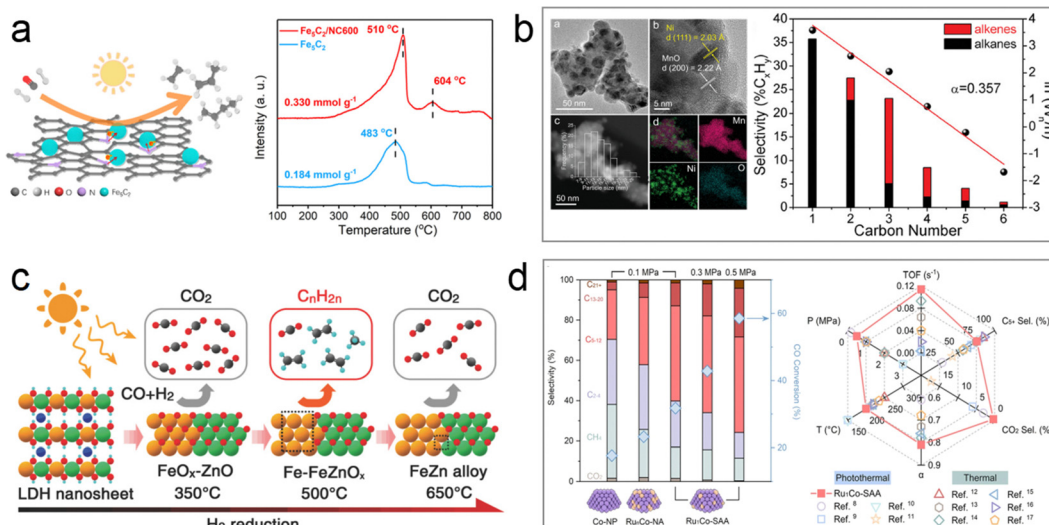


Fig. 8 (a) Scheme and CO adsorption ability of Fe₅C₂/NC600.⁷⁵ (b) Characterization data and product selectivity of the Ni/MnO catalyst.⁷⁶ (c) The CO hydrogenation selectivities of the Fe-x photocatalysts derived from ZnFeAl-LDH nanosheets at different temperatures.⁷⁷ (d) Comparison of FTS performance of Ru₁Co-SAA with other catalysts.⁸⁰

investigated a series of Fe₅C₂-based catalysts with different supports (hydrophobic silica, hydrophilic silica, α -Al₂O₃, γ -Al₂O₃, and α,γ -Al₂O₃) *via* a one-step wet-chemical method to explore the influence of metal-support interaction on the photothermal catalytic FTO process. It was found that the weak interaction between the active phase and α -Al₂O₃ supports favored the formation of Fe₅C₂, contributing to high selectivity for light olefins.

Research on Ni-based catalysts for the photothermal FTO process has also been conducted. One study focused on developing Ni-containing nanoparticles supported on MnO catalysts (Ni/MnO) derived from the reduction of NiMn mixed metal oxide.⁷⁶ The optimized Ni/MnO catalyst with a Ni:Mn ratio of 2:1 demonstrated excellent performance in FTO, achieving a high selectivity of light olefins (33%) at 14.9% CO conversion under UV-visible light irradiation (Fig. 8b). Characterization techniques such as XAFS and XPS analysis of the Ni-500 catalyst revealed the presence of MnO-supported Ni nanoparticles, which induced modifications in the electronic structure and valence of the Ni nanoparticles, resulting in the formation of Ni^{δ+} sites. This slight change in nickel valence hindered the strong hydrogenation ability typically associated with Ni⁰, leading to C-C coupling reactions that produced alkenes.

In one-step FTO processes, preventing the high selectivity for the by-product of CO₂ resulting from the WGS reaction remains a challenge. To address this issue, Zhang's group developed a series of Fe-based heterostructured photocatalysts by H₂ reduction of ZnFeAl-LDH precursor nanosheets at different temperatures (300–650 °C).⁷⁷ The Fe-500 catalyst (reduced at 500 °C), comprising Fe and FeO_x supported on ZnO and Al₂O₃, exhibited high selectivity (42%) for light olefins and low selectivity (11.4%) for CO₂ at a conversion of 20.9% in the photothermal FTO reaction. DFT calculations indicated that the abundant interface between Fe and FeO_x in the

Fe-500 heterostructured catalysts, along with moderate intermediate binding energies, contributed to the high selectivity for light olefins and suppressed CO₂ evolution (Fig. 8c). The author further investigated Co-based heterostructured catalysts derived from ZnCoAl-LDH precursor nanosheets.⁷⁸ Surprisingly, the Co-Co₃O₄/ZnO-Al₂O₃ catalyst exhibited high selectivity (36%) for light olefins at a CO conversion of 15.4%. The heterogeneous structure of oxide-modified metallic Co nanoparticles in this catalyst weakened the hydrogenation capacity of olefins, resulting in high selectivity for low carbon olefins.

In addition to light olefins, higher hydrocarbons (C₂₊) are valuable products in the FTS process. Zhang *et al.* reported a partial phosphidation strategy for preparing TiO₂-supported Ni₂P/Ni heterostructure catalysts for photothermal FTS reactions.⁷⁹ Precise control over the degree of phosphating in Ni/Ni₂P catalysts was achieved by adjusting the input amount of NaH₂PO₂ during synthesis. The optimized Ni/Ni₂P-based catalyst for CO hydrogenation exhibited remarkable C₂₊ selectivity of 70.7% at a CO conversion rate of 20.7% under Xe lamp irradiation and demonstrated excellent stability in flow reaction system testing. DFT calculations indicated that metallic Ni facilitated CO activation, while Ni₂P/Ni favored C-C coupling. The coexistence of both metals provided an efficient pathway for CO hydrogenation to C₂₊ products, inhibiting over-hydrogenation to methane.

Metal alloys such as Fe, Co, Ni, and Ru can also achieve high CO conversion rates and selectivity for specific products. Zhang's group recently developed an Al₂O₃-supported RuCo single atom (Ru₁Co-SAA) catalyst derived from LDH topological transformation for converting syngas into C₅₊ liquid fuels *via* the photothermal catalytic FTS process.⁸⁰ Characterization of the Ru₁Co-SAA structure confirmed the successful preparation of isolated Ru atoms on the surface of metallic Co nanoparticles. The Ru₁Co-SAA catalyst exhibited higher CO conversion

activity (58.6%) and C₅₊ product selectivity (75.8%) compared to Al₂O₃-supported Co nanoparticles or RuCo nanoalloys (Fig. 8d). Furthermore, the FTS performance of Ru₁Co-SAA at low pressure was comparable to that of traditional FTS catalysts under higher pressure conditions. Chemisorption experiments and DFT calculations revealed that the Ru-Co coordination environment in Ru₁Co-SAA promoted CO dissociation and C-C coupling of CH_x^{*} intermediates while inhibiting H₂ activation and over-hydrogenation of CH_x^{*} intermediates. This promoted the effective growth of carbon chains to liquid products. This work is expected to inspire the design of more bimetallic catalysts for photothermal catalytic systems to convert small C1 molecules into high-value chemicals.

4.1.2 Water-gas shift reaction. The water-gas shift reaction (WGS: CO + H₂O → CO₂ + H₂) plays a vital role in the modern chemical industry, which is highly significant, involving the conversion of CO and H₂O into CO₂ and H₂, making it essential for hydrogen production. To reduce energy consumption in H₂ production, researchers are actively seeking catalysts that efficiently activate water in the WGS reaction at low-temperature (below 250 °C).^{81,82}

A recent study conducted by Zhang *et al.* presented a remarkable discovery regarding the activity of noble-metal Au clusters and Pt₁-Pt_n clusters on α-MoC in low-temperature WGS reactions, which achieved unprecedented rates of H₂ production (Fig. 9a).⁸³ However, the utilization of noble metals for large-scale H₂ production is impractical due to their high costs and the substantial amount of heat energy required from electricity or fossil fuel combustion. Consequently, it becomes crucial to prioritize the design and development of non-noble metal catalysts capable of activating water and efficiently driving WGS reactions using clean energy at lower temperatures. Previous research has demonstrated that semiconductor photocatalysts can drive the WGS reaction at room temperature when exposed to light irradiation. Nevertheless, the hydrogen production rates achieved through photocatalysis fall significantly below industry standards.^{84–88}

In contrast, Cu-based photothermal catalysts for WGS have shown the ability to produce hydrogen at rates comparable to those of traditional high-temperature thermal catalysts when operated under light irradiation at 250–350 °C.^{85,86,89,90} The group led by Ye reported that CuO_x/Al₂O₃ exhibits excellent catalytic activity (122 μmol g_{cat}^{−1} s^{−1} H₂ evolution and >95% CO conversion) in the solar-driven WGS process under light irradiation, surpassing noble-metal-based catalysts (Au/Al₂O₃ and Pt/Al₂O₃) in efficiency (Fig. 9b).⁸⁶ This solar-driven WGS process incurred no electric or thermal power costs while achieving 1.1% light-to-energy storage. However, the presence of an oxygen vacancy at the interface between Cu and Cu₂O in this catalyst limited reaction kinetics due to its singularity. To address this, CeO₂ was introduced as a promoter to facilitate oxygen transport from the H₂O reduction active site to that of CO, resulting in a low-CO-residual WGS reaction under H₂-rich conditions at a reaction temperature as low as 225 °C.⁸⁷ Photocatalyst-enhanced photothermal catalysis over the CeO₂-loaded Cu_{1.5}Mn_{1.5}O₄ catalyst injects photocarriers into active sites and significantly reduces the apparent activation energy (decreased by 61%) (Fig. 9c).

However, it should be noted that photothermal catalysts for the WGS process exhibited inferior performance at temperatures below 250 °C when compared to thermal noble metal-based catalysts.^{91–95} By leveraging the LSPR effects in metal nanoparticle-based catalysts, such as Au, Ag and Cu, it becomes possible to significantly lower the operating temperature of the WGS reaction. The LSPR excitation generated hot electrons from copper nanoparticles, which were then transferred to adsorbates like water molecules, leading to enhanced activation of these adsorbates. This approach showed promise in overcoming the high energy barrier for water dissociation, resulting in improved WGS reaction activity under mild conditions. Zhao *et al.* synthesized a novel LDH-derived Cu-based catalyst (LD-Cu) for photo-driven WGS reactions, consisting of Cu nanoparticles dispersed densely on an amorphous alumina

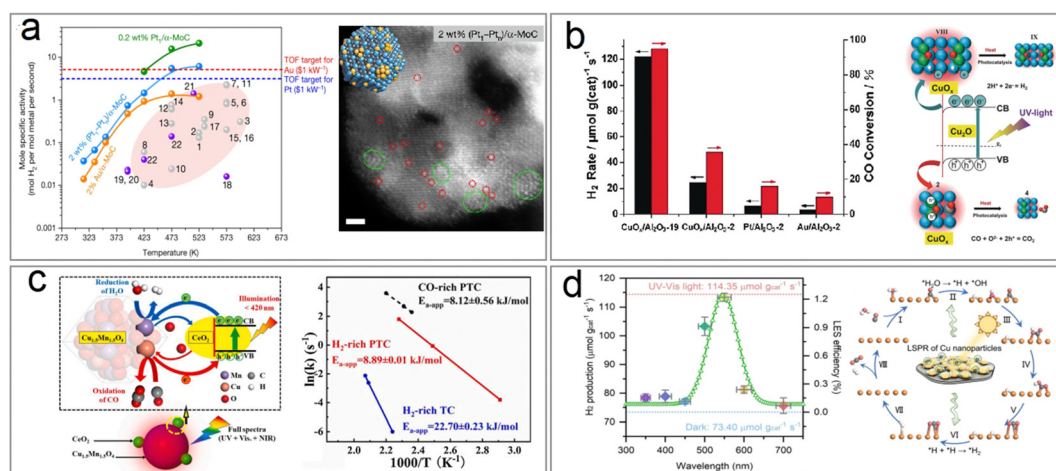
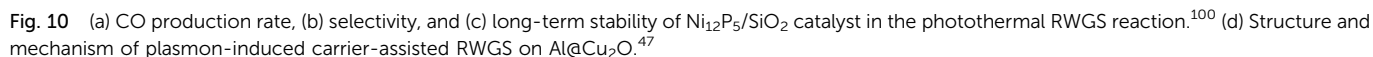


Fig. 9 (a) WGS performance and morphology of the Pt/α-MoC catalyst.⁸³ (b) WGS activity and mechanism of the CuO_x/Al₂O₃ catalyst.⁸⁶ (c) WGS reaction mechanism and the apparent activation energy of the CeO₂/Cu_{1.5}Mn_{1.5}O₄ catalyst.⁸⁷ (d) WGS reaction activity and mechanism of the LD-Cu catalyst.⁹⁶



The utilization of low-density carbon materials as supports can enhance the active mass loading and significantly improve



the overall CO productivity.¹⁰⁴ Very recently, Wang *et al.* presented a potassium-modified carbon-supported cobalt (K^+ -Co-C) catalyst that emulates the structure of a lotus pod.¹⁰⁵ As a result of the designed lotus-pod structure, which incorporated an efficient photothermal C substrate with hierarchical pores, an intimate Co/C interface featuring covalent bonding, and exposed Co catalytic sites exhibiting optimized CO binding strength, the K^+ -Co-C catalyst exhibited exceptional performances in the photothermal RWGS reaction, achieving a record-breaking rate of $758 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$, accompanied by an exceptional selectivity for CO at 99.8%, surpassing typical photochemical CO_2 reduction reactions by three orders of magnitude.

4.2.2 CO_2 methanation. Hydrogenation of CO_2 to methane, known as the Sabatier reaction, can proceed through different reaction pathways involving intermediate CO or formate species. Ye's group demonstrated the significant potential of group VIII metals (Ru, Rh, Ni, Co, Pd, Pt, Ir, and Fe) in enhancing the photothermal conversion of CO_2 . Catalysts such as Ru- Al_2O_3 , Rh- Al_2O_3 , and Ni- Al_2O_3 exhibited reaction rates several orders of magnitude higher compared to other photocatalysts.³⁸ Another investigation by Ma's group focused on the selectivity of Fe-based oxides and Fe-based carbides for CO_2 hydrogenation products.⁴² Fe_3O_4 exhibited 100% selectivity for CO production, while Fe_3C favored CH_4 production with 97% selectivity. By adjusting the carbonization conditions of the precursors, a series of iron base oxides and iron base carbides

can be prepared (Fig. 11a), allowing for a comparison of their selectivity in CO_2 hydrogenation products.

A recent development in the field involved a Pd-loaded WN- WO_3 heterostructure, which acted as a direct Z-scheme catalyst, broadening the absorption spectrum of solar energy for the photothermal-assisted conversion of CO_2 and H_2O into CH_4 .¹⁰⁶ The catalytic activity reached $40.6 \pm 0.7 \text{ mmol h}^{-1} \text{ g}^{-1}$ for CH_4 due to the unique carrier transfer mode of the Z-scheme catalyst. Under sunlight illumination, the WN- WO_3 heterostructure can efficiently separate and migrate photoinduced carriers, resulting in more energetic hot electrons involved in the reaction (Fig. 11b). The local photothermal effect facilitated the migration of gas molecules and carriers, thereby enhancing CO_2 conversion efficiency. Recent studies have also explored Ni nanoparticles supported on barium titanate perovskite for photothermal catalytic CO_2 conversion, achieving high CH_4 yields with nearly 100% selectivity. The dominant reactivity was attributed to a nonthermal hot-electron-driven pathway, aided by the local photothermal effect.¹⁰⁷

To further advance photothermal catalytic CO_2 hydrogenation, the effect of SMSI has also been investigated. For instance, Ru- Al_2O_3 -x-L, which is rich in defects, was grown *in situ* on aluminum foil using an ultraviolet pulsed laser, and then ultra-small Ru nanoparticles were loaded in a controllable manner to prepare Ru- Al_2O_3 -x-L, which achieved effective photothermal catalytic CO_2 methanation.¹⁰⁸ The willow fluff structured Al_2O_3 -x-L can effectively capture light and ensure a high light



Fig. 11 (a) Preparation strategy for photothermal catalysts with varying degree of hydrogenation/carbonization.⁴² (b) Schematic illustration of the charge-carrier migration mechanism according to the type-II and Z-scheme heterojunction for WN- WO_3 .¹⁰⁶ (c) (d) Schematic illustration of the flow reactor system and outdoor flow reactor system for photothermal CO_2 methanation.¹⁰⁸ (e) The proposed reaction pathways and B(OH)_x frustrated Lewis pair reaction pathway for CO_2 methanation.¹⁰⁹ (f) and (g) Schematic of the nanoscale greenhouse effect in $\text{Ni}@\text{SiO}_2$ -30 and T_{local} of different catalysts under different illuminations.¹⁰³ (h) and (i) Schematic of the new photothermal catalytic CO_2 methanation system and the CO_2 conversion rates of the catalysts.¹¹⁰

In the realm of photothermal catalysis, the release of thermal radiation into the surrounding environment represents wasted heat energy. To address this issue, Cai *et al.* developed a catalyst composed of nickel nanocrystals encapsulated in nanoporous silica with 30 nm-thick shells, known as Ni@p-SiO₂.¹⁰³ This catalyst demonstrated superior photothermal catalytic efficiency for CO₂ hydrogenation (Fig. 11f). When exposed to light illumination at 2.8 W cm⁻², the Ni@p-SiO₂ catalyst reached a maximum temperature of 334 °C, as measured using a contacting thermocouple. In comparison, the reference catalysts (Ni/SiO₂·Al₂O₃ and Ni-NC) only achieved temperatures of 314 and 300 °C, respectively. These results highlight the enhanced photothermal catalytic efficiency conferred by the core-shell structure. As the thermocouple had limitations in precisely reflecting the local temperature (T_{local}) of the catalysts, the authors estimated T_{local} based on the gas composition under reaction equilibrium conditions. The findings revealed that Ni@p-SiO₂ exhibited the highest T_{local} of 852 K, further confirming its potent photothermal effect (Fig. 11g). This supraphotothermal phenomenon originated from the greenhouse-like engineering of the SiO₂ shell, which acted as both heat insulation and infrared shielding, minimizing heat loss

4.2.4 Hydrocarbon production. While photothermal catalytic CO₂ hydrogenation has successfully produced C1 chemicals, there is a growing interest in synthesizing higher value-added C₂₊ hydrocarbon products.¹¹⁵ Although significant progress has been made in obtaining C1–C3 hydrocarbons from CO₂ hydrogenation, more efficient methods are required

to produce these valuable compounds. Presently, most catalysts employed for multi-carbon generation necessitate noble metal supports, combinations of metallic elements and various oxide catalysts, or the construction of complex catalyst structures. However, recent studies have shown promising results in achieving C_{2+} hydrocarbons through photothermal catalytic approaches. For instance, a CoFe-based photothermal catalyst derived from layered double hydroxide has been observed to produce C_{2+} hydrocarbons (Fig. 12a).⁴⁶ Additionally, Zhang *et al.* reported a dual-functional Au–Ru/TiO₂ catalyst capable of decomposing H₂O to H₂ while hydrogenating CO₂, enabling the conversion of CO₂ and H₂O into fuels through photothermal coupling catalysis.¹¹⁶ This study investigated thermocatalytic CO₂ hydrogenation, photothermal catalytic CO₂ hydrogenation, photothermal catalytic H₂O splitting to produce H₂, and photothermal catalytic reduction of CO₂ and H₂O. Au/TiO₂ exhibited high selectivity and productivity in thermocatalytic CO₂ hydrogenation, while Ru/TiO₂ demonstrated superior formation rates of CH₄ and C₂H₆. Although Au–Ru/TiO₂ shared similar

characteristics to Ru/TiO₂, its activity was slightly lower due to the partial blocking effect of Au. However, the production rates of CH₄ and C₂H₆ increased with temperature elevation. Under photothermal catalytic conversion of CO₂ and H₂, Au–Ru/TiO₂ exhibited significantly higher activities (Fig. 12b).

Recently, a Fe/FeO_x heterogeneous structure supported on MgO–Al₂O₃ mixed metal oxide, derived from hydrogen reduction of the MgFeAl–LDH precursor, has also been employed for photothermal catalytic CO₂ hydrogenation.¹¹⁷ The catalyst exhibited a surprising C_{2+} selectivity of 52.9% at a CO₂ conversion rate of 50.1% under UV-visible light irradiation. The coexistence of Fe and FeO_x was found to be favorable for promoting the C–C coupling reaction, thereby enhancing the selectivity of C_{2+} products (Fig. 12c). Notably, there was no discernible difference in performance between photothermal catalysis and thermal catalysis processes for CO₂ hydrogenation to C_{2+} .

In another work, Ning *et al.* prepared a Co⁰–Co^{δ+} structure catalyst through *in situ* photothermal activation. Co–CoO_x/MgAl₂O₄ achieved a C_{2-4} yield of 1303 μmol g^{−1} h^{−1} under light

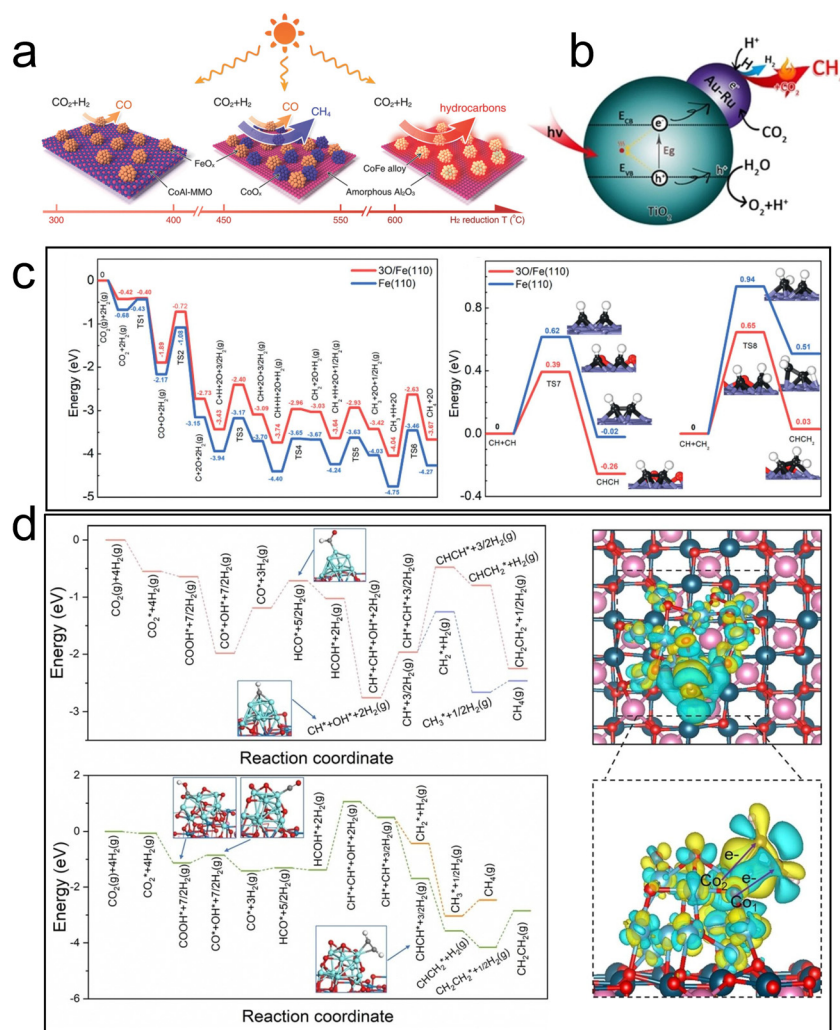


Fig. 12 (a) Illustration of selectivity in CO₂ hydrogenation over different CoFe-x catalysts.⁴⁶ (b) Coupling of thermocatalysis and photocatalysis in CO₂ hydrogenation over Au–Ru/TiO₂.¹¹⁶ (c) Potential-energy profile of possible pathways for CO₂ conversion at active sites.¹¹⁷ (d) C–C coupling mechanism of Co⁰ and Co⁰–Co^{δ+} over Co–CoO_x/MgAl₂O₄ by theoretical calculations.¹¹⁸

irradiation.¹¹⁸ The selectivity of C_{2–4} total organic carbon reached 62.5%, and the ratio of olefin to alkane reached approximately 11. Experimental and theoretical results confirmed that the two active sites at the interface effectively adsorbed and activated CO₂ to form C1 intermediates through the Co⁰ site. The introduction of the Co^{δ+} electron-deficient state effectively reduced the reaction energy of the key CHCH* intermediate, thus promoting the formation of low carbon olefin C₂₊ hydrocarbons (Fig. 12d). This study offers a novel approach to designing photothermal catalysts for the conversion of CO₂ to C₂₊ hydrocarbons through photoreduction.

4.3 Methane conversion

Methane, a colorless and odorless gas, serves as a vital building block in the chemical industry. It is primarily known for being the main component of natural gas and methane clathrates, which are found deep beneath the ocean floor. This versatile hydrocarbon feedstock plays a crucial role in the synthesis of fuels and other essential chemicals. The commercial production of H₂ heavily relies on catalytic steam reforming technology, along with partial oxidation and coal gasification methods. Therefore, it is evident that the conversion of CH₄ holds immense practical significance for the chemical industry.

4.3.1 Methane oxidation. Complete oxidation of methane (COM, CH₄ + 2O₂ → CO₂ + 2H₂O) is thermodynamically

favorable, but the resulting products have relatively low value compared to other chemical compounds. Partial oxidation of methane (POM) to value-added liquid commodities (like CH₃OH and HCHO, HCOOH, *etc.*) proves to be a more attractive option from a catalysis perspective.¹¹⁹ Recently, Tang's group constructed AuCu–ZnO photothermal catalysts modified with highly dispersed two-site cocatalysts (AuCu), achieving a breakthrough in the quantum yield of methane conversion at room temperature, reaching 14.1% (365 nm) (Fig. 13a–d).¹²⁰ On the basis of this work, the authors utilized a Pd single atom cocatalyst and co-modified oxygen vacancies in an indium oxide catalyst (Pd-def-In₂O₃), thereby extending the utilization range of the solar spectrum into visible region (Fig. 13e).¹²¹ They achieved direct conversion of methane under 420 nm visible light irradiation, with the yield of carbon-liquid products reaching nearly 100 μmol h^{−1} and the primary product selectivity (CH₃OH and CH₃OOH) as high as 82.5%. Mechanistic studies revealed that Pd single atoms and oxygen vacancies acted as photogenerated holes and electron acceptors, respectively, synergistically promoting carriers' separation and transportation. Isotope experiments and electron paramagnetic resonance spectroscopy demonstrated that O₂ was the sole source of oxygen for methanol production, while H₂O generated hydroxyl radicals (•OH) through photogenerated hole activation, which then activated methane molecules (Fig. 13f).

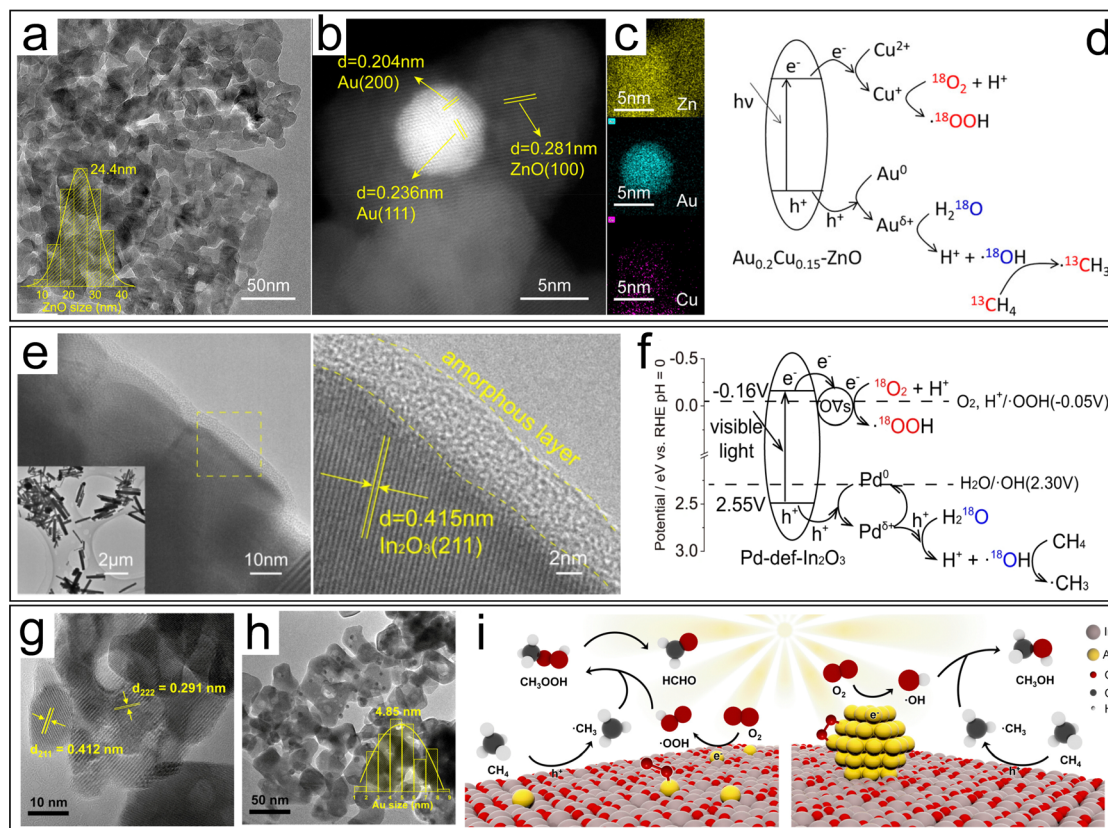


Fig. 13 (a) TEM image of ZnO. (b) HAADF-STEM and (c) EDS-mapping images of Au_{0.2}Cu_{0.15}–ZnO. (d) Methane conversion mechanism of AuCu–ZnO.¹²⁰ (e) HRTEM images and (f) CH₄ conversion mechanism of Pd-def-In₂O₃.¹²¹ TEM images of (g) Au₁/In₂O₃ and (h) AuNPs/In₂O₃. (i) Proposed mechanism of photocatalytic conversion of CH₄ to HCHO or CH₃OH on Au₁/In₂O₃ and AuNPs/In₂O₃, respectively.¹²²



Very recently, Jiang *et al.* achieved high yields and selectivity for CH_3OH (6.09 mmol g^{-1} , 97.62%) and HCHO (5.95 mmol g^{-1} , 89.42%) by precisely controlling the efficient path of free radicals ($\cdot\text{OOH}$ and $\cdot\text{OH}$) formed during the reaction process. They achieved this by adjusting the band structure of the semiconductor and controlling the size of the active site (either Au single atoms or Au nanoparticles) in the $\text{Au}/\text{In}_2\text{O}_3$ catalyst (Fig. 13g–i).¹²²

4.3.2 Non-oxidative coupling of methane. Non-oxidative coupling of methane (NOCM) is an attractive reaction that directly converts methane to C_{2+} and H_2 . However, conventional catalytic NOCM processes face challenges due to the high stability of CH_4 molecules and the extremely strong C–H bond

energy, necessitating elevated temperatures for activation. Unfortunately, these high temperatures often lead to side reactions, such as coke formation and catalyst deactivation. The introduction of photocatalysts offers a promising solution by overcoming the CH_4 activation barrier, opening up new possibilities for this process. One notable example is $\text{Pt}/\text{black TiO}_2$ (Pt@BT-O) photothermal catalysts, which exhibited remarkable alkane dehydrogenation properties under near-infrared light and at room temperature (Fig. 14a and b).¹²³ The authors achieved a conversion rate of 8.2% of methane into propane with a selectivity of 65%, which is impressive considering that ethane is typically the dominant product. The proposed mechanism involves intramolecular dehydrogenation of methane, resulting

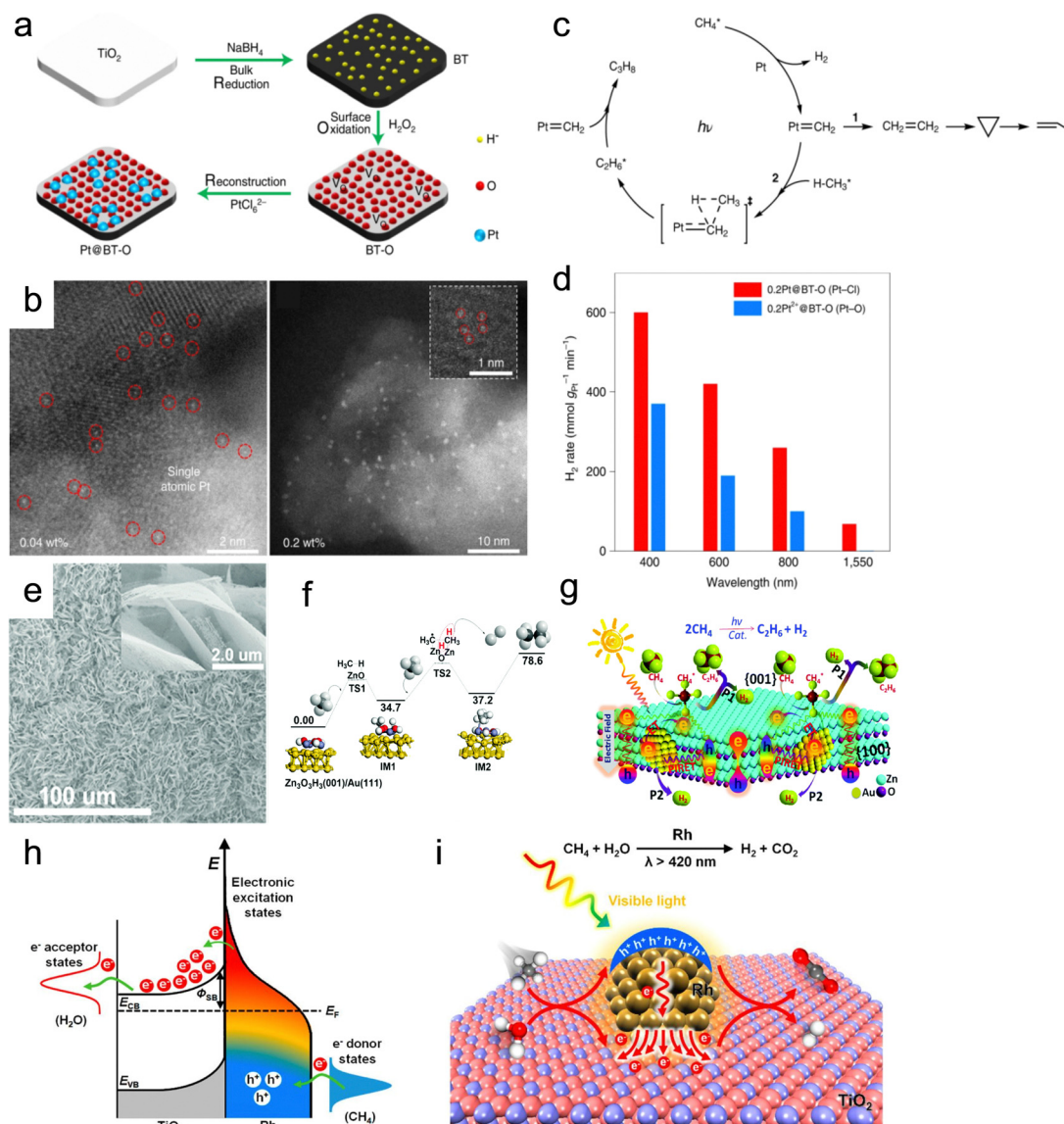


Fig. 14 (a) Synthesis and (b) characterization of the Pt@BT-O catalyst. (c) Proposed mechanism and (d) catalytic activity of catalysts for cyclohexane dehydrogenation.¹²³ (e) SEM image of the Au/ZnO photothermal catalyst. (f) Potential energy diagram for the methane coupling reaction on $\text{Zn}_3\text{O}_2\text{H}_3(001)/\text{Au}(111)$ clusters. (g) Schematic description for the dehydrogenative coupling of methane into ethane over Au/ZnO .¹²⁴ (h) Schematic of energy transfer from photoexcited hot carriers to adsorbate states. (i) Mechanism description for the SRM reaction on Rh/TiO_2 under visible light illumination.¹²⁵



4.3.4 Dry reforming of methane. Photothermal catalytic dry reforming of methane (DRM: $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$) has emerged as an alternative to traditional thermal DRM, offering sustainable and low-temperature advantages. Extensive literature studies suggest that Ni-based catalysts are promising candidates for DRM in both thermal and photo-driven catalysis.¹²⁷ Recently, Hu *et al.* reported a unique nickel semi-metallic catalyst with a single-layer Ni cluster stabilized by Al_2O_3 , exhibiting 100% atomic utilization efficiency and remarkable catalytic performance in photothermal DRM.¹²⁸ This catalyst demonstrated exceptionally high yields of H_2 and CO , reaching 8573.0 and 9614.3 mmol $\text{g}_{\text{Ni}}^{-1} \text{min}^{-1}$, respectively, which were one order of magnitude higher than those for Ni nanoparticles. Moreover, the change in DRM kinetic process

In recent times, the integration of plasmonic ‘antenna’ metal nanoparticles with catalytically active ‘reactor’ materials has emerged as a remarkable strategy to enhance the efficiency, selectivity, and specificity of photocatalytic reactions. This innovative configuration harnesses the local optical field generated by the antenna to effectively convert the catalyst into a highly efficient photocatalyst. Zhou *et al.* synthesized a series of photothermal catalysts with different Ru loadings on the MgO–Al₂O₃ composite support by a coprecipitate method, and the impact of Ru concentration on the photothermal catalytic performance of Cu–Ru surface alloys was investigated, revealing that isolated Ru atoms on the Cu surfaces exhibited excellent DRM activity (Fig. 15b).¹³⁰ Through temperature programmed oxidation and thermal catalysis of isotopic reactants, it was determined that methane was the sole source of coke production. The authors speculated that CH₄ and CO₂ molecules first dissociated on the catalyst surface to form H^{ads}, C^{ads}, O^{ads} and CO^{ads}, respectively. The desorption of H₂ was accelerated by the hot carrier through the electron transition mechanism, which inhibited the reaction between H^{ads} and O^{ads}, leading to high photocatalytic selectivity. This inhibition can effectively promote the removal of carbon and improve the stability of the catalyst. In addition, H^{ads} was more likely to react with O^{ads} in the thermal catalytic process, and the lower decarbonization efficiency of O^{ads} led to lower selectivity and stability of the thermal catalytic reaction. The excellent photothermal catalytic performances with long term stability (50 h) and high selectivity (>99%) can be attributed to the light-excited hot carriers and single-atom active sites.



Fig. 15 (a) Schematic and DRM performance of the Ni/Ga₂O₃ catalyst.¹²⁹ (b) Schematic of enhanced selectivity and stability in Cu–Ru surface alloys.¹³⁰ (c) Oxygen vacancy formation energy of the Pt/CeO₂ catalyst.¹³¹ (d) Schematic diagram for the light-driven DRM reaction over the Rh/Ce_xWO₃ catalyst.³

The construction of interfaces between single atoms and oxide catalysts with a synergistic effect has been proven to be effective in improving atomic utilization, reducing reaction energy consumption, and enhancing catalytic activity. For instance, the DRM reaction was catalyzed by a Pt monatomic catalyst supported by CeO₂ (Pt/CeO₂) with different morphologies at low temperature (300–450 °C).¹³¹ Experimental and theoretical results demonstrated that rod-like CeO₂-R with abundant defects provided better anchoring for Pt monatoms, while Pt doping induced surface reconfiguration of CeO₂, significantly reducing the oxygen vacancy formation energy of CeO₂-R. The Pt–O lattice structure at the interface facilitated CH₄ oxygen-assisted dissociation, leading to CO formation through CH_xO intermediates. CO₂ was adsorbed and dissociated at the Pt–CeO₂ interface, generating CO and O lattice species to complete the catalytic cycle (Fig. 15c). Similar photo-induced redox cycles can occur in other heteronuclear bimetallic photocatalysts with oxygen bridging bonds. Yang *et al.* reported a highly active and coke-resistant DRM photocatalyst consisting of 3 nm Rh nanoparticles uniformly dispersed on Ce_xWO₃ nanosheets.³ This catalyst utilized full-spectrum sunlight without the need for an external heat source and achieved a light-to-chemical energy efficiency of 4.65% under mild conditions. Metal-to-metal charge transfer induced by light facilitated the redox cycle, improving the catalyst's reaction activity and stability. Rapid oxygen migration assisted in the removal of carbon deposits and reduced the reaction start-up temperature. The authors attributed the catalyst's high performance, including H₂ and CO evolution rates of 88.5 and 152.3 mmol g_{Rh}^{−1} h^{−1}, respectively, to the strong CO₂ absorption on the Ce_xWO₃ surface, the high mobility of oxygen and the electron transfer from Ce to W species (Fig. 15d). This construction of a heteronuclear bimetallic photocatalyst with oxo-bridge bonds provides valuable insights for the design of low-temperature DRM catalysts.

5. Summary and outlook

In summary, photothermal catalytic C1 chemistry offers a cleaner pathway for fuel synthesis using solar energy, which is particularly crucial in the face of climate change and the need for energy structure transformation. Supported catalysts with excellent optical properties and high specific surface area offer an ideal platform for photothermal catalysis. In this paper, we review the mechanism of photothermal catalysis, the design strategy for supported photothermal catalysts, and recent research progress in photothermal catalysis for C1 chemistry, including CO conversion (Fischer–Tropsch synthesis and water-gas-shift reaction), CO₂ conversion (reverse water-gas-shift reaction, methanation, methanol and higher hydrocarbon production), and methane conversion (oxidation, non-oxidative coupling, steam reforming, and dry reforming). Although significant progress has been made in the development of supported photothermal catalysts with excellent optical properties and high specific surface area, the field of photothermal catalysis is still in its early stages. Several challenges and prospects for future work can be identified:

(1) In order to further improve the performance of photothermal materials, it is still challenging to design materials with extremely high light absorption over a wide wavelength range, photothermal conversion ability, catalytic ability, and material stability. Advancements in this area are crucial to enable the cost-effective mass production of photothermal materials for everyday life and industrial applications.

(2) Distinguishing the differences between photocatalysis and thermal catalysis pathways in the context of photothermal processes is essential. Current temperature measurement methods, such as thermocouples or infrared cameras, provide macroscopic measurements but do not accurately reflect the local temperature of nanoparticles or fully capture the photothermal catalytic mechanism. Exploring new thermometry

(3) By harnessing the power of light and heat, we can transform harmful gases like CO_2 and CH_4 into valuable polycarbon alkanes/olefins and other high-value chemicals. But this technology has even greater potential than just reducing emissions – it can also help us tackle industrial waste gases that would otherwise go unused. With further research and development, we can unlock a whole new world of possibilities for creating sustainable, profitable products from what was once considered waste.

There are no conflicts to declare.

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