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Jinqiang Zhang

Haijun Chen

Xiaoguang Duan

Hongqi Sun  
*Edith Cowan University*

Shaobin Wang

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# Photothermal catalysis: From fundamentals to practical applications

Jinqiang Zhang<sup>a</sup>, Haijun Chen<sup>b,\*</sup>, Xiaoguang Duan<sup>a</sup>, Hongqi Sun<sup>c,\*</sup>, Shaobin Wang<sup>a,\*</sup>

<sup>a</sup>School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

<sup>b</sup>Jiangsu Key Laboratory of Process Enhancement and New Energy Equipment Technology, School of Mechanical and Power Engineering, Nanjing Tech University, Nanjing 211816, Jiangsu, China

<sup>c</sup>School of Science, Edith Cowan University, 270 Joondalup Drive, Joondalup, WA 6027, Australia

Photothermal catalysis is an innovative approach that integrates photochemical and thermocatalytic processes to enable an efficient use of full-spectrum sunlight in catalyzing various chemical reactions for energy conversion and environmental governance. This approach has demonstrated competitive performance and energy efficiency compared to conventional techniques, making it suitable for large-scale applications. In this review, we will comprehensively examine the fundamentals and classification of photothermal catalysis and discuss detailed design principles of various types of photothermal catalysts, focusing on enhancing solar light absorption, improving internal electric field for more energetic hot carriers (EHC) and localized thermal energy (LTE), interfacial engineering for robust and directed EHC transferring, and regulating EHC and LTE for continuous 24/7 operation. We will also report photothermal catalysis in a diverse range of chemical reactions. Moreover, we will introduce the latest technologies for synthesizing robust photothermal catalysts and advanced solar concentrators for pilot testing in the production of solar fuels at scale. Finally, the future opportunities and challenges of the promising but fledgling field will be discussed, which is expected to transform conventional chemical industries into a clean and sustainable manner.

**Keywords:** Photothermal catalysts; Design principles; Solar conversion; Chemical fuel production; Upscaling technology

## Introduction

Our world has been experiencing a global energy crisis, which has become exacerbated in the aftermath of the COVID-19 pandemic, with widespread shortages and soaring prices in oil, gas, and electricity markets worldwide. Although the world possesses 46.6 times as high as its annual consumption levels of proven oil reserves, the depletion of fossil fuels as non-renewable energy is inevitable [1]. Additionally, burning fossil fuels emits a vast amount of carbon dioxide into the atmosphere, causing global warming and climate change [2,3]. It is estimated that human

activities, especially the combustion of fossil fuels, have increased the Earth's global average temperature by approximately 1 °C since the pre-industrial period, and this number is currently increasing by more than 0.2 °C per decade. The effects of climate change on the environment are already noticeable, with glaciers and ice sheets reducing, river and lake ice breaking up earlier, and plant and animal ranges shifting. As a result, it is crucial to transform the conventional framework of energy utilization, which relies mainly on fossil fuels, into clean and renewable energy sources.

Solar energy is a highly sustainable source of energy that can be captured using various technologies such as solar photovoltaics (PV) [4], solar thermal converters [5], and concentrated solar power (CSP) systems [6]. At the top of the Earth's

\* Corresponding authors.

E-mail addresses: Chen, H. (chenhj@njtech.edu.cn), Sun, H. (h.sun@ecu.edu.au), Wang, S. (shaobin.wang@adelaide.edu.au).

atmosphere, about 1360 W per square meter ( $\text{W/m}^2$ ) of solar radiation can be received on average, while the amount of solar radiation on the Earth's surface is around 1000 to 1200  $\text{W/m}^2$  due to atmospheric absorption and scattering [7]. Despite the abundance of solar energy available, it only accounts for a small portion of the global primary energy supply. In 2020, the international energy agency reported that combined solar PV and solar thermal power accounted for merely 2% of the world's total primary energy supply. As such, highly efficient solar energy capturing and converting technologies are required to maximize the utilization efficiency of full-spectrum sunlight.

One of the promising pathways for the efficient transportation of solar energy is solar fuels, which are synthetic fuels produced from solar energy driven chemical reactions [8]. Solar fuels are considered to be the most economically viable and efficient solution for clean energy transportation and can be produced at a scale in an environmentally friendly way [9]. There are two pathways for solar energy to be converted into useful forms: solar-to-energetic hot carriers (EHC) [10] and photo-localized thermal energy (LTE) [11]. Photocatalysis is an example of a solar-to-EHC process where light irradiation is used to excite EHC in photocatalysts for chemical reactions [12,13]. The emergence of photocatalysis technology is a milestone in environmentally sustainable energy research [14]. However, the low reaction rate of photocatalysis ( $R_{\text{photo}} \propto I^{0.5}$ ,  $I$  represents light intensity) and the unfavourable selectivity to the target products significantly limit the widespread utilization of solar energy resources [15]. Additionally, most photo-induced thermal energy in a photocatalytic process is lost by cooling systems, leading to inefficient energy utilization. Therefore, a well-designed photo-driven catalytic system with a high catalytic activity and minimal energy loss is essential for maximizing the utilization efficiency of global solar irradiance and mitigating the dependence on conventional fossil fuels.

Photothermal catalysis has been proposed as a promising alternative to conventional photocatalysis and thermocatalysis for energy transformation and environmental remediation due to its unprecedented light harvesting efficiency, superior throughputs, and moderate reaction conditions [16,17]. This technology integrates solar energy mediated photochemical processes and solar light-induced thermocatalysis into a single unit, creating a complementing and synergistic effect. When the catalyst materials absorb light, EHC are generated to directly participate in chemical reactions [18,19], while those that fail to participate in will be converted into heat by thermalization [20]. Consequently, photothermal catalysis compensates for the disadvantages of photocatalysis and thermocatalysis, improving reaction selectivity and reducing reaction barriers. By using full-spectrum solar light, photothermal catalysis has raised the reaction rates to an industrial level, making it a promising solution for a large-scale production of solar fuels [21,22].

To upscale photothermal catalysis technology, two key components are required: efficient and stable photothermal catalysts that are scalable and precise for high-throughput processes, and development of green and cost-effective technological processes that minimize energy loss [23]. To achieve these objectives, researchers have been utilizing materials science, nanotechnol-

ogy, and computational modelling to engineer various photothermal materials such as metal-, semiconductor-, carbon-based and single atom materials, as well as their hybrids [24–26]. Furthermore, cutting-edge technologies such as 3D printing have been successfully utilized for a precise and large-scale preparation of photothermal materials [27,28]. The design and optimization of reaction facilities also play a crucial role in determining the efficiency of solar energy conversion and mass distribution and transfer [23]. Light-focusing devices, for instance, significantly impact the intensity and duration of light to activate the catalyst and drive the reaction, thus its integration with reactors have been designed to reduce energy loss [29]. Although photothermal catalysis has witnessed rapid growth and remarkable performance improvements, as a field in its infancy, the concept of photothermal catalysis is still not clearly defined and catalyst design strategies are still lacking. Therefore, a comprehensive review of fundamental investigations and large-scale applications is both necessary and timely.

In this review, we aim to present the fundamental principles underlying photothermal catalytic processes, explore the key considerations in catalyst design and discuss the technological processes involved in scaling up the production of solar fuels through the photothermal catalytic processes (Fig. 1). The review begins with a brief introduction to the fundamentals of photothermal catalytic technology, including the origins of EHC, LTE and their interactions, as well as the classification of this technology. Emphasis will be put on the development of new types of photothermal materials for intensified full-spectrum sunlight absorption, enhanced generation and directed accumulation of EHC and LTE and their efficient regulations. The goal is to achieve highly efficient and stable harvesting of solar energy for robust and continuous contribution to photothermal catalysis. The versatile applications of photothermal catalysis in chemical reactions towards green energy generation are then systematically discussed, including liquid–solid, gas–solid and solid–solid phase reactions. Additionally, the technological process involved in material scaling manufacture and high-flux sunlight capture for catalyzing chemical reactions on a large scale is briefly reviewed. Further perspectives are presented on the integration of photothermal catalytic technology into traditional chemical blocks, aiming at exploring efficient photothermal catalysts for high solar energy conversion efficiency and yields of solar fuels, while renovating traditional facilities of chemical industry production in cost-effective and low energy loss manners. This review is anticipated to provide new insights toward the understanding and engineering of the key components in upscaling applications of photothermal catalysis, further accelerating the development of this important research area.

## Fundamentals of photothermal catalysis

Photothermal catalysis is a technique sharing the same goal with photocatalysis to harvest solar energy for initiation of chemical processes, but completely differs from photocatalysis in reaction mechanism. In this process, when a catalyst absorbs photons, it converts solar energy into two essential components: EHC and LTE (Fig. 2) [30]. The EHC can be used to directly inject into



FIG. 1

Schematic illustration of the photothermal catalysis from fundamentals, catalyst design and application in diverse chemical reactions for industrial production of solar fuels.

the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the reactants for redox reactions or assist in lowering the specific bonding energy required for thermocatalytic processes [20]. Meanwhile, the LTE obtained from the cooling of hot carriers can be utilized to overcome energy barriers that prevent reaction initiation or accelerate reaction kinetics and photo-excited charge dynamics in photochemical processes [31]. The participation of these two components makes photothermal catalysis more advantageous than single component-driven conventional photocatalytic and thermocatalytic processes.

For instance, dry reforming of methane with  $\text{CO}_2$  (DRM) is an industrialized route to produce syngas that can be used for hydrogen generation and Fischer-Tropsch synthesis of high value-added chemicals and fuels, such as methanol and gasoline [2,32,33]. As a highly endothermic reaction, critical temperatures and pressures are required to overcome the thermodynamic energy barrier of DRM [34]. Here, photothermal catalysis can help highlight benefits in terms of energy efficiency, cost, safety, and environmental impact by triggering the DRM process at ambient conditions of room temperature and pressure [35,36]. In addition, coupling photochemical processes with thermocatalysis has been shown to yield better performance and selectivity for syngas than photocatalysis or thermocatalysis alone [37–39]. Moreover, the photothermal catalytic technology offers greater control over reaction conditions compared to thermocatalysis, as the temperature of the photothermal catalytic reaction can be precisely adjusted by modifying the wavelength and intensity of the light source [33,40–42]. Therefore, photothermal catalysis is an exciting area of research with great potential for advancing our understanding of catalytic processes and developing new technologies for energy conversion.

In the following sections of the paper, the origins and interactions of EHC and LTE in photothermal catalytic processes will be elucidated. The types of photothermal catalysis will also be clarified to help design and develop highly efficient catalysts for energy conversion and preparation.

### Photochemical processes

A photo-to-electron process is a term widely referred in photovoltaics and photocatalytic technologies to describe the conversion of solar energy into electrical energy [45]. This process involves the absorption of photons (light energy) by a material, such as a semiconductor or plasmonic metal nanoparticles, to excite electrons and generate a flow of electric current [46–48]. The mechanism of semiconductor-based photocatalysis involves the excitation of electron-hole pairs due to the suitable band structure upon absorbing equivalent photons of light [49]. As a result, the excited electrons and holes can participate in chemical reactions with adsorbed molecules, generating reactive intermediates that lead to the desired reaction [50]. More specifically, when a photocatalyst is exposed to light, it absorbs photons to excite electrons from the valence band (VB) to the conduction band (CB), creating electron-hole pairs [51]. These excited electrons and holes can separate and move to the surface of the photocatalyst, where they participate in redox reactions with adsorbed molecules on the surface (Fig. 2a) [43]. Inorganic (e.g., metal oxides [52,53], transition metal dichalcogenides [54–56], and black phosphorus [57]) and organic semiconductor-based photocatalysts (e.g., carbon nitride [58,59], metal organic frameworks [60,61] and covalent organic frameworks [62]) have been developed and used in various applications, including water splitting [21,63,64],  $\text{CO}_2$  reduction [65], and organic pollutant degradation [66]. Despite the promising potential, the weak internal electrical field in semiconductor-based photocatalysis always results in fatigue charge carriers and short diffusion length of EHC, thereby leading to poor photo-to-electron conversion efficiencies [67].

Plasmonic metal nanoparticles, especially those made of Au, Ag, and Cu, have demonstrated the great potential as photo-to-electron conversion materials [68]. The localized surface plasmon resonance (LSPR) effect plays a crucial role in plasmonic catalysis and allows it to be distinguished from semiconductor-based photocatalysis [24,69]. When sunlight strikes plasmonic nanometals and the photon's energy matches the metal's work function, the energy becomes stored in the collective resonant oscillations of

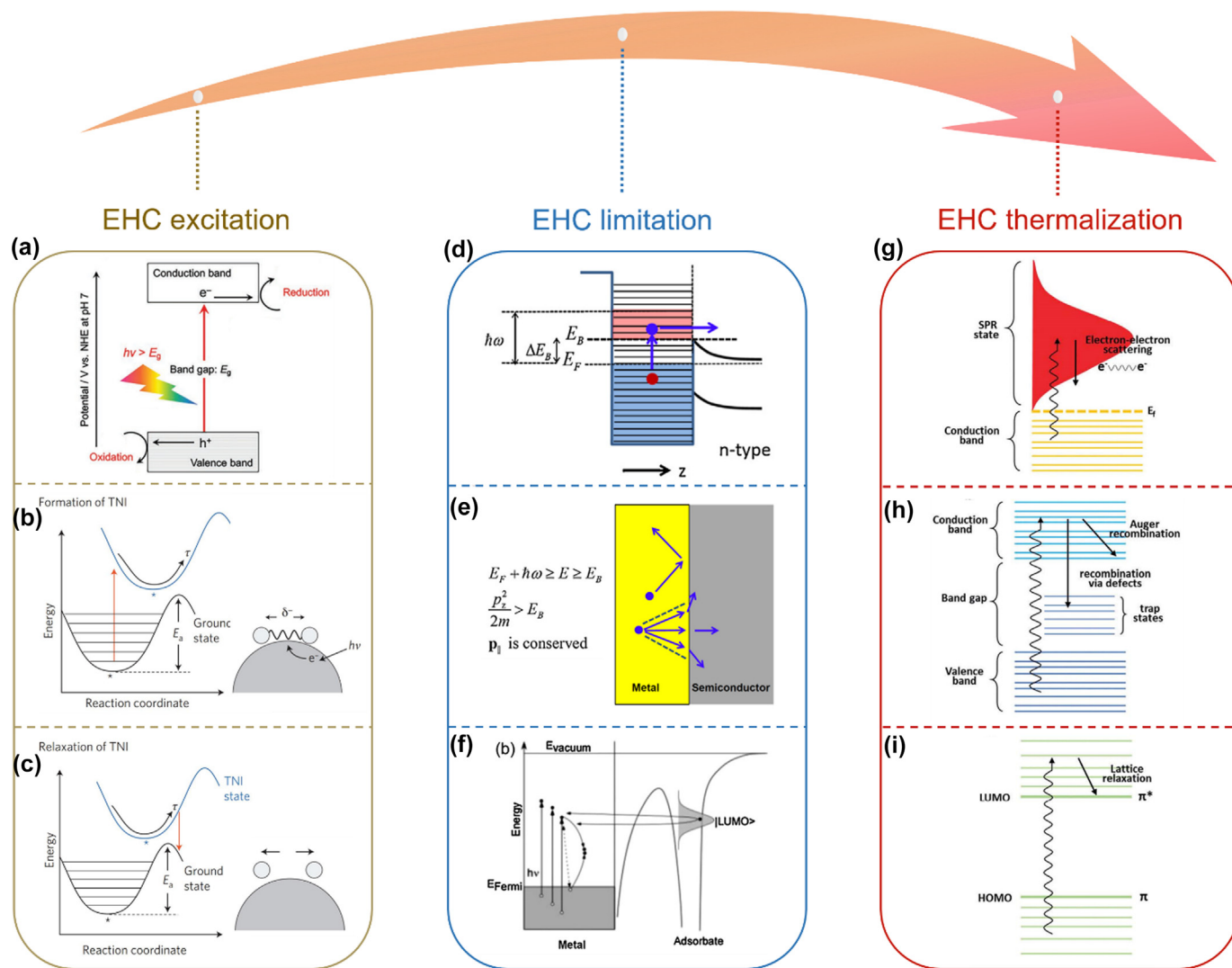


FIG. 2

Fundamentals in photothermal catalysis, including (a-c) EHC excitation, (d-f) EHC limitation for injection into HOMO/LUMO of reactants, and (g-i) EHC thermalization. (a) Mechanism of EHC generation in a semiconductor-based catalyst [43]. (b-c) EHC excitation pathway of a plasmonic nanometal [19]. Proposed mechanism for electron-induced reactant molecular dissociation on a photo-excited plasmonic metal.  $E_a$  stands as the activation barrier for dissociation [44]. (d-f) Requirements for EHC to be injected into a semiconductor and an adsorbate [20]. Photothermal effect of (g) plasmonic nanometal, (h) semiconductor and (i) carbon-based and organic materials [7].

conduction electrons, resulting in the LSPR effect. Although only a tiny fraction of photo-excited hot electrons is emitted in the form of radiative emission, most of these electrons generate photo-excited charge carriers through intraband or interband extinction, also known as Landau damping [70]. These hot carriers are capable of driving catalytic reactions, provided their energy is sufficient to exceed the LUMO of the reactant molecules. Plasmonic hot carrier-induced catalysis follows a transient negative ion (TNI) mechanism [71]. The adsorbate begins on its ground-state potential energy surface, followed by electron-scattering leading to the formation of TNI (Fig. 2b). The adsorbate then follows the potential energy surface of TNI and obtains kinetic energy along the reaction coordinate. After a short duration, the electrons decay back to the metal Fermi level, and the adsorbate returns to the ground-state potential energy surface with increased vibrational energy (Fig. 2c). If the energy transfer exceeds the activation energy, the reaction takes place.

In comparison to semiconductor photocatalysts, a critical feature of plasmonic photocatalysis is that the plasmonic nanoparticles exhibit stronger capability to absorb light in the visible and near-infrared regions, enabling a full-spectrum sunlight utilization. Additionally, plasmonic-enhanced EHC driven photocatalysis exhibits a linear dependence on the reaction rate with respect to light intensity ( $R_{\text{photo}} \propto I^n$ , where  $I$  represents light intensity and  $n > 1$ ), leading to significant activities [72]. However, the use of nanometals, particularly coinage metals, in plasmonic photocatalysis raises concerns due to their scarcity and environmental impact. Alternatively, titanium nitride (TiN) emerges as a promising plasmonic material to exhibit superior solar light harvesting efficiency and satisfactory catalytic performance [73–75]. Notably, TiN holds a promise for future large-scale applications due to its significantly higher natural abundance compared to costly materials like Au or Ag. By utilizing TiN, plasmonic photocatalysis can achieve efficient

light absorption and catalysis while addressing environmental and scalability issues.

### Photo-to-thermal processes

Photo-to-thermal conversion is an innovative technology that harnesses solar energy to produce heat in a sustainable and eco-friendly manner. The process relies on the non-radiative relaxation, which indirectly converts irradiation into heat, as well as absorption of infrared (IR) radiation, which directly converts solar radiation into thermal energy. In a Schottky heterojunction, the energy of the excited electrons in plasmonic nanometals must be within the limitations of  $E_F + \hbar\omega \geq E \geq E_F + E_B$  and  $p^2/2m > E_B + E_F$  for the hot electrons to be injected into the semiconductor (Fig. 2d-e) [20]. However, if the hot carriers fail to overcome the Schottky barrier or the anti-bonding orbital of the reactant molecule (Fig. 2f), hot electrons will release their energy through Ohmic damping and transfer them to phonon modes, leading to an increase of temperature on the nanometals and their surroundings (Fig. 2g).

Additionally, non-radiative relaxation occurs on semiconductor-based catalysts through either Auger recombination or Shockley-Read-Hall recombination (Fig. 2h). This leads to the dissipation of excessive energy as lattice vibrations or phonons, resulting in heat generation. The dissipation of energy in the form of phonons can cause the local heating of the lattice, resulting in a temperature distribution reliant on optical absorption and bulk/surface recombination. The optically excited charge carriers then diffuse and recombine, establishing a temperature distribution that leads to the photothermal effect of semiconductor materials.

Furthermore, carbonaceous and organic materials exhibit a photothermal effect that is highly dependent on the  $\pi$  to the  $\pi^*$  orbitals, which requires a lower energy input (Fig. 2i) [76]. When a material is illuminated by light whose energy matches an electronic transition within the molecule, an electron would be promoted from the ground state to a higher energy orbital. The excited electrons relax by means of electron phonon coupling, hence, the light energy absorbed is transferred from the excited electrons to vibrational modes throughout the atomic lattices, leading to a temperature rise in the material.

Consequently, the photo-to-thermal process always follows the photoelectrical process in photothermal catalysis. Only the hot carriers that are not effectively output for redox reactions can be decayed into LTE, which forms the foundation regarding the classification of photothermal catalysis and the design and development of photothermal catalysts. Besides, advanced technologies, such as transient absorption spectroscopy, are highly required to distinguish the photochemical and photo-to-thermal processes for mechanistic investigations, considering the varying lifetimes of hot carriers ranging from fs to ns in the photothermal catalysis.

### Interactions between photochemical and thermocatalytic processes

Photocatalysis and photo-driven thermocatalysis are two interrelated processes and significantly contribute to photothermal catalytic performance. The difference is that photocatalysis employs solar energy to excite electrons, elevating their energy levels and

resulting in reactive intermediates such as free radicals and TNI for chemical reactions, while photo-driven thermocatalysis utilizes solar energy to generate localized heat and thereby initiate chemical processes. Combining these two processes in a single photothermal catalytic unit can have a multifaceted promoting effect. Specifically, traditional thermocatalytic reactions typically require critical reaction conditions, such as high temperature and pressure. However, photoexcitation has been harnessed to unlock low-temperature equilibrium regimes and increase catalyst temperature, thereby promoting thermocatalytic reactions [77]. Additionally, EHC's participation in thermocatalytic processes increases selectivity by injecting into specific reactive intermediates [40]. Thermal energy, in turn, can be used to overcome the limitations of photocatalysis and promote the excitation and generation of EHC [78,79]. Thus, visible and near infrared light can be used to drive photochemical reactions when thermal energy is supplied to the photothermal catalytic system [80]. Moreover, this cooperation is effective because elevated reaction temperature significantly reduces the redox potentials of reactants, enabling EHC's involvement in redox reactions [81].

Nonetheless, suppressing effects between photochemical and thermocatalytic processes in photothermal catalysis also exist. Specifically, at higher temperature, the charge dynamics will slow down and EHC decay rates promote. The contribution from EHC to photothermal catalysis in such conditions therefore remains a topic of debate. Additionally, we have experimentally found that photochemical and thermocatalytic processes compete for active sites on a photothermal catalyst, with thermocatalysis occupying more active sites when the temperature reaches the minimum onset temperature of thermocatalysis, resulting in a diminished EHC output [82]. As such, it is vital to quantify the contributions of EHC and LTE to photothermal catalysis and optimize their interactions to maximize light harvesting efficiency and photothermal catalytic performance.

### Classification of photothermal catalysis

Based on the above discussions on photochemical and photo-to-thermal processes, photothermal catalysis can be categorized into three groups, depending on the extent of the contribution from thermal energy to the catalytic process. These categories are thermal-dominated photothermal catalysis (TPT), carrier-thermal coupling catalysis (CTC), and hot carriers dominated photothermal catalysis (CPT) (see Fig. 3). It is important to note that externally heated photocatalysis represents a distinct type of photothermal catalysis where a portion of the thermal energy is supplied through external heating [82]. With the advancement of light-concentrating devices, solar concentrating technology is expected to eventually replace the need for external heating, initiating chemical reactions in a more sustainable and cleaner manner [83,84]. This particular process can be further classified into TPT and CTC processes based on the combined contribution of thermal energy, including both photo-generated thermal energy and externally supplied thermal energy, to the overall catalytic efficiency.

In TPT, most of the photo-excited hot carriers cannot be injected into the HOMO/LUMO of the reactants and decay in the form of heat due to ohmic damping. Consequently, the contribution of most hot carriers to TPT catalytic throughput is

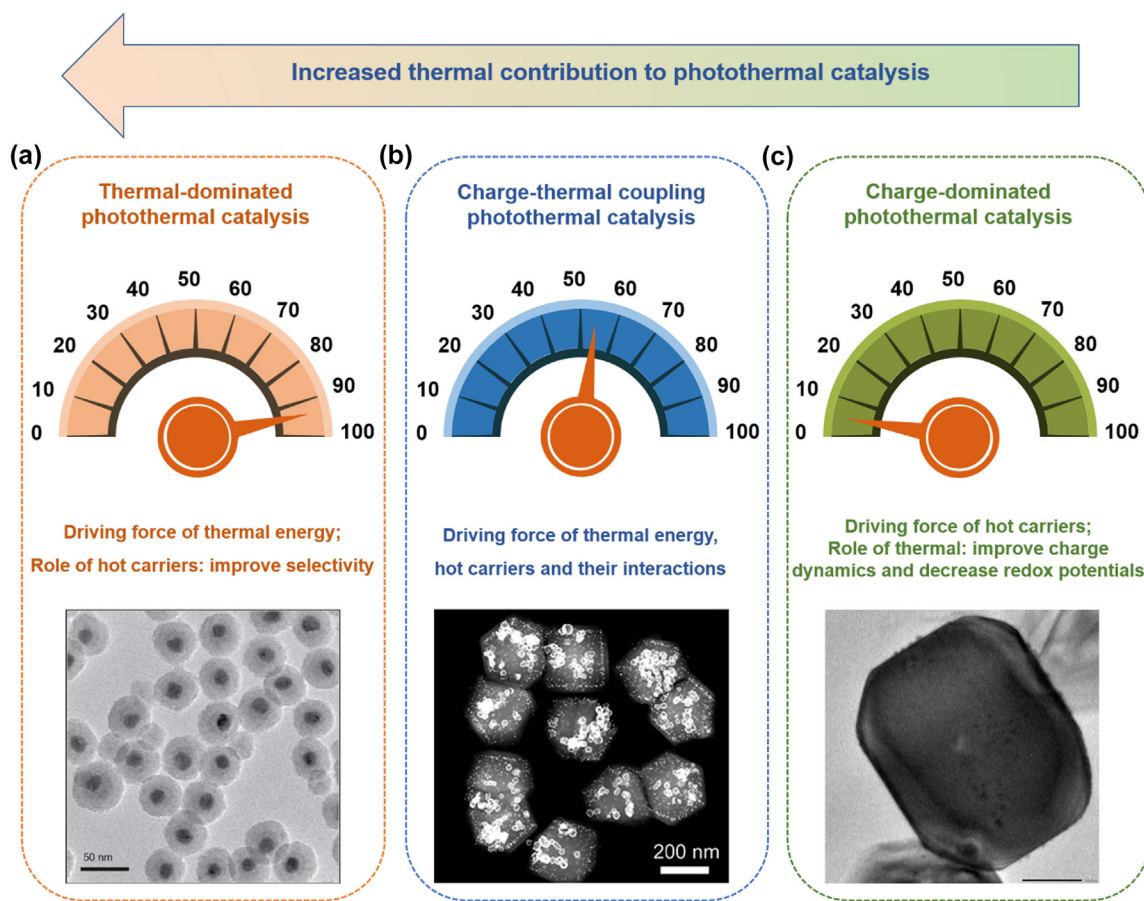


FIG. 3

Classification of photothermal catalysis into (a) thermal-dominated photothermal catalysis (a representative catalyst of  $\text{Ni}_{12}\text{P}_5@\text{SiO}_2$  [93]), (b) carrier-thermal coupling catalysis (a representative catalyst of  $\text{AuPt}@\text{MOF}$  [90]) and (c) hot carriers dominated photothermal catalysis (a representative catalyst of  $\text{SrTiO}_3:\text{Al}$  [21]).

predominantly attributed to induced thermal energy rather than direct injection. Only the EHC with enough energy to weaken or break specific bonding for intermediates are responsible for catalytic activity. For instance, Group VIII transition metal nanoparticles (e.g., iron, cobalt, and nickel) on  $\text{Al}_2\text{O}_3$  exhibit weaker plasmonic properties in the visible and near-infrared spectral range due to the filled d-band [85,86]. This, in turn, reduces the efficiency of directly reducing/oxidizing adsorbed molecules. Instead, the localized temperature on the catalyst can be rapidly elevated to  $\sim 400^\circ\text{C}$  within half an hour of light illumination, leading to an efficient DRM by TPT for syngas production.

By contrast, once the photo-excited hot carriers are energetic enough and photo-generated LTE in a photothermal catalytic process fails to overcome the thermodynamic reaction barrier of chemical processes, the yield or throughput of the reaction is highly dependent on photo-excited hot carriers for directly participating into the redox reactions of reactants. This is known as a CPT process. The essence of CPT is a photochemical process, where thermal energy exists for accelerating the dynamics of photo-induced charge carriers and lowering the redox potentials of reactants. The CPT technology has been widely applied in water splitting related processes, such as water splitting for green hydrogen and  $\text{CO}_2/\text{N}_2$  reduction reaction with water, where photo-induced EHC serves as the main driving force to realize

water dissociation. Catalysts involved in the CPT process include semiconductor-based (e.g.,  $\text{TiO}_2$  [87],  $\text{C}_3\text{N}_4$  [88] and  $\text{CdS}$  [54]) or classical plasmonic metal (e.g., Ag, Au and Cu) materials [89].

In most cases, especially gas–solid phase reactions, contributions of EHC and thermal energy co-exist, and the process is known as CTC. In a CTC process, a part of hot carriers is used for photocatalysis, while the others recombine with the liberation of heat for thermocatalysis. Consequently, photocatalysis mediated by hot carriers from Landau damping and the thermal catalysis process induced through Ohmic damping jointly determine the synergistic catalysis in CTC. A bimetallic system integrating an coinage metal and a transition metal is a typical CTC catalyst [90]. The photocatalytic process on the IB metal and photo-driven thermocatalysis on the transition metal collectively determine the photothermal catalytic performance.

Although experimental results have confirmed the existence of EHC and LTE in CTC processes, accurately quantifying the contributions from photothermal and photocatalytic processes to the overall catalytic throughput remains a challenge. Many studies focus on determining the localized temperature to differentiate the thermocatalytic contribution from the CTC processes. However, there are several challenges related to reactor setup, measurement instrumentation, and categorization of catalytic systems [91]. These challenges lead to unduplicated

temperature gradients within the catalyst bed under light irradiation in thermocatalysis, thereby resulting in controversial mechanistic studies within CTC processes [16,92]. Therefore, it is imperative to rationally design catalysts and reactors to unravel the intrinsic solar conversion mechanism in photothermal catalytic reactions. By addressing these design considerations, a deeper understanding of the complex interplay between photothermal, photocatalytic, and thermocatalytic processes can be achieved, enabling the development of more efficient and sustainable catalytic systems for solar energy conversion.

### Design strategies for photothermal catalysts

The success of photothermal catalytic reactions depends on the interplay between EHC and LTE. As such, a photothermal catalyst plays a crucial role in choreographing these two ‘dancers’ by inducing different behaviors. Developing efficient photothermal catalysts is therefore necessary to promote the scaling application of photothermal catalysis. However, despite the rapid growth of the field, there is still a lack of clarity in the concept and design principles of photothermal catalysts, which can cause confusion for those new researchers to the field. To address this gap in knowledge, we aim to provide a comprehensive concept of photothermal catalysts by categorizing them into different types that contribute to various photothermal processes, such as CPT, TPT, and CTC. Additionally, we propose strategies for optimizing photothermal catalysts to control and enhance the contributions of EHC and LTE, maximizing solar harvesting and the efficient production of solar fuels. These optimized strategies will ultimately lead to more robust and efficient photothermal catalytic operations.

#### Concept of photothermal catalysts

Photothermal catalytic activities have been observed in a wide range of materials, including semiconductors, nanometals, black materials, and their hybrids. To gain a deeper understanding of the above classified CPT, TPT and CTC processes, we can describe photothermal catalysts as  $P_xB_{1-x}$ , which consists of photo-to-electron components and/or black materials (Fig. 4a). When  $x$  is close to 1, the photothermal catalyst is mainly a photocatalyst and is commonly used in the CPT process. However, in most photocatalytic systems, photothermal effect is often overlooked due to the dissipation of thermal energy by the cooling water system. An experimental work has revealed that the temperature of water solution can be increased from 25 to 57 °C in 4 h with a 300 W xenon lamp irradiation during a solar driven water splitting reaction using semiconductors (i.e.,  $TiO_2$  and  $g-C_3N_4$ ) as catalysts [88]. Besides, the enhancement of photothermal effect on chemical synthesis was also observed when heating was left in photocatalysis in the absence of cooling system, fully confirming the nonnegligible photothermal effect in a CPT process [45]. When  $x$  is close to 0, the photothermal catalyst is always a black material such as carbon, amorphous boron, MXene, thermoelectric, transition nanometal, and their hybrids [94,95]. This material is highly effective in converting full spectrum sunlight into thermal energy and is often used in TPT processes. For example, amorphous boron has demonstrated outstanding TPT catalytic performance in  $CO_2$  reduction by rapidly increasing the localized

temperature to 462 °C in just 10 min [96]. For  $0 < x < 1$ , the photothermal catalyst is a hybrid that combines both a photocatalyst and a black material, allowing EHC from the former to synergize with the LTE of the latter [97]. This hybridization is popular in CTC processes, where it takes advantage of both EHC and LTE. Numerous materials have been used in these hybrids, such as bimetallic integration of coinage and transition metals (e.g., Au-Pt [90], Cu-Ru [42], and Au-Ru [36]), transition metal/semiconductor hybrids (e.g., Pt/ $TiO_2$  [82] and Ru/ $HNb_3O_8$  [98]), and semiconductor/black material hybrids (e.g.,  $TiO_2$ /graphene [99] and  $Bi_2Se_3/g-C_3N_4$  [100]).

Defining different types of photothermal catalysts is not straightforward due to the varying contributions of EHC and LTE in different chemical reactions. For instance, transition nanometal-loaded carbon (e.g., Fe@C hybrid [94]) or insulator materials (e.g., VIII group nanometal/ $Al_2O_3$  [86]) are generally black and have been reported as TPT catalysts in  $CO_2$  reduction processes but are considered as CTC catalysts (e.g., Ru/C [10]) in ammonia synthesis processes. Similarly, a modified semiconductor material can function as a CPT catalyst (e.g.,  $C_3N_4$  and  $TiO_2$  [88]) in water splitting reactions but may act as a CTC catalyst (e.g.,  $In_2O_{3-x}/In_2O_3$  [101]) in gas–solid phase reactions. Therefore, accurately classifying a photothermal catalyst depends on understanding the specific contributions of EHC and LTE in a chemical reaction.

#### Catalyst design strategy

Photothermal catalysts play a crucial role in converting solar light into useful energy through photochemical and thermocatalytic processes. Such catalysts must possess several key factors, including a high absorption ability to induce and regulate electron and lattice heating (EHC and LTE), and catalytic sites. While the latter component has been extensively discussed in the literature [102], we will here focus on broadening the response of full-spectrum sunlight, internal electric field (IEF) modulation for more generation of EHC and LTE, interfacial engineering for directional transferring of EHC and LTE, and management of EHC and LTE in exploring highly efficient photothermal catalysts for 24/7 photothermal catalytic operations (Fig. 4b).

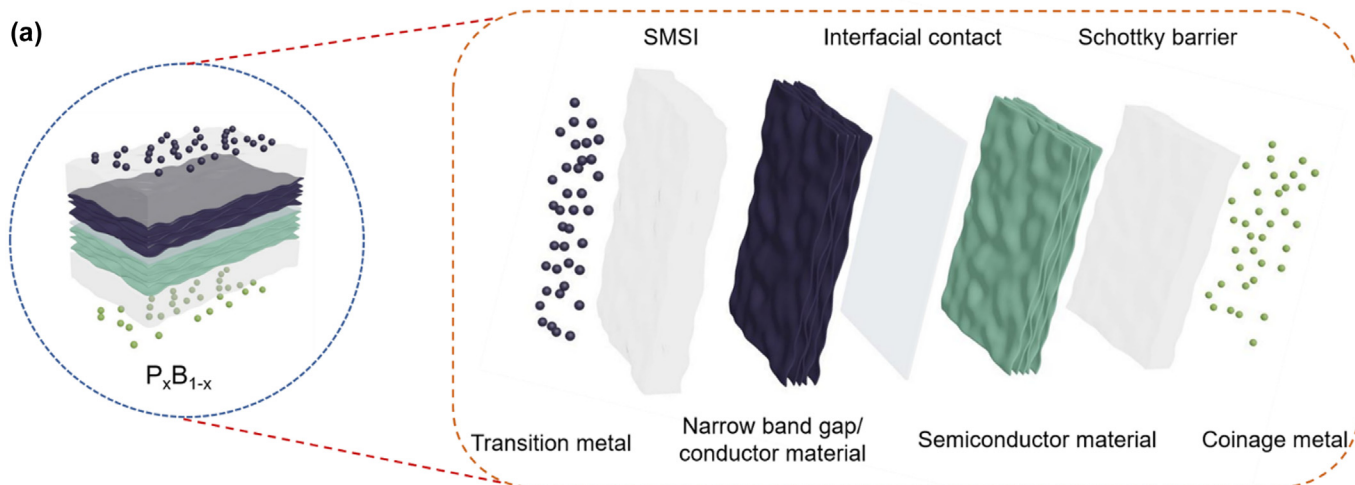
#### Enhancing absorption of full spectrum sunlight

Photon absorption is the initial and essential step for enhancing the efficiency of photothermal catalysis. For optimizing the absorption of full-spectrum sunlight, several tactics can be considered for the different components of  $P_xB_{1-x}$  (Fig. 5).

##### (1) Band regulation

An energy band gap exists between the CB and VB of semiconductor materials, and this gap affects the light wavelengths that a material can absorb. As such, band regulation plays an imperative role in determining the extent of a material’s exposure to light. Heteroatom doping is a frequently-used strategy for introducing impurities into a semiconductor’s crystal lattice intentionally. Various changes can be induced in the electronic band structure of the semiconductors (Fig. 5a), including (i) creation of an extra intraband energy states; (ii) narrow of the band-gap; and (iii) impurity band formation in degenerately doped





(b)

### Design principles of photothermal catalysts for enhancing each step in photothermal catalysis

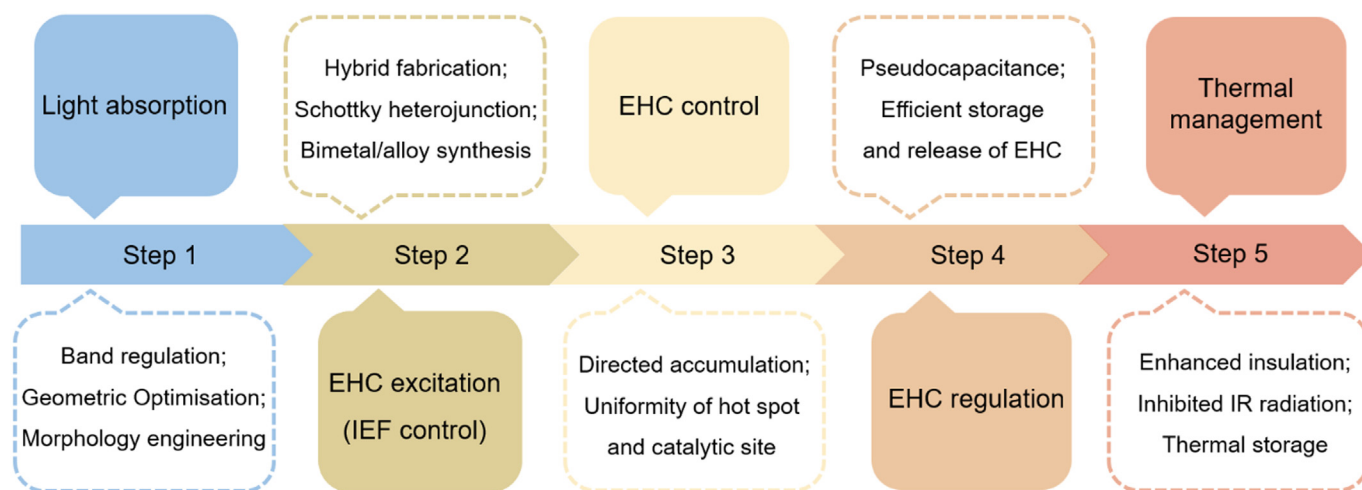


FIG. 4

(a) Definition of a photothermal catalyst of  $P_xB_{1-x}$ . (b) Design principles of photothermal catalysts for enhancing performance at each step, including light absorption, EHC excitation, EHC control, EHC regulation and thermal management, in photothermal catalysis.

transition metal semiconductors, which will broaden the absorption range of the materials and thereby refine the light-harvesting efficiency. In general, metal doping tends to have a greater impact on the optical properties of a material than non-metal doping despite of the negative environmental and economic impact of metals [103,104].

In the same way, vacancy engineering is used to transform the band structure of a semiconductor by introducing defects or vacancies in the crystal lattice. In a perfect crystal lattice, each atom has a specific position and coordination number with its neighbouring atoms. When a vacancy is introduced, it creates an empty space, leading to a defect in the lattice, and can alter the electronic properties of the semiconductor. The introduction

of vacancies always results in the formation of mid-gap states within the band gap, modifying the semiconductor's light-responsive ability and its photo-to-electron/thermal abilities, thereby affecting photothermal catalytic throughput. The defects created always function as catalytic sites in thermocatalytic processes. Zhao et al. prepared a three-dimensionally ordered macroporous structured materials,  $LaSrCoFeO_{6-\delta}$ , with a visible light response ability, and the oxygen vacancies on its surface allowed the material to be employed in thermal catalysis [105]. As such, the more EHC and LTE by oxygen engineering hastened the activation of  $CO_2$  nonpolar molecules, leading to higher selectivity and conversion yield of  $CO_2$  to  $CH_4$  in comparison to thermal catalysis.

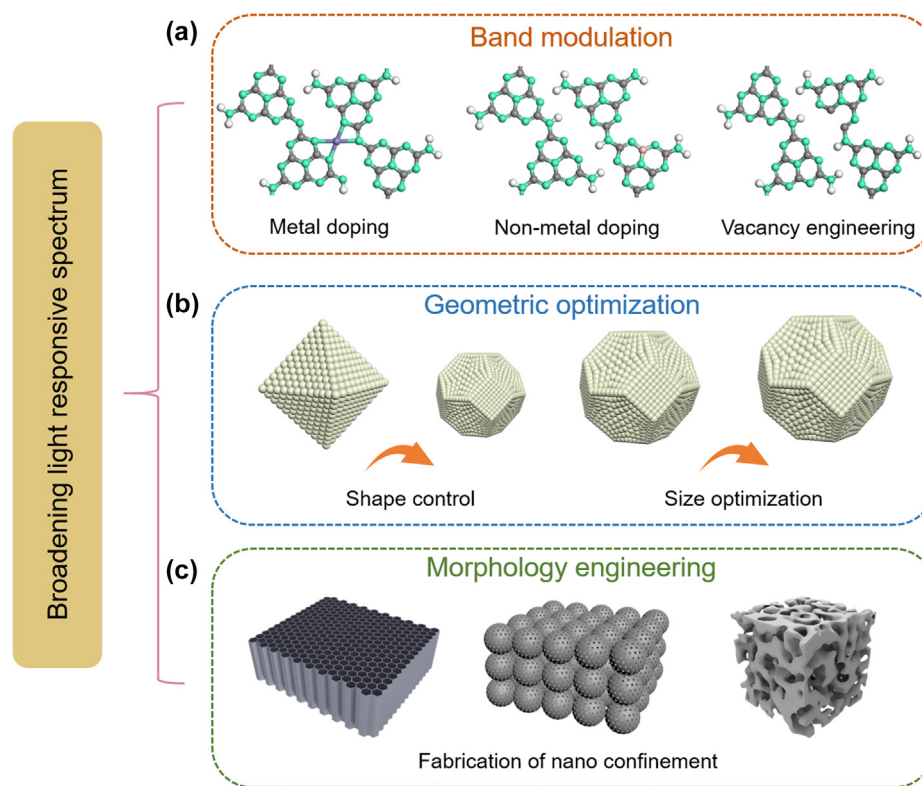


FIG. 5

Strategies for broadening sunlight absorption. (a) Band modulation of a semiconductor. (b) Geometric optimisation of a nanometal. (c) Morphology engineering of black materials.

While band controlling can narrow the band gap and improve the solar light absorption of semiconductors, it can also result in a loss of redox potentials due to lowered band structures. Elevation of the redox ability is a competing process that must be considered to improve the light harvesting efficiency.

## (2) Optimization of geometric features

Unlike the dependency of light absorption in semiconductors on band structure, the absorption cross-section of plasmonic nanometals is significantly influenced by the metal nature, size and shape (Fig. 5b). When a plasmonic metal nanoparticle is illuminated by light, the electric field of the light can drive collective oscillations of the free electrons in the nanoparticle, generating a resonance termed as LSPR. The LSPR of IB-group metals engender strong interactions between light and the matter, thereby elevating light absorption in specific regions of the electromagnetic spectrum. Initially, the light responsive ability of a nanometal is determined by the nature.

It can be clearly seen from Fig. 5b that Au and Ag are strong plasmonic metals that can effectively scatter and absorb light in the visible and near-infrared regions, while Cu has a relatively weak plasmonic response but a high electron mobility. Besides, the wavelength of light that matches the LSPR resonance of a metal nanoparticle depends on the particle's size. Specifically, the LSPR resonance shifts to longer wavelengths with an increasing nanoparticle size, owing to the reduced confinement of electrons. As a result, smaller nanoparticles exhibit higher absorption efficiency than larger nanoparticles resonant at

longer wavelengths, for a given wavelength of incident light [106]. In addition, the light-absorption properties of plasmonic metal nanoparticles are influenced by their geometric parameters, such as shape and crystal structure. Different shapes can lead to different resonant modes, affecting the absorption properties. For instance, spherical nanoparticles exhibit a dipolar resonance mode, while nanorods can exhibit both dipolar and quadrupolar resonance modes. Asymmetric shapes, like nanocrescents or nanostars, can display multiple resonance modes, resulting in enhanced absorption over a wider swath of wavelengths [106].

## (3) Morphology engineering

Morphology engineering is a common method to increase light harvesting and minimize surface light reflection in black materials, which are typically narrow band gap semiconductors or conductors (Fig. 5c). One effective way to accomplish this is through introducing confined spaces, such as porous nanostructures, which can decrease the effective refractive index of the material and minimize the angular dependence of the incident light. Additionally, the pores in nanostructures act as optical microcavities to enhance light-material interaction through multiple light reflection and scattering, further improving the harvesting efficiency of full spectrum sunlight. For instance, carbon nanotubes demonstrate strong one-dimensional excitonic absorption in the near-infrared range due to their unique electronic structure, which enables strong light absorption properties.

Overall, band regulation, geometric optimization and morphology engineering can effectively improve the light responsive capability of semiconductor, nanometal and black materials, respectively. However, challenges remain in realizing full-spectrum sunlight absorption. Combining these approaches is a prudent path towards achieving maximal efficiency. The success of heterojunctions, such as rhodium (Rh), chromium oxide ( $\text{Cr}_2\text{O}_3$ ), and cobalt oxide ( $\text{Co}_3\text{O}_4$ ) on InGaN/GaN nanowires, suggests that more combinations of different components and related modification strategies can lead to a high utilisation efficiency sunlight [107]. Therefore, attempts on more combinations are expected to achieve 100% harvesting efficiency for full spectrum sunlight.

#### *Modulation of IEF for more EHC and LTE*

The generation of efficient EHC and LTE is a core requirement for photothermal catalytic activity, for which the IEF of the photothermal catalyst plays a central role. Various IEF modulation strategies are used in different types of photothermal catalysts to achieve effective EHC and LTE generation for chemical reactions, which will be reviewed and discussed below.

IEF manipulation is a process of breaking the symmetry of materials, which can be easily realized by the heterostructure fabrication technique in semiconductors. The Fermi level equilibrium at the contact area is formed by different semiconductors with distinct work functions, leading to electron transfer and creating IEF to drive photo-excited charge carriers separated by the heterojunction. Currently, type II, Z-, and S-scheme heterostructures are predominantly reported for semiconductor-based heterojunctions (Fig. 6a). In the type II regime, photo-excited hot carriers move from a higher CB/VB to a lower CB/VB, resulting in faster separation of charge carriers but reduced redox abilities and a higher possibility of LTE. On the other hand, the Z- or S-scheme heterosystem permits photo-excited hot electron transfer from a semiconductor with a lower CB to the VB of another semiconductor for combination, leaving hot carriers at higher redox potentials for more EHC.

An intensified electric field can also be achieved at the interface between a metal and a semiconductor in Schottky heterojunctions, leading to more EHC and LTE for photothermal catalysis. When a metal is brought into contact with a semiconductor, a depletion region is formed at the interface due to the difference in work function. This depletion region results in a built-in electric field, which promotes the charge separation and improves the charge dynamics. In a Schottky heterojunction for an enhanced electric field, the metal and support materials are carefully chosen to optimize the electric field at the interface. For example, platinum with a high work function can be used in contact with  $\text{TiO}_2$  to create a Schottky heterojunction with a high built-in electric field (Fig. 6b). However, interfacial charge separation channels cannot be created when Pt is loaded on  $\text{Al}_2\text{O}_3$ , which leaves an enhanced electric field on the surface of Pt nanoparticles [108].

Bimetallic structures can also be used to enhance the electric field as Schottky heterojunctions. A LSPR effect can be produced by combining two different metals, resulting in a strong electromagnetic field enhancement at the interface. Accordingly, a range of bimetallic nanoparticles (e.g., PtAu, RuCu, and CoNi)

have been manufactured. As an example, a RuAu bimetallic catalyst was constructed and showed significantly strengthened electrical field compared to the monometallic materials, despite lacking a contact interface (Fig. 6c) [36]. Consequently, a higher photothermal catalytic DRM performance was achieved due to the increase of EHC and LTE. In contrast, a metal alloy as a homogenous solid material composed of two or more metallic elements displayed different properties (e.g., reflective index) from those of the individual metals, allowing for optimized IEF. Thus, AgPt alloy nanoparticles with controlled geometric features have been studied, showing promising IEF enhancement and modulation principles (Fig. 6d) [110].

In general, the IEF of photothermal catalysts can be notably improved using various modification strategies, which significantly promote more EHC and LTE to participate into chemical reactions. However, selectively generating EHC and LTE remains a challenge and needs to be overcome, particularly considering their paradoxical contributions in photothermal catalysis, which lacks precise characterization techniques and reaction design. Recently, a significant study from Linic's group demonstrated that the plasmon-induced activation of reactants via electronic excitation or photothermal heating plays a critical role in driving LSPR-induced chemical reactions [111]. Therefore, future efforts should focus on the precise generation and contribution of EHC/LTE to specific reactions to rationally utilize solar energy.

#### *Interfacial effect on electron transfer*

The efficiency of a photothermal catalytic process is determined by two factors: hot spots, the region of energy accumulated, and catalytic sites, the region with a low thermodynamic barrier. EHC and LTE are the driving forces to support the photochemical and thermocatalytic processes, respectively, and both are accumulated at the hot spots of the catalyst [112]. Therefore, a unification of hot spots and catalytic sites can double the effectiveness of the photothermal catalytic process, otherwise will reduce the effectiveness by half (Fig. 7a) [113]. The interfacial effect plays a crucial role in determining the accumulation region of EHC and LTE and is essential for controlling the transfer of EHC after generation. However, the random directions of IEF at the interface of semiconductor heterojunctions pose a challenge in achieving effective charge accumulation at the active sites. For addressing this issue, an integrated carbon nitride homojunction with a tandem IEF was developed to achieve fast charge separation and effective accumulation of hot electrons on the catalyst surface for efficient hydrogen reduction (as shown in Fig. 6a) [109].

The same problem also occurs at the Schottky barrier, where an induced IEF is always employed for a rapid separation of EHC. Manipulating IEF at the metal-support interface is highly desired to accumulate more EHC and LTE at the catalytic sites for highly efficient outputs. The reaction temperature has been evidenced to play a crucial role in changing the accumulation region of EHC and LTE. At low temperatures, the interfacial effect plays a decisive role in EHC assembly and TPT catalysis, while it weakens as the temperature increases owing to the weakened charge dynamics (Fig. 7b) [108]. Modulating the electronic structure of the support can also tune the interfacial effect and

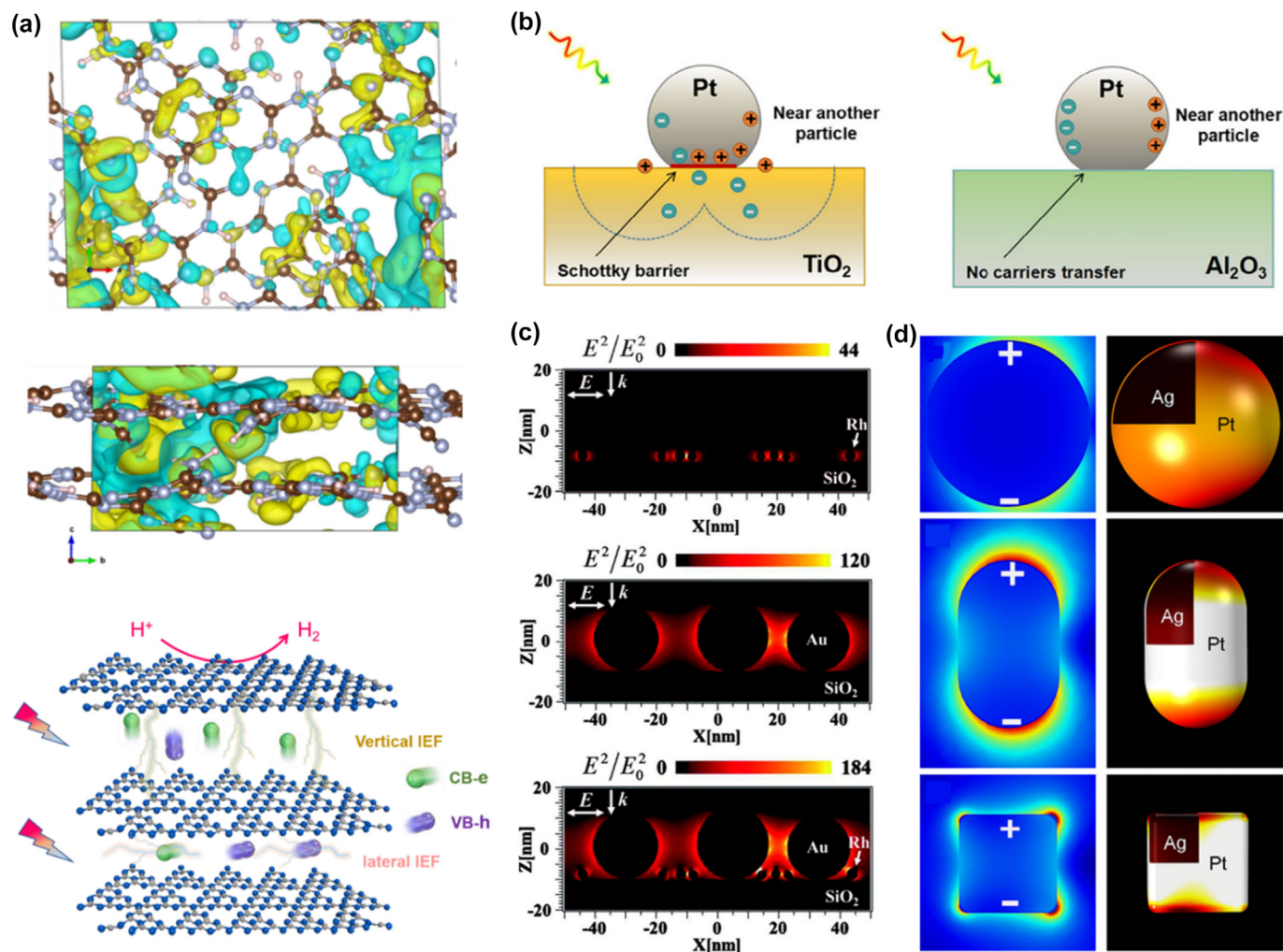


FIG. 6

IEF enhancement for more EHC and LTE. (a) Tandem IEF for a directed charge flow in a semiconductor [109]. (b) Schottky barrier for charge intensification at metal support interface [108]. Bimetal nanoparticle (c) [36] and its morphology engineering (d) [110] for enhanced IEF.

improve photothermal catalytic performance. For example, the classical support metal strong interaction (SMSI) effect observed in  $Ru/TiO_2$  increases the electron density of  $Ru$  nanoparticles (NPs) under illumination [114]. However, in the DRM reaction process, the dissociation of C–H bonds of  $CH_4$  occurs on electron-deficient sites on the metal surfaces and is the rate-determining step. Consequently, an inconsistency between hot spots and catalytic sites inhibits the SMSI effect on solar-driven photothermal DRM. To address this issue, Jia et al. modified the electronic structure of the  $TiO_2$  support by introducing oxygen vacancy, creating an interfacial effect to manipulate the photo-induced electrons transfer to the support. The resultant suppressive SMSI effect created electron-deficient sites on  $Ru$  NPs, improving  $CH_4$  dissociation and intensifying photothermal catalytic DRM (Fig. 7c).

Additionally, the strength and configuration of interfacial coordination play a critical role in the dynamic motion of a metal on a support, thus determining the catalyst stability. Single atom catalysts (SACs) have a simple metal-support configuration

that is useful in probing catalytic mechanisms. A Pd-SAC, for instance, displays exceptional activity and stability in photothermal catalytic hydrogenation of  $C_2H_2$  with  $H_2$  when atomically dispersed Pd on nitrogen-doped graphene (Fig. 7d) [115]. This is because of the strong coordination between the Pd and nitrogen atoms and the lower EHC accumulation at the metal-support interface, which results in less Pd aggregation. However, when an atomic metal is immobilized on semiconductor-based materials such as  $TiO_2$  and  $g-C_3N_4$ , metal aggregation tends to occur after photothermal catalytic chemical reactions (Fig. 7e). It has been discovered that surface migration of metal-SACs can be accelerated by the initial SAC loading, photogenerated electrons, and reactive intermediates, leading to metal nanoparticle agglomeration [88,116,117]. Therefore, accurate modulation of the interfacial effect to control charge transfer is critical for achieving highly efficient and stable photothermal catalysis for chemical reactions.

Overall, interfacial engineering is an effective approach for controlling the directional flow of EHC and LTE. However, there

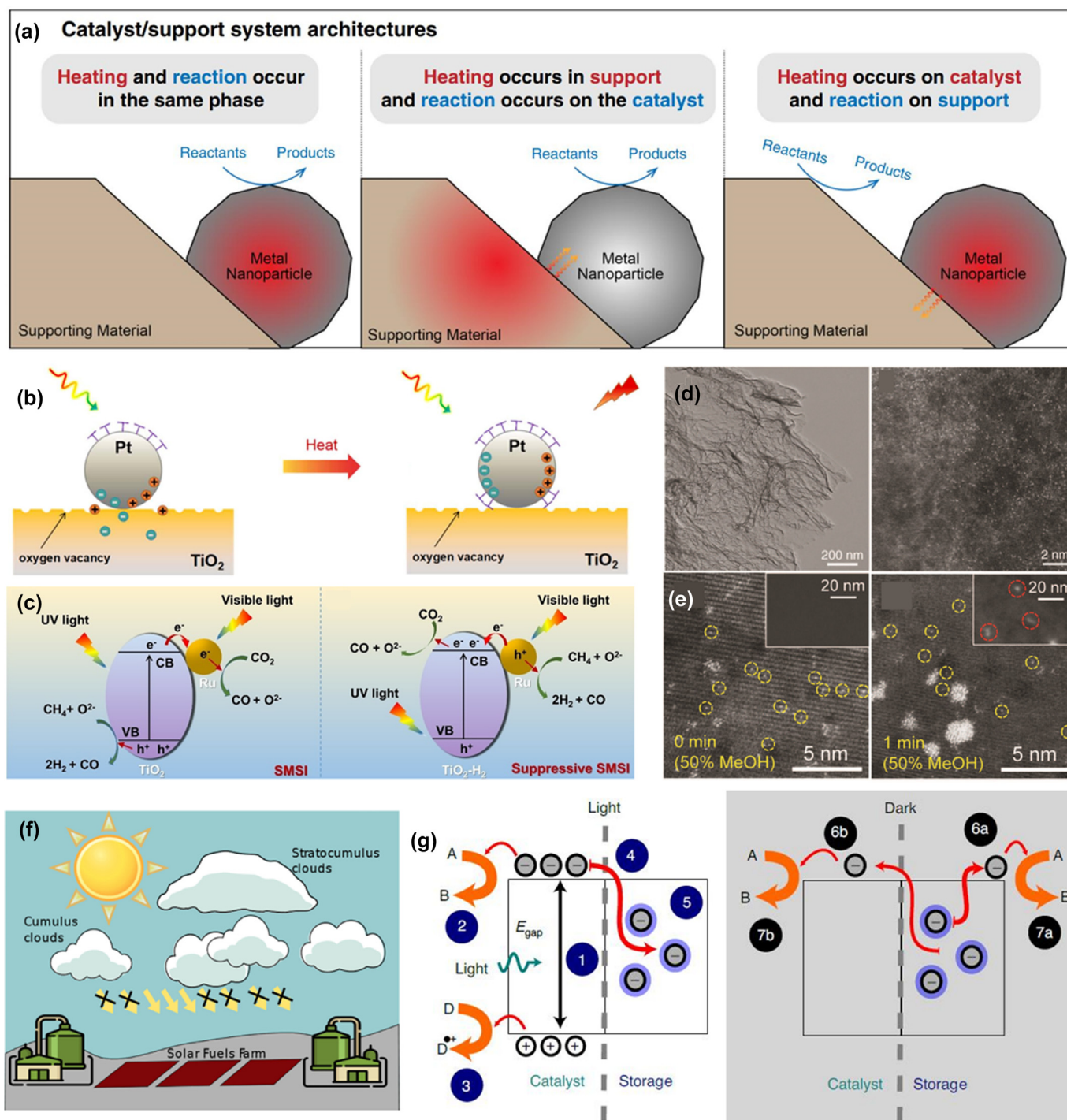


FIG. 7

(a) Relationship between hot spots and catalytic sites in photothermal catalysis [113]. (b) Temperature dependent interfacial effect on photothermal catalysis [108]. (c) Suppressing SMSI of Ru/TiO<sub>2</sub> to tailor electron transferring pathway in photothermal catalytic DRM [114]. (d) Pd/N-graphene single atom catalyst for photothermal catalytic hydrogenating C<sub>2</sub>H<sub>2</sub> with H<sub>2</sub> [115]. (e) Photothermal effect induced atomic metal aggregation to nanoparticle [116]. (f) Solar fuels production in the dark using supercapacitor CO<sub>2</sub> photocatalysts when the sun does not shine, circumventing intermittency and cloud cover. (g) Mechanism of a persistent photocatalyst system on the storage and release of photo-induced electrons [118].

is a lack of research focused on distinguishing between the hot spot and catalytic site in photothermal catalysts. In some cases, these two concepts have been confused. It is crucial to determine the hot spot and catalytic site during the design of a highly efficient photothermal catalyst, not just for the development of

photothermal hybrid catalysts and the mechanistic investigations. Moreover, the presence of EHC at the metal-support interface can impact catalyst stability, thus it is essential to pay close attention to the catalyst reconstruction process in photothermal catalysis to accurately elucidate the reaction mechanism.

### Photo-carriers regulation

Photothermal catalysis has demonstrated great potentials to large-scale productions of solar fuels. Whereas, intermittent availability of sunlight is the biggest obstacle for 24/7 solar-driven catalytic operations. It has been reported that 40% of power losses occur in photovoltaic systems during overcast days, so EHC cannot be excited in the dark (Fig. 7f) [119]. As a result, regulation of EHCs enabled by catalyst design for robust participation into photothermal catalysis is highly important but challenging for practical application of photothermal catalysis. To address this, researchers are proposing the modification of photocatalysts with energy-storing materials to generate electrons or holes persistently, even in the absence of sunlight. Pseudocapacitance, which determines the surface electrochemical charge storage by surface redox reactions or ion adsorption/desorption, plays a vital role in these photocatalysts (Fig. 7g) [118]. When hot electrons serve as the primary charge carriers for catalysis and the intensity of light exceeds a certain threshold, photo-excited hot electrons migrate across the heterojunction of the photocatalyst and accumulate within the pseudocapacitor, typically composed of electron-storing materials like  $\text{WO}_3$ ,  $\text{SnO}_2$ , or  $\text{TiO}_2$ . Meanwhile, excessive holes are effectively eliminated by hole scavengers. During periods of darkness, the discharge of electrons from the pseudocapacitor drives the reduction reaction, ensuring continuous catalytic operations even in the absence of light. Conversely, hole-storing materials such as  $\text{Ni}(\text{OH})_2$  are employed to facilitate a continuous oxidation process. This inherent 24/7 capability of energy-storing materials offers a more compact and efficient alternative to integrating photovoltaic and battery systems, thereby minimizing energy losses. Presently, researchers are dedicated to enhancing the electron storage capacity of these photocatalysts through advancements in materials science and engineering. These ongoing efforts aim to extend the post-illumination catalytic period beyond the current limit of eight hours. Furthermore, the emerging field of photothermal catalysis presents significant opportunities for further research and development, with the potential to achieve even longer post-illumination catalytic periods.

### Photo-thermal management

As another indispensable anticipator in photothermal catalysis, efficient heat management by catalyst modification is crucial for achieving high catalytic activity and selectivity. Several strategies reported can enhance the light-to-thermal energy efficiency, including insulation, prohibition of infrared radiation, and thermal storage. Thermal insulator substrates, which have low thermal conductivity, can trap the heat generated by the catalyst, resulting in increased temperature and process efficiency. Common insulator substrates such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{ZrO}_2$  can be shaped and sized to optimize the substrate for specific catalytic processes. Interesting works have been reported by Ozin et al. in encapsulating a nanometal into  $\text{SiO}_2$  shell and  $\text{SiO}_2$  sphere pore channel (Fig. 8a) [83,120]. The high light transmittance and heat insulation effect of  $\text{SiO}_2$  slow down the heat conduction between the catalyst and the glass fibre filter for a high localized catalyst temperature. Similarly, a ZIF material with strong light absorbance and heat insulating has been employed to iso-

late graphene, which can not only lower thermal conduction but also enhance the light-to-thermal efficiency (Fig. 8b) [121].

Additionally, a significant amount of heat is always lost in the form of infrared radiation in photothermal catalysis, which reduces the catalyst temperature and process efficiency. To enhance photothermal catalysis, it is possible to prohibit or limit infrared radiation by using materials or coatings that are reflective to or absorbing infrared radiation. Cu with near-zero IR radiation was coated on  $\text{Bi}_2\text{Te}_3$  film. The superior solar-to-thermal conversion from  $\text{Bi}_2\text{Te}_3$  and low-IR radiation from Cu can increase the temperature of the catalyst (Fig. 8c) [122].

Thermal storage is a similar process with persistent photocatalysis for mitigating the problem of intermittent sunlight. Phase change materials (PCMs) are one of the latent heat storage materials that can store significant amounts of heat without temperature fluctuation. However, organic solid-liquid PCMs have limitations such as low thermal conductivity, leakage, and lack of energy conversion ability, which challenge their practical use [124]. 2D MXenes, specifically  $\text{Ti}_3\text{C}_2\text{T}_x$ , have an internal light-to-heat conversion efficiency of up to 100% [124]. Its unique 2D and lamellar structure enables the highly anisotropic heat transfer process, where interlayer heat transfer processes occur with larger thermal resistance than intralayer transfers as it involves more complicated transfer pathways (Fig. 8d). The superior light-to-thermal efficiency and unique nanostructure of MXenes make them potential candidate for thermal conversion and storage. Therefore, Tang et al. fabricated a new phase change composite made up of stacked  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets and polyethylene glycol (PEG). The resulting composite showed excellent photo-to-thermal storage efficiencies of up to 94.5% under actual solar light irradiation (Fig. 8e). Despite a significant progress being made on thermal storage materials, their use is still confined to laboratory scale. Furthermore, combining thermal storage materials with photothermal catalysts remains an area of active research.

In summary, various strategies have been successfully implemented to enhance specific steps in photothermal catalytic processes, such as solar absorption, modulation of IEF, and regulation of EHC and LTE, resulting in more robust and efficient catalysis. However, since photothermal catalysis is a chain process, improving one step may inhibit another. For instance, narrowing the band gap of a semiconductor to improve solar absorption may hinder the generation of EHC. Moreover, achieving enhancements in all steps of photothermal catalysis requires precise fabrication of multi-component heterojunctions. Therefore, the optimization and integration of different approaches in a photothermal hybrid catalyst are essential to maximize light harvesting efficiency, catalytic throughput, and post-illumination catalysis in photothermal catalysis.

## Applications

Photothermal catalysis is a promising field that combines the benefits of photothermal heating and catalysis to facilitate powerful chemical reactions. Its mild reaction conditions and superior efficiency make it a potential candidate for revolutionizing different industries in a financially viable and eco-friendly man-

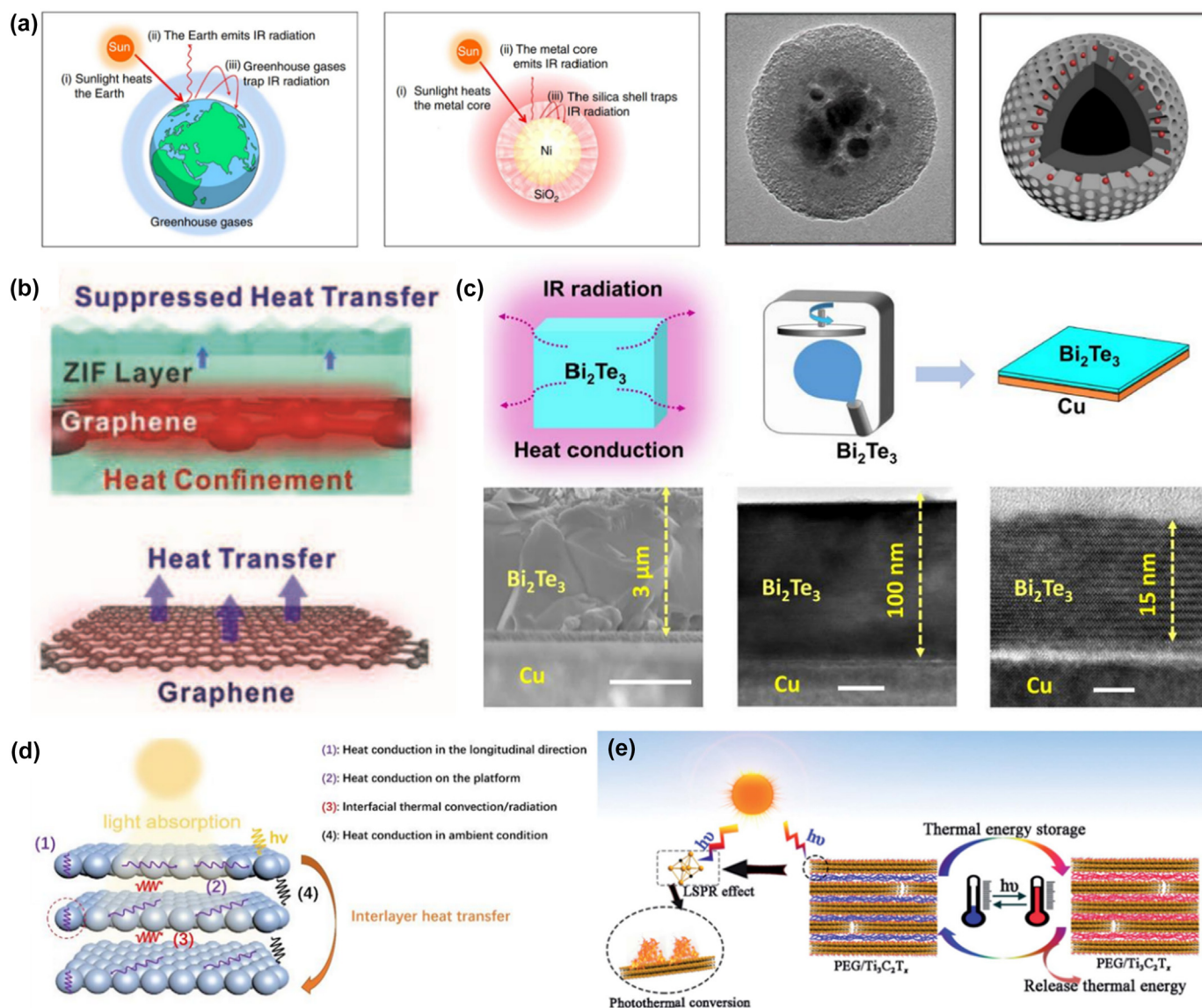


FIG. 8

(a) SiO<sub>2</sub> confinement [83,120] and (b) ZIF layer coating for decreasing thermal conduction rate [121]. (c) Cu coating for reducing infrared radiation [122]. (d) Heat conduction mechanism in 2D MXene [123]. (e) PEG/MXene for thermal storage [124].

ner, thus overcoming many of the obstacles facing the world today.

However, the photothermal effect in a catalytic process is highly dependent on the surrounding medium. When a nanometal catalyst is immersed in water, heat can be rapidly dissipated into both the substrate and the surrounding medium. This heat dissipation can be expressed using Fourier's law.

$$\mathbf{q} = \sum_i k_i A_i \nabla T \quad (1)$$

where,  $\mathbf{q}$  is the total heat dissipation (or total heat generation because the system is at a steady state),  $k_i$  is the thermal conductivity of the material at surface  $A_i$ , which is the surface area of heat dissipation, and  $(\partial T/\partial x)$  is the thermal gradient.

Hence, the temperature gradient occurs due to the heat transfer within the catalyst and the surrounding medium. In a liquid–solid phase reaction, the temperature rise of the bulk solution is generally limited due to the large specific heat capacity of water

(4200 J kg<sup>-1</sup> K<sup>-1</sup>). By contrast, gases exhibit lower heat transfer coefficients than solids and liquids, resulting in an indiscernible temperature gradient when photothermal catalysts are surrounded by a gas. Therefore, the surface of the nanometal experiences an obvious increase in temperature compared to the minimal change experienced by the substrate. The different temperature leads to different photothermal effects. Based on the effect of the surrounding medium of the catalyst on the photothermal effect, we here divide the application of photothermal catalysis into liquid–solid phase, gas–solid phase, and solid–solid phase reactions (Fig. 9).

#### Liquid–solid phase reactions

Photothermal catalytic liquid–solid phase reactions mainly occur at low temperatures in the bulk solution, which is typically less than 100 °C. Although the low thermal driving force may not be sufficient to overcome the activation barriers of thermocatal-

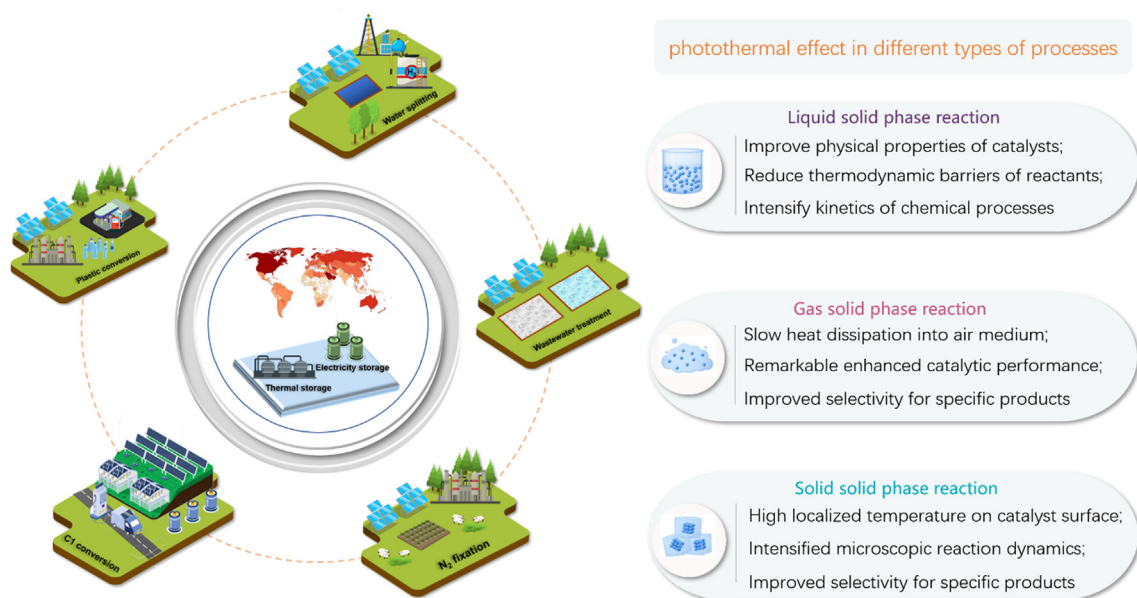


FIG. 9

Photothermal transfer in a diverse range of chemical reactions, including gas–solid, liquid–solid and solid–solid phase reactions, with related photothermal effects.

ysis, it can improve the physical properties of catalysts, enhance charge dynamics and intensify reaction thermodynamics and kinetics. These reactions are useful in various applications, such as pharmaceutical synthesis [45], wastewater treatment [125], and the production of renewable energy through photothermal catalytic water splitting [107].

Hydrogen, which is an eco-friendly and promising renewable energy option with a high energy density of approximately 120 MJ/kg, has captured a significant attention. In photothermal catalytic water splitting, the process may be primarily dependent on CPT, where EHC acts as the primary driver for hydrogen reduction. Photothermal effects in this process, such as lowering the electrical impedance, reducing the band gap, and increased light absorption of the photothermal catalyst, can significantly enhance the hydrogen evolution performance [88]. Furthermore, the photothermal effect can increase catalyst wetting ability, which in turn decreases bubble adhesion and bubble radius for detachment from the surface, leading to vivid improvements in reaction kinetics [126].

For liquid–solid phase chemical synthesis, EHC plays a vital role in producing high-value chemicals and fuels and LTE promotes the injection of EHC into HOMO and LUMO of adsorbents. For instance, CPT catalysis has been utilized in the selective oxidation of 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (1,4-DHP) to produce bioactive compounds such as antihypertensive agents and calcium channel blockers. Increased temperature in the CPT process not only enhances charge dynamics and band structures but also reduces the reduction potential of 1,4-DHP, which is beneficial for the output of EHC into the HOMO/LUMO of 1,4-DHP [45]. Additionally, the photothermal effect has demonstrated its capability in TPT processes to improve reaction kinetics, as evidenced by a photothermal nanoconfinement reactor with high localized temperatures inside hollow carbon nanospheres for improved micropollutant degradation and modulated degradation pathways [125].

Despite the significant improvements in the performance of liquid–solid phase reactions by photothermal catalysis, understanding the actual reaction mechanism on the catalyst surface remains elusive. While photothermal catalysis can dissipate heat into the bulk solution in a liquid–solid phase reaction, superheating always occurs at the liquid–solid interface [127], heating the liquid above its boiling point and enabling reactant molecules metastable. Therefore, it is crucial to reveal the surface temperature of the catalyst using advanced characterization and monitoring techniques underlying the real reaction mechanism on catalyst surface, which is beneficial for catalyst developments and reaction optimizations [91].

#### Gas-solid phase reactions

Catalytic gas–solid phase processes are commonly used in the chemical industry to produce fertilizers, chemicals, and fuels by accelerating the conversion of gases (reactants) into other gases (products). However, traditional gas–solid phase catalysis often requires high temperature, high pressure, and significant energy consumption. Photothermal gas–solid phase catalysis has emerged as a promising approach to convert fossil fuels into cleaner energy sources at ambient conditions using photothermal catalysts. Due to the low heat conduction coefficient of gases, the temperature of the catalysts can be rapidly increased and is positively correlated with the intensity of light irradiation. By concentrating sunlight using a light concentrator, the intensity can be increased up to 1000 to 10000 mW/cm<sup>2</sup>, resulting in the temperature of over one thousand degrees on the catalyst surface, which can easily initiate the conversion of stubborn molecules such as CO<sub>2</sub> and CH<sub>4</sub>.

For instance, DRM reaction, which is highly endothermic, can only occur at high temperatures and pressures in the presence of a catalyst. However, the high temperature and pressure required for this reaction are energy-intensive, and the catalysts used are expensive and subject to deactivation over time. As a result,



researchers have developed a series of photothermal DRM catalysts, including group VIII nanometals and their bimetallic systems with coinage metals. These state-of-the-art photothermal catalytic DRM processes surpass conventional thermocatalysis while using mild conditions, ensuring highly efficient conversion of the two greenhouse gases to energy-rich syngas in a green and sustainable manner [35,128–130].

Photothermal catalysis not only enhances performance but also changes the reaction pathway. Two photothermal catalytic mechanisms, CTC and TPT, have been widely reported, with the latter actually being a thermocatalytic process. In the TPT process, reaction selectivity can only be controlled by modifying the catalyst, whereas EHC in the CTC process can selectively decrease the activation energy for specific intermediates, thus increasing reaction selectivity. CO<sub>2</sub>, produced as a by-product of human activities such as burning fossil fuels, is an important feedstock for fuel production, and a high product selectivity is highly desirable in this process. Liu et al. utilized rhodium nanoparticles to improve performance in the CTC for catalytic carbon dioxide hydrogenation reaction, reducing the activation energy and producing selectively a desired but kinetically unfavourable product (Fig. 9) [72]. Mild illumination of rhodium nanoparticles resulted in almost exclusive methane production, as hot electrons were injected into the anti-bonding orbital of a critical intermediate. Without illumination, CO and CH<sub>4</sub> were equally produced. The reduced activation energy and super-linear dependence on light intensity led to the photothermal catalytic methane production rate at ambient conditions exceeding the thermocatalytic rate at 350 °C.

EHC and LTE have demonstrated excellent reactant conversion and better product selectivity in photothermal (CTC and TPT) catalytic gas–solid phase reactions at moderate conditions. Although thermal energy promoted EHC has made significant contributions to the CTC process, temperature can also accelerate the excited state decay and charge recombination processes. Additionally, competition between EHC and LTE exists on the active site of the photothermal catalyst in the CTC process. Therefore, optimizing reaction conditions and precisely quantifying the contributions of EHC and LTE are crucial to maximize solar energy utilization and catalytic throughput.

#### *Solid-solid phase reactions*

Solid-solid phase reactions involve the interaction between two or more solid materials, resulting in the formation of new chemical compounds. One example is the pyrolysis of waste plastics, which can convert the wastes into chemicals or high-value products. However, this process often requires high electricity or fuel consumption, making it inefficient and environmentally unfriendly. To address this, Luo et al. have applied photothermal catalysis to convert plastic waste into high-value fuels. By optimizing the catalyst, they were able to control the selectivity of gas and liquid products (Fig. 9) [131]. While photothermal catalysis offers a promising approach to achieving a clean and sustainable environment, more research is needed to fully understand the mechanisms of this technology in solid–solid phase reactions. With further development, photothermal catalysis could play a significant role in turning waste into valuable resources.

Table 1 demonstrates the efficacy of various types of photothermal catalysis for chemical reactions, highlighting the potential of this technology for energy conversion and environmental governance. However, it is worth noting that the photothermal catalytic performance varies depending on factors such as light intensity, reaction type, and chemical process. Therefore, optimizing reaction conditions and expanding the use of photothermal catalysis to more critical chemical processes is the next step.

#### **Upscaling photothermal catalysis**

Photothermal catalysis is a process that utilizes solar light to produce EHC and LTE for catalytic chemical reactions. The application of photothermal catalysis in sustainable chemistry has been proposed as a strategy to renovate the traditional chemical processes and color ‘green’ to fuel production. A few pilot studies of photothermal catalysis have been conducted, which involve two different types: a rooftop demonstrator that uses a waveguide photoreactor coated with a supercapacitor photocatalyst (Fig. 10a) and a solar fuel farm that uses either a plate-type catalyst bed or a concentrator (Fig. 10b–c) [22,119]. Therefore, light concentrators and catalyst scaling manufacture technologies are essential to realize photothermal catalysis for an industrial-scale production.

#### *Solar concentrators*

For the photothermal catalytic reaction to occur, an efficient, reliable, and suitable light source is required to provide the necessary intensity and wavelength of light. Solar concentrator systems have been developed to concentrate sunlight and provide the required energy for the reaction. These systems fall into four categories: parabolic trough, central power tower, parabolic dish, and double concentration, which can facilitate temperatures in the range of 500–700, 1600, over 1800, and over 1500 K, respectively. The selection of the corresponding system depends on the required temperature for the reaction. Stephane et al. utilized a parabolic dish to concentrate solar light, resulting in the delivery of 16 MW/m<sup>2</sup> flux of solar irradiation to the chemical reactor [134]. To decrease the energy loss within solar concentrator systems, they further integrated a solar light concentration system with the reaction into one solar reactor. This was achieved by coupling a primary sun-tracking paraboloidal concentrator to a secondary planar rotating reflector [84]. As a result, the reaction temperature could be ramped up to above 1400 °C, which allowed the use of the full solar light spectrum (Fig. 10d).

#### *Scaling synthesis technology*

Scaling up the synthesis of photothermal catalysts is essential for their practical use in various industrial applications. Advanced manufacturing technologies are necessary to ensure cost-effective and reproducible manufacturing, which can also reduce the cost of the catalyst and make it more accessible for a wider range of applications. In addition, minimizing variations in the catalyst's composition, size, and shape can improve the reliability of the catalytic process.

Photolithography is an advanced technique for batch manufacturing plate-type catalysts with a wide range of patterns and shapes, including complex geometries and high-resolution fea-

TABLE 1

## Typical examples of different types of photothermal catalysis for chemical reactions.

Reaction type	Catalyst	Solar light	Reaction	Activity
CPT-liquid solid phase	Rh/Cr <sub>2</sub> O <sub>3</sub> /Co <sub>3</sub> O <sub>4</sub> /InGaN/GaN NWs [107]	3,800 mW cm <sup>-2</sup>	water splitting	H <sub>2</sub> : ~5 mmol cm <sup>-2</sup> h
CPT-liquid solid phase	SAAg-g-CN [117]	300 W Xe lamp	water splitting	CO: 498 μmol h <sup>-1</sup> g <sup>-1</sup>
CPT-liquid solid phase	Bi <sub>2</sub> Se <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub> [100]	300 W Xe lamp	CO <sub>2</sub> reduction	CO: 8.2 μmol h <sup>-1</sup> g <sup>-1</sup>
TPT-liquid solid phase	Hollow carbon nanospheres [125]	300 mW cm <sup>-2</sup>	Phenol removal	Phenol: 0.09 min <sup>-1</sup>
TPT-gas solid phase	Ru/Al <sub>2</sub> O <sub>3</sub> [86]	846.5 mW cm <sup>-2</sup>	Sabatier reaction	CO <sub>2</sub> : 18.16 mol h <sup>-1</sup> g <sup>-1</sup>
TPT-gas solid phase	Pd@Nb <sub>2</sub> O <sub>5</sub> [97]	25 kW cm <sup>-2</sup>	Reverse water gas shift	CO: 4.9 mol h <sup>-1</sup> g <sup>-1</sup>
CTC-gas solid phase	Ru/graphene [132]	0.5 W cm <sup>-2</sup>	Fischer-Tropsch synthesis	CO: 14.4 mol·mol <sub>Ru</sub> <sup>-1</sup> ·h <sup>-1</sup>
CTC-gas solid phase	Cu-Ru alloy [16]	9.6 W cm <sup>-2</sup>	Ammonia decomposition	H <sub>2</sub> : 1200 μmol s <sup>-1</sup> g <sup>-1</sup>
CTC-gas solid phase	Rh/SrTiO <sub>3</sub> [42]	19.2 W cm <sup>-2</sup>	Dry reforming of methane	H <sub>2</sub> : 34 mol (mol Ru) <sup>-1</sup> s <sup>-1</sup>
CTC-gas solid phase	copper/zinc oxide/alumina [133]	600 mW cm <sup>-2</sup>	CO <sub>2</sub> hydrogenation	MeOH: 245 g kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>
CTC-solid solid phase	Ni-TiO <sub>2</sub> -γ-Al <sub>2</sub> O <sub>3</sub> [131]	1.5 mW m <sup>-2</sup>	Plastic pyrolysis	Selectivity for hydrocarbon: 53.46%

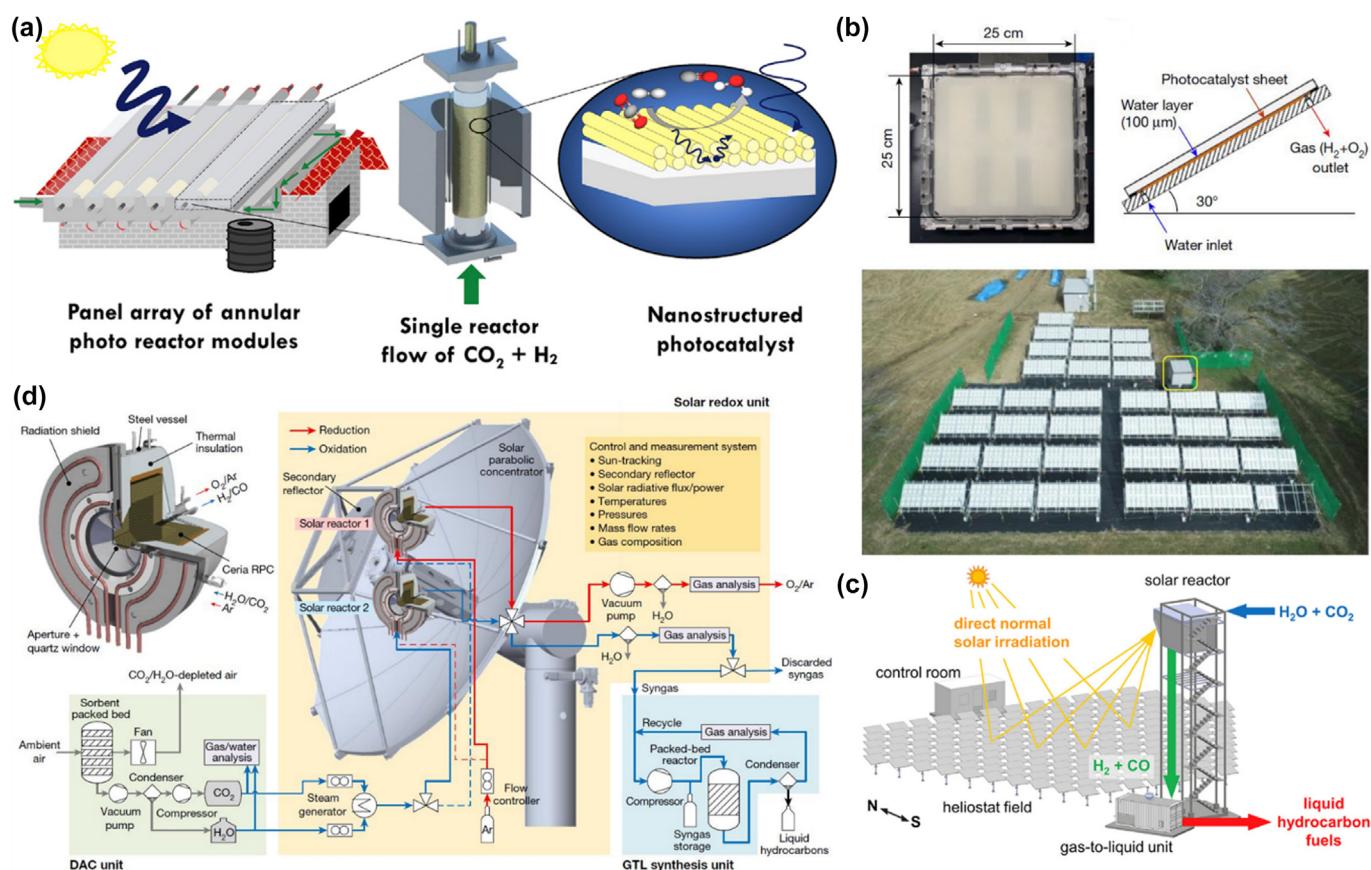


FIG. 10

Pilot tests of photothermal catalysis. (a) A rooftop demonstrator that uses a waveguide photoreactor coated with a supercapacitor photocatalyst [119]. (b) A solar fuel farm uses a plate-type catalyst bed [22]. (c) A solar concentrator system for photothermal catalysis [23]. (d) An integral reactor for photothermal catalysis [84].

tures. This technique is ideal for creating precise and reproducible patterns of catalysts on a substrate, including semiconductor and heterojunction based photothermal catalysts. For example, Au microelectrode chips were successfully fabricated on a glass slide using photolithography (Fig. 11a) [135]. Additionally, electrospinning is a versatile and widely used technique for scaling up the synthesis of flexible materials. This process involves generating a jet of polymer solution or melt using an electrostatic field, which can be adapted to incorporate catalyst particles or nanoparticles into the resulting fibers. Electrospin-

ing technology has been widely used for the fabrication of almost all types of nanostructured photothermal catalysts, including carbonaceous, semiconductor-based, heterojunction, and supported metallic catalysts (Fig. 11b) [136]. Chemical vapor deposition (CVD) is also a popular technique for scaling up the synthesis of two-dimensional photothermal catalyst films. This versatile and efficient process can deposit thin films of catalyst materials onto a variety of substrates. The technique involves the reaction of one or more precursor gases in a high-temperature chamber, resulting in the formation of a solid or



chemical reactions is to differentiate the contribution of EHC to photothermal catalytic throughput. However, the existence of EHC in the photothermal catalytic process is still under debate. Rational experimental design and exploring high-resolution microscopy are necessary to resolve this issue. Meanwhile, unifying hot spots and catalytic sites on photothermal catalysts can yield a double output. While most research has focused only on the active site, the importance of hot spots has been overlooked. Distinguishing these two essential regions via multiscale computational simulation and in situ/operando characterizations is highly important.

- (iii) Photothermal catalysis possesses considerable potential for expanding its application beyond its current scope. While its role in the reduction and conversion of CO<sub>2</sub> into low-carbon molecules is crucial for addressing greenhouse gas emissions and achieving carbon neutrality, there is further potential for the development of higher-value fuels. Photothermal tandem catalysis, in particular, holds a promise for high efficiency and selectivity in coupling C–C bonds and generating multi-carbon products, thereby presenting an encouraging pathway for green chemical synthesis. Through the integration of photothermal catalysis with other catalytic processes, the conversion of CO<sub>2</sub> can be optimized to produce valuable fuels and feedstocks, advancing the goal of a sustainable and resource-efficient future.
- (iv) In accelerating the industrialization of photothermal catalysis, it is necessary to develop safe and energy-efficient assembly reactors. In addition, there is a need for coupling technologies that can scale the synthesis of different types of photothermal catalysts. To ensure consistent and reliable performance of photothermal catalytic reactions at a large scale, accurate process control is essential. Advanced monitoring and control systems must be used to measure key process parameters and adjust operating conditions in real-time as needed. By addressing these challenges, photothermal catalysis can be rapidly advanced towards commercialization and implementation in a wide range of industrial applications.

## Data availability

No data was used for the research described in the article.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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