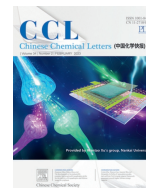




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Photothermal catalysis for CO₂ conversion

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ABSTRACT

The conversion of carbon dioxide into useful fuels or chemical feedstocks is of great importance for achieving carbon emission peak and carbon neutrality. The harvesting and conversion of solar energy will provide a sustainable and environmentally friendly energy source for human production and living. Very recently, photothermal catalysis has been proved to exhibit great advantages in reducing the reaction temperature, promoting the catalytic activity, and manipulating the reaction pathway in comparison with traditional thermal catalysis. In this review, we firstly introduced the fundamental mechanisms and categories of photothermal catalysis to understand the synergy or the difference between photochemical and thermochemical reaction pathways. Subsequently, the criteria and strategies for photothermal catalyst design are discussed in order to inspire the development of high-efficiency photothermal catalytic route by achieving intense absorption of broadband solar energy spectrum and high conversion capability of solar-to-heat. Recent progress in CO₂ reduction achieved by photothermal catalysis was summarized in terms of production types. In the end, the future challenges and perspectives of photothermal catalytic CO₂ reduction are presented. We hope that this review will not only deepen the understanding of photothermal catalysis, but also inspire the design, preparation and application of high-performance photothermal catalysts, aiming at alleviating non-renewable fossil energy consumption and carbon emissions for early carbon emission peak and carbon neutrality.

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1. Introduction

At present, the production of approximately 95% of the world's chemical products relies on catalytic routes. Unfortunately, the energy input driving catalytic process is largely dependent on traditional non-renewable fossil fuels (coal, oil, and natural gas). The tremendous consumption of non-renewable energy sources has resulted in excessive carbon emissions leading to severe environmental and climate problems. In recent years, the exploration and application of renewable energy sources have attracted numerous attention in order to replace or promote the existing catalytic processes [1–7]. Solar energy as a renewable energy source provides, directly or indirectly, most of the energy needed for human production and living. Hence, photo-driven and photo-assisted catalytic chemical transformations have been extensively investigated. Recently, photothermal catalysis has developed into an effective

process to extensively harvest solar energy including low-energy visible and infrared light spectrum [8]. Light-induced fascinating properties such as “hot electrons” generation, local temperature rise, vacancies engineering, can couple photochemical and thermochemical pathways [5,6,9–11], thereby efficiently activating adsorbed species towards outstanding catalytic activity enhancement.

Since the pioneering work of Fujishima and Honda in 1972 [12], the photocatalysis field has witnessed decades of booming development. However, the semiconductor-based photocatalysis suffers from the fast recombination of photo-generated carriers and the insufficient absorption/utilization of the whole solar spectrum, thereby retaining low photocatalytic efficiency until now [9,13–18]. The research work in 1987 reported that the introduction of photo can lead to a significantly enhanced reaction rate in the methanation reaction, which is 4 to 5 times higher than that of non-illuminated catalysis [19]. Wavelength-dependent performance investigation suggested the dominate contribution of bandgap excitation in catalyst. One year later, photo-generated heat effect rather than intrinsic photochemical route was suggested to make the main contribution for methanation reaction [20]. Since then, the contribution of light through thermochemical and/or photochemical pathways comes to the forefront

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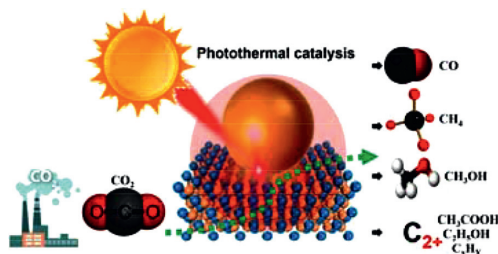


Fig. 1. Illustration for photothermally catalyzing CO₂ conversion.

of research. Thermochemically dominant route in CO₂ conversion has been widely found in Ni-based catalyst for dry reforming of methane (DRM) catalysis [21], Group VIII nanocatalysts for CO₂ hydrogenation [22], Pd@Nb₂O₅ for photothermal hydrogenation (PTH) catalysis [23], Ru@layered double hydroxide [24], CoFe@alumina [25], and so on. These cases suggested that the heat converted from light drives the catalytic process just the same as conventional thermal catalysis. The achievement of CO₂ reduction at ambient temperature only through light-irradiation-induced photo-driven thermocatalysis (PDT) route demonstrated great advantages including lowering/eliminating fossil energy input and preventing catalysts' sintering/degradation/deactivation [2,3,26,27]. In recent years, the amount of researches about photochemistry pathway in photothermal catalysis witnessed a gradual increase, which can be summarized into heat-assisted photocatalysis and/or light-assisted thermocatalysis. Heat-assisted photocatalysis can solve the problem of the slow reaction rate in PDT by lowering activation energy barrier, accelerating the mobility of photo-generated electron and hole in semiconductor and the mass transfer [28]. The utilization of light irradiation in light-assisted thermocatalysis demonstrated the special role of light in mediating the reaction pathways in PDT [4,29,30].

Photothermal catalysis is essentially based on sunlight harvesting and conversion, which has developed into challenging and dynamic research area. In this review (Fig. 1), the fundamental mechanisms and categories of photothermal catalysis were firstly introduced. Subsequently, the criteria and strategies for photothermal catalyst design are discussed. Recent progress in CO₂ reduction achieved by photothermal catalysis was summarized in terms of production types. In the end, the future challenges and perspectives of photothermal catalytic CO₂ reduction are presented. We hope that this review will not only deepen the understanding of photothermal catalysis, but also inspire the design, preparation and application of high-performance photothermal catalysts, aiming at alleviating non-renewable fossil energy consumption and carbon emissions for early carbon emission peak and carbon neutrality.

2. Photothermal catalysis

2.1. Different mechanisms of photothermal effect

Nowadays, inorganic and organic materials have been reported to own the capabilities of converting incident light energy into thermal/heating energy with the light irradiation driving. As shown in Fig. 2, the present photothermal mechanisms can be summarized into three different ways, i.e., thermal vibration of molecules, plasmon-induced localized heating, and non-radiative relaxation in semiconductors based on the understanding of the difference in the interactions of light and matter [3,31]. Of course, some special material system may couple one or more of the three photothermal mechanisms.

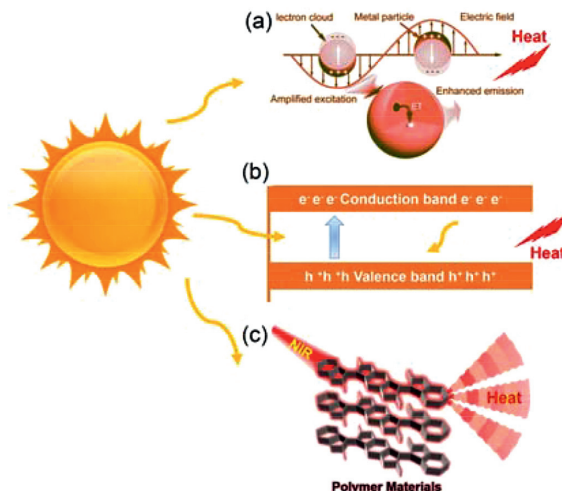


Fig. 2. Illustration of different generation forms of photothermal effects. (a) Plasmonic localized heating, (b) non-radiative relaxation in semiconductors, (c) thermal vibration in molecules.

2.1.1. Plasmonic localized heating

Recent pioneering work has indicated that plasmonic catalysts can induce local heating and provide hot carriers to initiate the CO₂ reduction reaction and/or modulate reaction pathways, leading to high solar-to-fuel conversion efficiency, which can be classified into two types of mechanism: plasmonic photocatalysis (photo-induced hot carriers) or photothermal catalysis (light-excited phonons). The collaboration of hot carriers and phonon modes is suggested to be more beneficial to the plasmonic photothermal catalysis. It is well-known that metallic elements Cu, Ag, and Au in group IB exhibit superior surface plasmon resonance (SPR) effects [32]. The inter-band excitations of Cu and Au have to overcome energy thresholds of 2.1 and 2.2 eV, respectively, implying the absorption capacity for visible light [33]. The size, the morphology and the types of plasmonic metals can modulate the local electromagnetic field and the localized surface plasmon resonance (LSPR) absorption [2,34]. The transfer of generated hot carriers from plasmonic metal to adsorbates are suggested to facilitate the activation of chemical bond and the conversion of intermediates through providing additional vibration energy. Photo-induced heat can mainly influence the catalytic reaction process in three ways. Firstly, photo-induced heat can excite the phonon modes, which drives the conversion of adsorbates on the surface of the plasmonic nanoparticle. Secondly, the key adsorption-desorption process of reactants in heterogeneous catalysis can be promoted leading to high reaction kinetics [4,35,36]. Thirdly, the yield and the selectivity of final products can be manipulated by photo-induced heat. The light and thermal properties of plasmonic catalysis can enhance the application efficiency of solar light leading to an attractive solar-to-energy conversion [32,33,37].

2.1.2. Non-radiative relaxation in semiconductors

Semiconductors can absorb the light energy close to or higher than their band gap. Then, two main processes dominate the relaxing of excited electrons to the lower-energy states, i.e., the recombination of photo-generated carriers (electrons and holes) through radiative relaxation and the excitation of phonons through non-radiative relaxation. The former emits photon resulting in energy loss [38–40]. The latter can produce local heating by lattice vibration. Therefore, photothermal conversion efficiency of catalyst is highly related to the band-gap width of semiconductors. Specifically, the semiconductors with narrow band gap are suggested to be more efficient in the conversion of light energy to heat energy

[41,42]. By contrast, low-energy light is scattered in the case of semiconductors with wide band gap, thereby playing a tiny role in photothermal conversion [2].

2.1.3. Thermal vibration in molecules

Currently, carbonaceous and polymeric materials have been reported to follow the thermal vibration mechanism [43,44]. Similar to the above semiconductors, the electron transition occurs when the energy of incident light matches that of electron transition in molecules. The photoexcited electrons at the lowest unoccupied molecular orbital (LUMO) relax back to the highest occupied molecular orbital (HOMO) through the electron-vibration coupling [45–47]. Thermal vibration in molecules will lead to heat generation in molecules. Moreover, the abundant conjugated π bonds in the reported material are suggested to allow low irradiation energy to achieve electron transition through π to π^* orbitals [48]. Then, the amount of π bonds can be modulated to tune the energy gap between LUMO and HOMO in molecules, thereby facilitating photothermal conversion efficiency.

2.2. Classifications of photothermal catalysis

In the absence of external heating, photo-driven thermocatalysis (PDT) highly requires an effective light harvesting, an excellent photo-to-heat conversion efficiency and efficient active sites [1,49]. Generally, we encounter low reaction kinetics in photocatalysis, which limits the rapid and efficient occurrence of the reaction. In the case of thermal-assisted photocatalysis (TAP), the energy bands of semiconductors satisfied thermodynamic requirements for photocatalytic CO_2 reduction. The coupled physical thermal energy can provide overall driving force to accelerate the reaction kinetics through reducing activation energy barrier, promoting the mobility of photo-generated carriers and the transfer rate of reaction mass, thereby enabling the photocatalytic CO_2 reduction. In the case of photo-assisted thermocatalysis (PAT), similar to traditional thermal catalysis, thermochemical pathway is dominant in CO_2 reduction. The introduction of light irradiation can modulate the adsorption and desorption of reactants/intermediate/product on the catalyst surface, thus achieving regulation of the reaction rate and production selectivity [27,50]. Photothermal co-catalysis (PTC) is suggested that both photo and heat play a synergistic or equally important role in the reaction.

2.3. Design principles of photothermal catalysts

As for the rational design of catalysts, we have to understand the light-induced photothermal effect and photochemistry process [51,52]. Current reports indicated that the effects of light can be summarized into three ways. Firstly, the electron-phonon interaction between catalyst and light solely straightforwardly provide localized photothermal heating to overcome the energy barrier for activating CO_2 molecules and accelerating subsequent conversion [53,54]. In this case, the mechanistic process is essentially the same as that of conventional thermal catalysis. The potential difference is that light irradiation can serve as multiple roles in CO_2 reduction process. If catalysts can provide a stable localized heating temperature, the requirement for physical heating will be dramatically decreased. Secondly, the role of light is discernible in light-assisted thermocatalysis or thermal-assisted photocatalysis [27,55,56]. As for heat-assisted plasmonic photocatalysis, heating has been verified to enhance photoexcited electron generation, thereby promoting the plasmonic photocatalytic activity through overcoming activation barrier, increasing quantum efficiency/yield, and optimizing intermediate species adsorption/desorption [57,58]. Another scenario is thermal-assisted photocatalysis. The positions of energy bands should satisfy thermodynamic requirements for

photocatalysis process under the light irradiation. The coupled thermal energy can provide overall driving force to accelerate the reaction kinetics, thereby enabling the photocatalytic CO_2 hydrogenation. Thirdly, in addition to the above two roles, light also exhibits other functions. Light irradiation has the ability to tune carbon deposition behavior from active carbon to graphitic carbon in SiO_2 encapsulated Ni nanocatalysts (Ni@SiO_2) through the reaction between excited hot electrons induced oxygen radical $\text{O}^\cdot$ and carbon species [59]. The amounts of oxygen vacancies in catalysts can also be *in situ* regulated by light irradiation, for example in CeO_2 -based catalyst [27,60–62].

3. Photothermally catalytic CO_2 conversion

Photothermal catalytic CO_2 reduction has attracted extensive attractions. However, the present productions of are C_1 fuels, such as CO , CH_4 , and CH_3OH are widely reported [2,57,63,64], some of which are listed below. By contrast, the formation of C_2 products definitely involved multielectron transfer and C–C coupling reaction pathways with typical thermodynamically intractable and kinetically retarded features. The photothermal conversion of CO_2 to C_2 products (CH_3COOH , $\text{C}_2\text{H}_5\text{OH}$, C_2H_4 , C_2H_6 , etc.) with higher energy density and broader application prospect has attracted extensive attention but is rarely reported [3,65]. The types of typical reactions, catalytic materials, and potential reaction mechanisms, in photothermal catalytic CO_2 conversion are described below.

Reverse water gas shift: $\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$

Dry reforming: $\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{H}_2 + 2\text{CO}$

Methane synthesis: $\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2$

Sabatier reaction: $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$

Methanol synthesis: $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$; $\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 3/2\text{O}_2$

4. CO production

Greenhouse-like catalytic strategy was reported to lock the light inside catalyst for photothermal catalytic CO_2 hydrogenation (Figs. 3a and b) [5]. A core-shell structure catalyst (denoted as Ni@p-SiO_2) was constructed by encapsulating nickel nanocrystals (Ni) into silica sheath (SiO_2) (Figs. 3a–e). Systematical experiments were conducted to clarify the origin of greenhouse-like photothermal effect in Ni@p-SiO_2 . A direct-contact thermocouple was used to measure the surface macroscopic temperature, while the local temperatures (T_{local}) was determined by indirectly calculating equilibrium constants in the equilibrated chemical reactions. Compared with the reference Ni nanocrystals (791 K T_{local}) and $\text{Ni/SiO}_2\cdot\text{Al}_2\text{O}_3$ (811 K T_{local}) (Fig. 3f), the Ni@p-SiO_2 showed a very high T_{local} of 852 K. In addition, the structure-activity relationship between the core-shell structure and photothermal efficiency was evaluated. They suggested that the presence of nickel core was beneficial to the absorption of incident photons. Theoretical simulation results indicated that thermal radiation and convection accounted for about 35% and 61% in heat dissipation, implying two dominant factors for photothermal effect enhancement. The SiO_2 shell in catalyst can serve as insulation media and infrared light trapper, which is also of significant in blocking heat dissipation pathway from hotspot Ni core to the surroundings. In addition, the existence of SiO_2 shell can well confine Ni core from irreversible aggregation, thereby leading to superior thermal stability of Ni active sites. As for the tests of photothermal CO_2 hydrogenation, CO is the predominant product (Figs. 3g and h). Ni@p-SiO_2 exhibited a CO_2 conversion rate of $344 \text{ mmol g}_{\text{Ni}}^{-1} \text{ min}^{-1}$ with a high thermal stability under 2.8 W/cm^2 illumination, which is about 12.3 and 8.8 times larger than the reference Ni nanocrystals and $\text{Ni/SiO}_2\cdot\text{Al}_2\text{O}_3$ samples (Figs. 3i and j). Greenhouse-like catalytic strategy by designing core-shell structure will inspire the development of novel

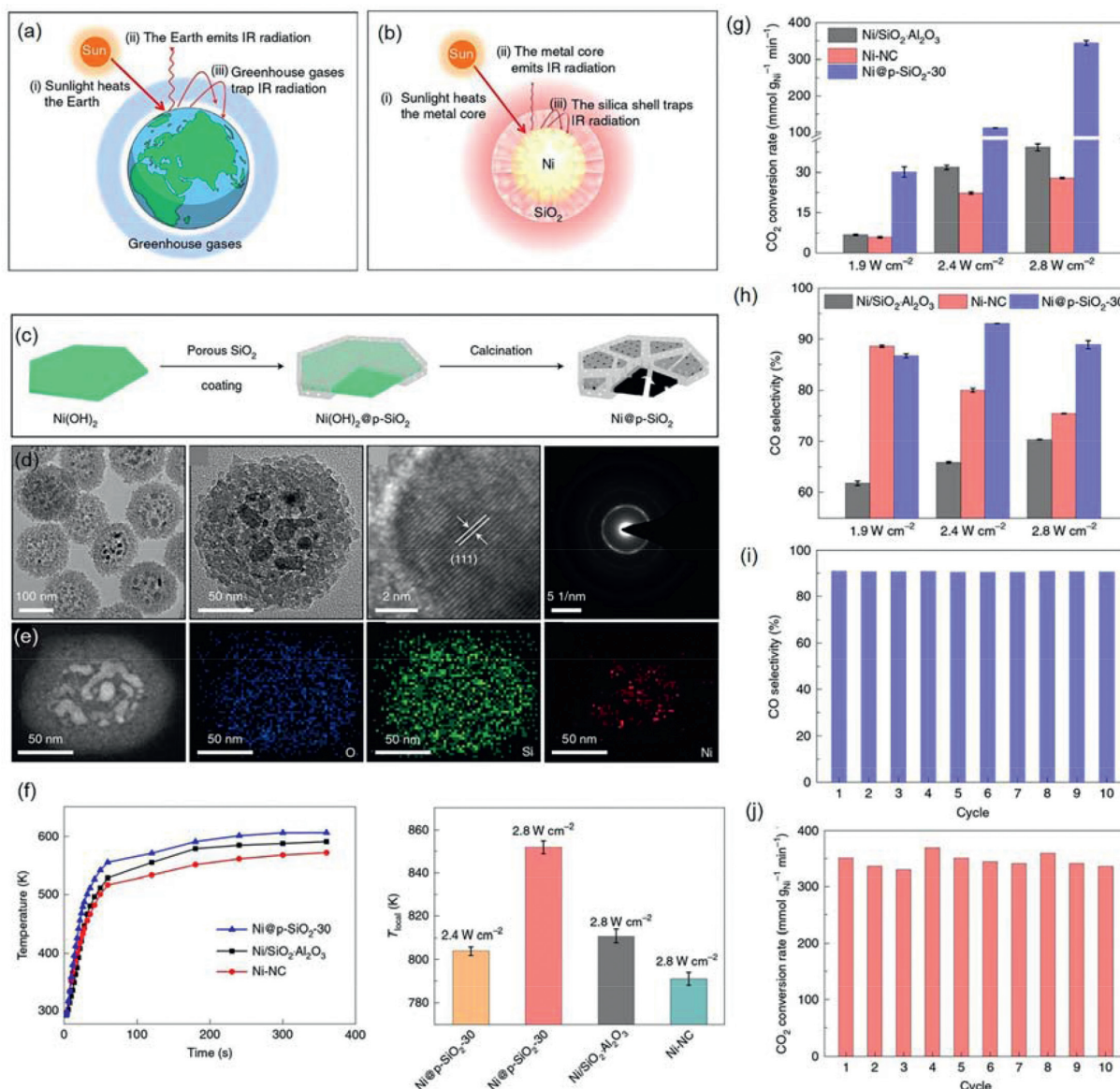


Fig. 3. (a) Schematic illustration of the Earth's greenhouse-like effect. (b) Mechanism description of the nanoscale greenhouse effect in Ni@p-SiO₂. (c) Illustration of the synthesis procedure for Ni@p-SiO₂. (d) Transmission electron microscopy (TEM) images, high resolution transmission electron microscopy (HRTEM) image, and selected area electron diffraction (SAED) pattern from left to right. (e) Elemental energy-dispersive X-ray spectroscopy (EDS) mapping of Ni@p-SiO₂-30. (f) Photothermal effect profiles via measuring the macroscopic surface temperatures of different samples under simulated 2.8 W/cm² sun-light illumination (left). Estimated local temperature (*T*_{local}) under 2.4 and 2.8 W/cm² illumination (right). Photothermal catalytic activity of Ni@p-SiO₂-30 in terms of (g) CO₂ conversion rate and (h) CO selectivity. Long-term stability tests in terms of (i) CO selectivity and (j) CO₂ conversion rate. Reproduced with permission [5]. Copyright 2021, Springer Nature.

photothermal materials in different application scenarios [5]. In addition, Co@p-SiO₂ nanoneedle arrays were reported with light absorption efficiency as high as 100% under entire solar illumination. The plasmonic excitation effects of Co nanoparticles and the antireflection effect of Co@p-SiO₂ nanoarrays are accounting for the strong sunlight absorption. The results strongly indicated that coating SiO₂ shell served as an effective strategy to enhance the light to heat conversion efficiency [35].

Composition modulations of other transition metals can also enable the production of CO [60,66–71]. Black color and high surface area are the two basic requirements for nanostructures to achieve high photothermal performance. Two-dimension (2D) black non-stoichiometric In₂O_{3-x} nanosheets were prepared by photoinduced defect engineering [60]. The 2D structure and the oxygen vacancies in catalyst can effectively regulate the structural and electronic properties, thereby leading to high conversion rate

of 103.21 mmol g_{cat}⁻¹ h⁻¹ and near-unity CO selectivity (Fig. 4a). Specially, oxygen vacancies in the catalyst are suggested to be bi-functional, which can not only promote the harvesting of light but also enhance the chemical adsorption of CO₂ molecules. A black non-stoichiometric/stoichiometric In₂O_{3-x}/In₂O₃ heterostructure was prepared to promote high optical absorption strength for heat or light application [66]. Hydrogen induction method was used to remove O-atoms from stoichiometric In₂O₃, leading to the formation of non-stoichiometric In₂O_{3-x} domains and ultimate amorphous phases. The resultant black heterostructure is featured with stoichiometric In₂O₃ core and non-stoichiometric In₂O_{3-x} shell, which demonstrated superior CO₂ hydrogenation activity with 100% selectivity to CO and a high turnover frequency of 2.44 s⁻¹. Specifically, In₂O_{3-x}/In₂O₃ heterostructure was suggested to display concurrent thermochemical and photochemical effects. The photogenerated electrons and holes are verified to transfer

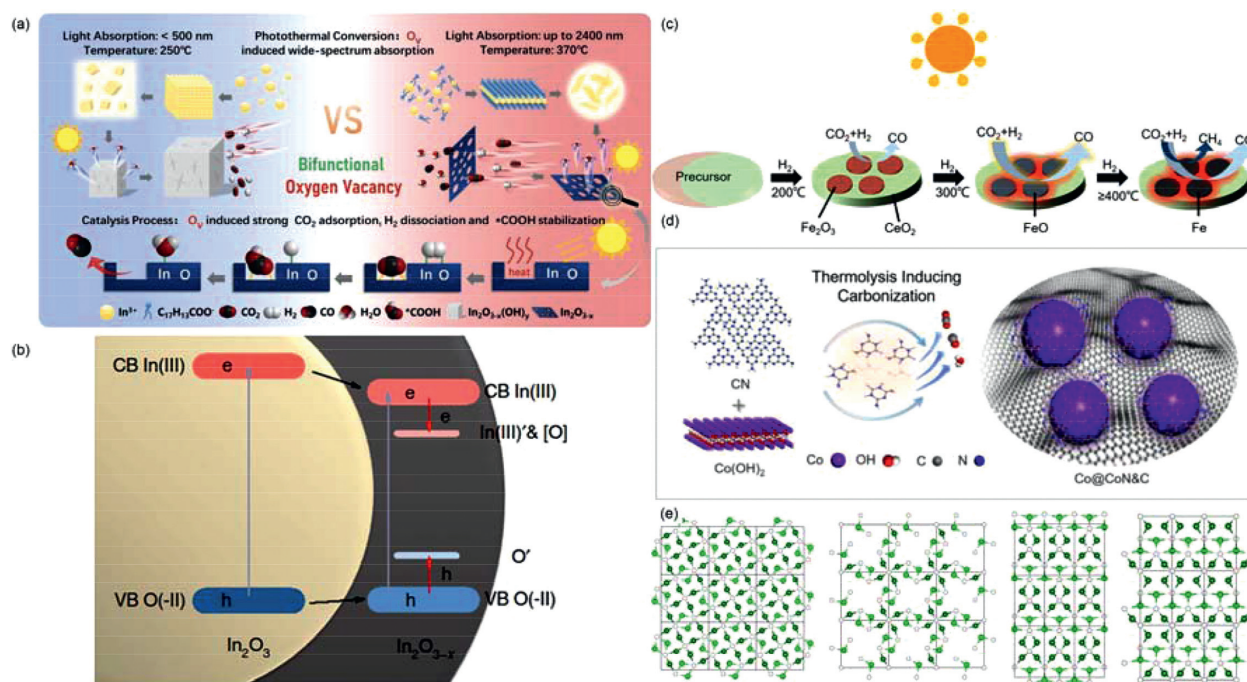


Fig. 4. (a) Schematic illustration of the formation mechanism of oxygen vacancy and catalytic route for black $\text{In}_2\text{O}_{3-x}$ nanosheets. Reproduced with permission [60]. Copyright 2020, Wiley-VCH. (b) Illustration of reaction pathway and the electronic band structure in $\text{In}_2\text{O}_{3-x}/\text{In}_2\text{O}_3$. Reproduced with permission [66]. Copyright 2020, Springer Nature. (c) The calcination temperature dependent photothermal activity. Reproduced with permission [67]. Copyright 2020, Springer Nature. (d) The preparation process of $\text{Co@CoN\&C}$. Reproduced with permission [68]. Copyright 2020, American Chemical Society. (e) Crystal structure of Ni_{12}P_5 (P-white, Ni-green) in the (001) orientation (two on the left) and in (010) orientation (two on the right). Reproduced with permission [69]. Copyright 2020, Springer Nature.

from the In_2O_3 core to the $\text{In}_2\text{O}_{3-x}$ shell for CO_2 hydrogenation reaction. The solar irradiation is also suggested to trigger CO_2 hydrogenation process at an oxygen vacancy through breaking the C–O bond in adsorbed CO_2 molecules by proton insertion (Fig. 4b). Researcher helped to understand the role of oxygen vacancies photothermal CO_2 reduction to CO by thermal coupled photoconductivity measurements [70]. The existence of oxygen vacancies can significantly increase photothermal CO yield on oxygen vacancies-rich TiO_2 catalyst by accelerating the electron transfer from catalyst to CO_2 molecules and promoting electron detrapping to photocatalyst conduction band. The metal oxide nanocomposites of $\text{FeO}-\text{CeO}_2$ were found to be an efficient and highly selective catalyst for photothermal CO_2 reduction reaction [67]. The valence state of Fe species plays an important role in the reaction selectivity. FeO is the active species for the high CO selectivity, while Fe^0 results in high CH_4 selectivity through Sabatier reaction (Fig. 4c). Fe_3O_4 catalyst was also reported with about 100% selectivity towards CO and a high conversion rate of $11.3 \text{ mmol g}^{-1} \text{ h}^{-1}$ in photothermal CO_2 conversion [71].

The non-noble Co-based catalyst was also reported with high activity for photothermal CO_2 reduction to CO. The $\text{Co@CoN\&C}$ catalyst was prepared by anchoring Co nanoparticles into atomic-scale dispersed Co–N species (Fig. 4d) [68]. The amount of carbon substrate and the size of Co nanoparticles are suggested to manipulate the thermodynamic and kinetic processes during catalytic reaction. Excessive carbon amount and larger Co nanoparticles can enhance the absorption of light and efficient. The increased local temperatures resulted in an enhanced hydrogenation ability for CH_4 . Moderate $\text{Co@CoN\&C}$ showed maximum conversion rate of $132 \text{ mmol g}^{-1} \text{ h}^{-1}$ with a high CO selectivity of 91.1%. The graphitic-carbon and Co nanoparticles enabled strong photon-matter interaction, thereby promoting the efficiency of light-to-heat conversion. The increased work temperature was thermodynamically favorable for CO_2 activation. The adsorption of CO_2 was improved by the graphitic-carbon layers. The existence of atomi-

cally dispersed Co–N species can decrease hydrogenation capability of catalyst, thereby kinetically modulating the reaction pathway. Taken together, the catalytic activity and the CO selectivity were both optimized.

Transition metal phosphides are found to serve as superior photothermal catalyst. Ni_{12}P_5 was selected as an archetype to study solar-driven CO_2 hydrogenation [69]. Ni_{12}P_5 owns a relatively special structural features with phosphorus lattice encapsulating highly dispersed nickel nanoclusters, which enable the highly efficient absorption of all solar spectrum (Fig. 4e). Ni_{12}P_5 was proved to be a superior photothermal catalyst offering a high CO production rate of $960 \pm 12 \text{ mmol g}^{-1} \text{ h}^{-1}$, approximately 100% selectivity and long-term structural stability in RWGS reaction. The ensemble effect of P was suggested to delivery highly dispersed Ni nanoclusters in catalyst and disadvantage the firm multi-coordinate bonding to CO, which provided unique reaction pathway in the form of linearly bonded nickel and carbonyl. The strong capability of light-harvesting endow Ni_{12}P_5 with a dramatically improved local temperature to actuate the RWGS reaction. Co_2P analogs also demonstrated strong light capture and high catalytic activity, implying a universal platform in photothermal CO_2 catalysis for metal phosphide materials.

Syngas (the mixture of H_2 and CO) is an exceptionally valuable chemical feedstock. The pathway of consuming two greenhouse gases by way of methane dry reforming ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$) is regarded as an environmentally friendly strategy. However, the desired reaction efficiency inevitably requires high temperatures (700 °C to 1000 °C) and the stability of catalyst suffers from coke generation. Recently, the strong interaction between light and bimetallic-alloy plasmonic nanostructures (Au–Pd and Au–Pt) has been studied for methane dry reforming reaction. The plasma resonance effect promoted methane dry reforming reaction was investigated on Au–Pt catalyst [36]. The photo-assisted thermal process exhibited high catalytic activity, which was about 2.4 times larger than that of PDT. The CO_2 reduction activation energies in

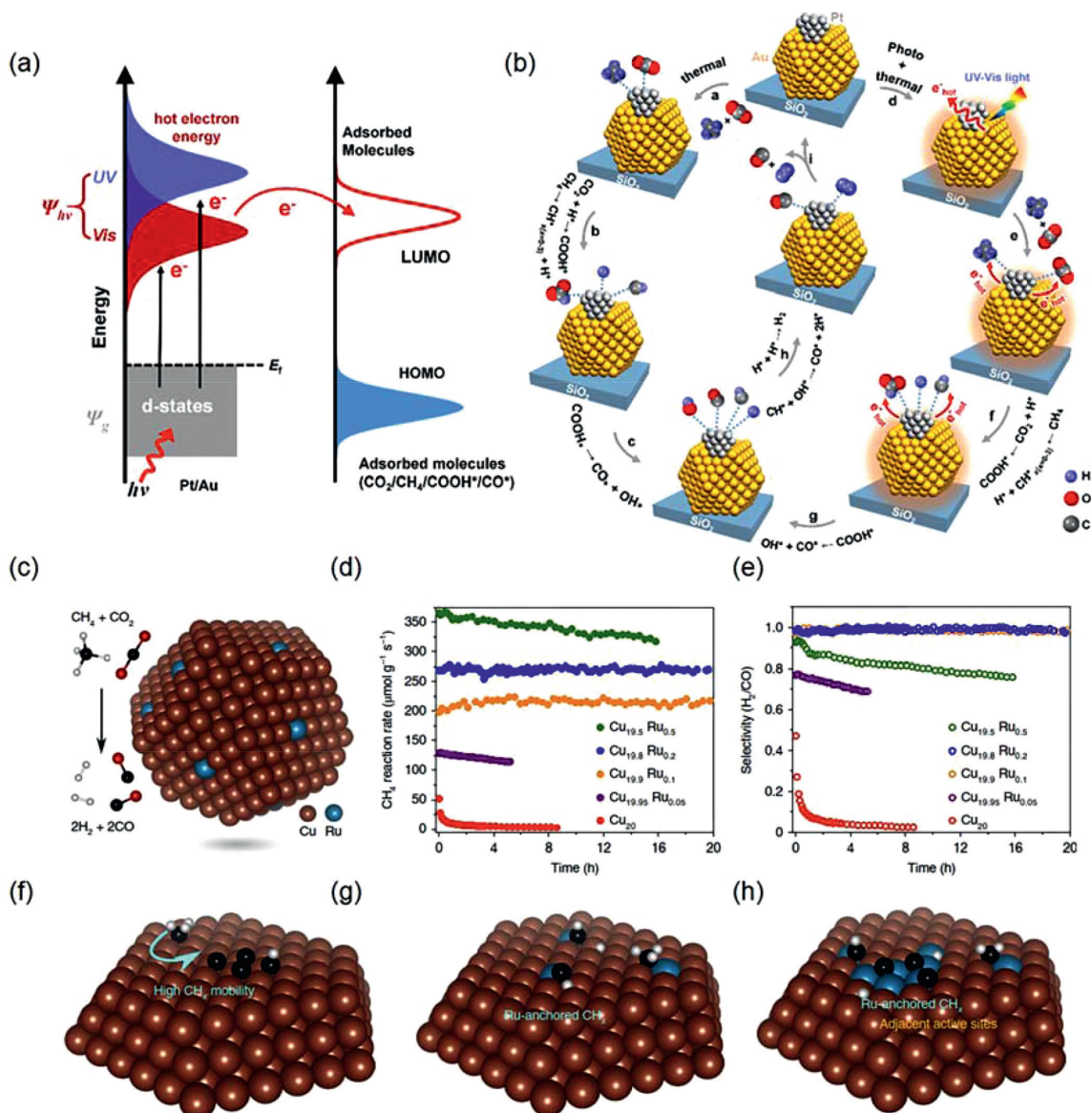


Fig. 5. (a) Schematic illustration of energy transfer. (b) Suggested methane dry reforming process on Pt-Au/SiO₂ under light irradiation. Reproduced with permission [36]. Copyright 2016, Elsevier B.V. (c) Proposed methane dry reforming process on Cu-Ru single-atom alloy catalyst. (d) Reaction rate and stability test and (e) production selectivity of photocatalytic dry reforming process on Cu-Ru single-atom alloy catalyst. Relationship between composition and coke resistance ability, i.e., (f) pure Cu, low Ru content (g) and (h) high Ru content. Reproduced with permission [6]. Copyright 2020, Springer Nature.

photo-assisted thermal process on Au-Pt is suggested to be decreased by ~30% compared with the activation energies in thermal process. The results of experiments, calculations, and simulations indicated that the effective absorptions in the range of UV and visible light in Au-Pt led to powerful electric fields and high yielding of hot electrons. Thus, the hot electron transferred to antibonding orbitals of adsorbed reactants/intermediate species on the surface of Au-Pt, thereby accelerating the products desorption for reaction rate promotion (Figs. 5a and b). However, the introduction of high content of Pd or Pt was suggested to decrease the plasma resonance effect in Au, thereby resulting in limited photocatalytic performance. A plasmonic photocatalyst composed of Cu nanoparticle and Ru single atom was reported to demonstrate desirable features of high reaction efficiency and coke resistance ability for light-driven low-temperature methane dry reforming. In this case, the Cu nanoparticle was used as plasmonic antenna for strong light absorption, thereby providing efficient production of hot carriers under light irradiation. The loaded single-

atom Ru served as reactive site. The non-uniform distribution of local electrons in Cu-Ru single-atom alloy nanoparticles indicated a further promotion in the production of hot carriers [6]. The resultant catalyst offered high catalytic activity with high turnover frequency (34 mol H₂ (mol Ru)⁻¹ s⁻¹) and superior long-term stability (over 50 h) under focused light irradiation (Figs. 5c-e). Note that no external heating was introduced. The structural design of plasmonic antenna and single-atom in the catalyst demonstrated great potential for high reaction efficiency and strong coking resistance in methane dry reforming (Figs. 5f-h). The synergistic catalysis of NiCo alloys also demonstrated photo-enhanced reactant activation in CO₂ conversion with CH₄ [72]. The light-to-fuel efficiency was up to 33.8%. The carbon deposition rate was as low as 0.011 g_c g_{cat}⁻¹ h⁻¹, which should be attributed to the favorable oxidation pathway from CH* to CHO* and the disadvantageous high energy barriers from the dissociation of CH* to C* species. The introduction of light illumination was suggested to lower apparent activation energy, thereby leading to superior light-driven CO₂

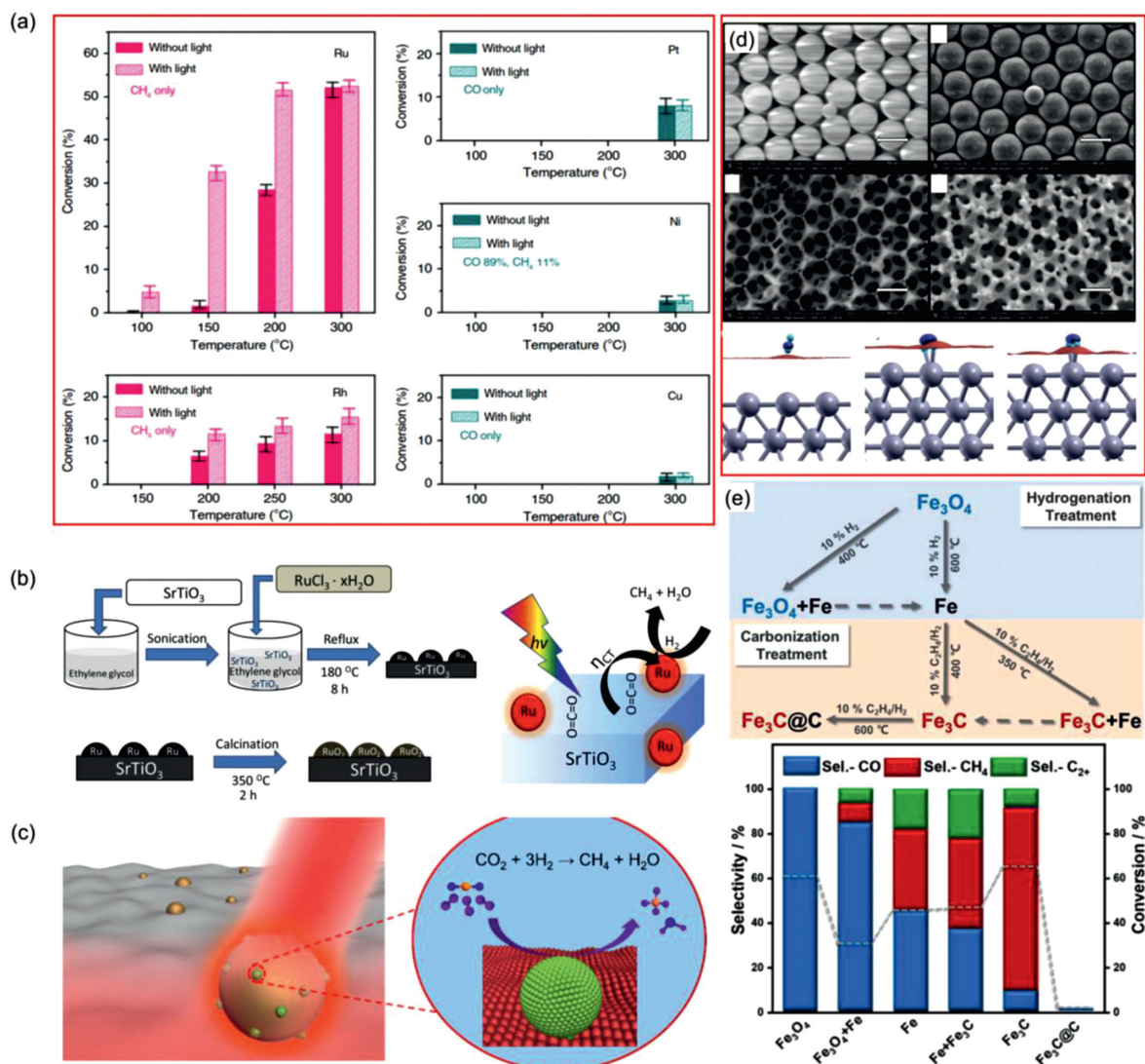


Fig. 6. (a) Light promoted catalytic performance. Reproduced with permission [73]. Copyright 2018, Springer Nature. (b) Preparation of RuO₂/STO catalyst and photothermal catalytic process. Reproduced with permission [74]. Copyright 2019, Elsevier B.V. (c) Schematic illustration of Rh/Al nanoantenna catalyst for photothermal CO₂ methanation. Reproduced with permission [75]. Copyright 2021, American Chemical Society. (d) SEM images of Ru/SiO₂ and Ru/i-Si-O and the difference in charge density on Ru isosurfaces for H₂ adsorption (Scale bar 500 nm). Reproduced with permission [76]. Copyright 2018, The Royal Society of Chemistry. (e) Preparation strategy for Fe-based photothermal catalysts with different hydrogenation/carbonization pathways and the catalytic performance of different Fe-based photothermal catalysts. Reproduced with permission [71]. Copyright 2020, American Chemical Society.

conversion in comparison with conventional thermal-driven process.

5. CH₄ production

The Sabatier reaction or Sabatier process involves the reaction of hydrogen with carbon dioxide at elevated temperatures and pressures in the presence of a nickel catalyst to produce methane and water. Optionally ruthenium on alumina makes a more efficient catalyst. It is described by the following reaction: $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$. The Ru-based catalysts have been verified to be active for Sabatier reaction. Different metallic catalysts of Cu, Ni, Ru, Pt, and Rh were studied for CO₂ hydrogenation. Among these metals, Ru catalyst exhibited significantly enhanced CO₂ conversion and almost 100% CH₄ selectivity upon light irradiation (Fig. 6a) [73]. The formed hybrid orbitals between CO₂ molecules and Ru surface enable strong CO₂ adsorption, leading to a reduced energy gap. The diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) analysis confirmed that the introduction of light can ac-

celerate CO₂ dissociation to CO. The energy consumption in light-assisted CO₂ hydrogenation was evaluated to be only 37% of that of conventional PDT, thereby indicating that the reaction temperature can be considerably decreased with light irradiation assistance. Ru/TiO₂ catalyst was reported for CO₂ hydrogenation towards CH₄ by coupling photo and thermal energies [28]. When the reaction was operated at low temperature of 150 °C and 1 atm, no CH₄ production was monitored without light illumination. Even in the case of 300 °C, the introduction of light can lead to about three times larger in terms of conversion rate in comparison with no light irradiation. Based on the analysis of energy bands, the light irradiation satisfied thermodynamic requirements for photocatalysis process. The coupled thermal energy can provide overall driving force to accelerate the reaction kinetics, thereby enabling the photocatalytic CO₂ hydrogenation [74–76]. Ruthenium oxide-based composition was also reported for CO₂ methanation reaction. The catalyst was prepared by depositing RuO₂ nanoparticles on perovskite semiconductor strontium titanate (SrTiO₃, STO) (Fig. 6b) [74]. With ultraviolet-visible (UV-vis) irradiation, the RuO₂/STO

sample showed a high CH_4 conversion rate of $14.6 \text{ mmol g}^{-1} \text{ h}^{-1}$. Mechanistic investigations strongly suggested a photothermal catalytic process, in which photo-generated electron-hole pair-based photocatalysis process contributed slightly. RuO_2 was transformed into metallic Ru under the reaction conditions. The high CO_2 adsorption and favorable charge transfer capacities of SrTiO_3 support contributed to the high efficiency in photothermal catalytic CO_2 methanation.

In the case of nickel, the main product was still CO when TiO_2 and Al_2O_3 were used as supports. When the support was replaced with barium titanate (BaTiO_3), CH_4 became the dominant production [1]. The results suggest that the interfaces between active metal sites and the support play a vital role in both the catalytic activity and product distribution. The underlying reaction mechanism still requires in-depth study. Metal-organic framework-derived Ni@C catalyst with highly dispersed Ni nanoparticles anchored on carbon matrix was reported to have outstanding catalytic performance for photothermal catalytic CO_2 methanation [77]. The optimal CH_4 production rate was evaluated to be $488 \text{ mmol g}^{-1} \text{ h}^{-1}$ under UV-visible-IR irradiation through the well-regulated pyrolysis of MOF-74 and therefore the carbonaceous matrix nature. The reactivity can last more than 12 h without significant particle aggregation or decay. Interestingly, an ambient experiment was used as a proof-of-concept to illustrate the great potential of Ni@C catalyst for photothermal catalytic CO_2 methanation through utilizing only solar energy. And, $\text{Co}/\text{Al}_2\text{O}_3$ catalyst prepared by a MOFs-templated approach exhibited high CH_4 production rate of $6036 \mu\text{mol g}^{-1} \text{ h}^{-1}$ with 97.7% CH_4 selectivity and superior durability in gas-phase photothermal CO_2 methanation [78]. Light irradiation can trigger intra- and inter-band electron transition in metal Co nanoparticles, leading to high light to heat conversion efficiency. UV-vis light irradiation was reported to generate oxygen vacancies which are active for reactant and intermediate adsorption for the enhancement of CO_2 methanation.

Rh/Al nanoantenna catalyst with Rh nanoparticles closely packed on Al nanostructures demonstrated a wide-spectrum sunlight-driven photothermal CO_2 reduction to CH_4 (from ultraviolet to the near-infrared region) [75]. The resultant Rh/Al nanoantenna catalyst exhibited a superior CH_4 production rate of $550 \text{ mmol g}^{-1} \text{ h}^{-1}$ and a nearly 100% selectivity under concentrated $11.3 \text{ W}/\text{cm}^2$ light irradiation (Fig. 6c). Operando spectroscopy indicated that the pathway of CO_2 methanation in Rh/Al nanoantenna catalyst should be a temperature-dependent multi-step process, in which CO served as the key intermediate. The Al nanostructure can generate localized surface plasmon resonance (LSPR) and provide a high surface temperature up to 700°C for activating adsorbed species. The surface Rh nanostructures offered rich active sites for CO_2 methanation. The nanoantenna effect in Rh/Al catalyst was verified to be effective for enhancing photothermal CO_2 -to-fuel conversion.

The support materials play very vital roles in catalytic activity [79]. The silica opal and inverted silicon opal photonic crystal were used as Ru supports and the prepared catalysts were named as Ru/SiO_2 and $\text{Ru}/\text{i-Si-o}$ (Fig. 6d), respectively [76]. The $\text{Ru}/\text{i-Si-o}$ catalyst exhibited a high rate as large as $2.8 \text{ mmol g}^{-1} \text{ h}^{-1}$ with a quantum efficiency of 3.1×10^{-4} at an irradiation intensity of $2470 \text{ mW}/\text{cm}^2$. The experimental results suggested that the exceptional light-harvesting properties should be responsible for the robust performance. The DFT analysis indicated that the i-Si-o support can trigger highly charged Ru surfaces, which can simultaneously achieve the destabilization of adsorbed CO_2 molecules and the adsorption and dissociation of H_2 molecules. Thus, a remarkable improvement for the Sabatier reaction was witnessed. When the same i-Si-o support was used and the active species is replaced by RuO_2 , the nanostructured $\text{RuO}_2/\text{i-Si-o}$ was prepared and demonstrated a very high conversion rates of $4.4 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$

for gas-phase photomethanation [80]. The mechanistic details were revealed by DFT calculations. The hydroxyl group formed between the adsorbed H and the oxygen on RuO_2 surface is important to facilitate the photomethanation reaction. The powerful use of light and heat in $\text{RuO}_2/\text{i-Si-o}$ catalysts enables photomethanation reaction to take place at ambient temperatures.

Non-precious transition metal catalysts have been also explored for CO_2 hydrogenation to CH_4 . The light irradiation with varied wavelengths and intensities was investigated to reveal the light-harvesting properties. The $\text{Co}_{10}/\text{CeO}_2$ catalyst exhibited high 94% selectivity to CH_4 and approximately 116% promotion in catalytic activity with blue light illuminating [61]. The light irradiation triggered the generation of hot electrons on Co surface, which can directly activate the adsorbed intermediates. As for the $\text{Cu}_{10}/\text{CeO}_2$, the localized surface plasmon resonance of Cu nanostructure resulted in 100% CO selectivity under green light illumination. The importance of CeO_2 support was further emphasized by comparing with Al_2O_3 support, in which intrinsic oxygen vacancies can localize charge density to enhance CO_2 hydrogenation. This research indicated that both metal site and support are very important for the design of high-performance photothermal catalysts. Various metal oxides supports, such as SiO_2 , ZrO_2 , CeO_2 , Al_2O_3 , and TiO_2 , have been investigated for CO_2 hydrogenation to CH_4 [41,56,78,81]. The morphology, chemical state, and vacancy/defect of support or the interface between the active metal and the supports plays a vital role in reaction activity and selectivity. Pure-phase $\theta\text{-Fe}_3\text{C}$ exhibited a high activity of $10.9 \text{ mmol g}^{-1} \text{ h}^{-1}$ for photothermal conversion of CO_2 to hydrocarbon products with a >97% selectivity under light irradiation (Fig. 6e) [71]. The phase transformation of the iron-based catalysts from Fe_3O_4 to $\theta\text{-Fe}_3\text{C}$ can well manipulate the main product distribution from CO to hydrocarbons under the same reaction conditions. The phase difference in Fe-based catalysts was confirmed to be related to different capabilities for CO adsorption and H_2 dissociation capabilities during CO_2 hydrogenation process. Meanwhile, spectroscopy techniques demonstrated that the types of intermediates and the capabilities for product formation/desorption can be regulated by the non-thermal effect of light. The use of cheap and commercial-available Fe_3O_4 as precursor indicated an efficient pathway to construct low-cost and high-activity Fe-based catalysts for photothermal CO_2 conversion.

5.1. Methanol synthesis

Methanol synthesis via H_2 -assisted CO_2 reduction is a significant route to convert CO_2 liquid fuel. Plasmonic Cu/ZnO catalyst was reported for methanol synthesis under ambient pressure (Figs. 7a and b) [82]. The production rate of methanol was promoted from $1.38 \mu\text{mol g}^{-1} \text{ min}^{-1}$ to $2.13 \mu\text{mol g}^{-1} \text{ min}^{-1}$ with visible light assistance. Visible light irradiation was also suggested to result in a favorable apparent activation energy of $49.4 \text{ kJ}/\text{mol}$. The experimental and theoretical results revealed that Cu nanoparticles were responsible for the generation of photo-excited hot electrons. The electron transfer between Cu metal and ZnO support interfaces can synergistically help the activation of reaction intermediates, thus resulting in high activity in photo-assisted methanol synthesis. Hybrid $\text{Au}\&\text{Pt}/\text{ZIF}$ structure was also reported for CO_2 hydrogenation. Pt nanocubes and Au nanocages were concurrently filled into ZIF-8 framework (Figs. 7c and d) [83]. Compared with the catalytic activity in dark, light irradiation can promote the turnover frequency by a factor of 13. The yield of methanol reached up to 0.6 mmol under the operating conditions of light irradiation and 150°C reaction temperature. The reference experiments suggested the roles of Pt nanocubes, Au nanocages, and ZIF-8 for the photothermal catalytic CO_2 hydrogenation. Specifically, Pt nanocubes functioned as active sites. Plasmonic Au nanocages can efficiently

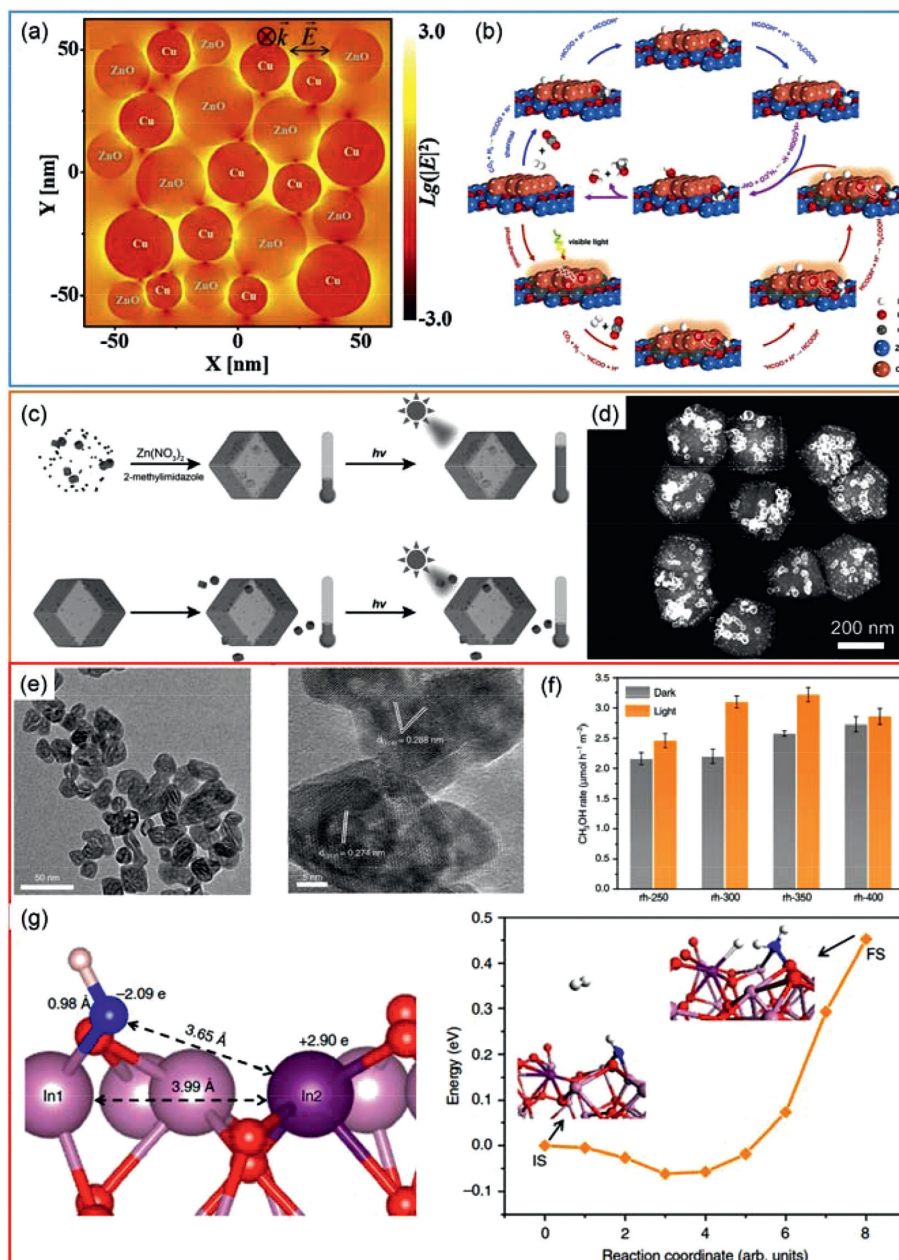


Fig. 7. (a) Simulated spatial distribution of the electro-magnetic fields over the Cu/ZnO catalyst under 580 nm irradiation. (b) Proposed mechanism for the visible light promoted methanol synthesis over the Cu/ZnO catalyst. Reproduced with permission [82]. Copyright 2019, Elsevier B.V. (c) Schematic illustration of the preparation and the photothermal effect under light irradiation, and (d) HAADF-STEM image of Au&Pt@ZIF. Reproduced with permission [83]. Copyright 2017, Wiley-VCH. (e) TEM and HRTEM images of rh- $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ nanocrystals. (f) Normalized CH_3OH production rate with and without light irradiation (270 °C). (g) Surface frustrated Lewis pairs on rh- $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ nanocrystals. Reproduced with permission [6]. Copyright 2019, Springer Nature.

enhance the conversion of light to thermal energy. The ZIF-8 shell was suggested to block the heat dispersion, thus leading to the generation of localized high-temperature region at the Pt active sites. The design strategy in Au&Pt@ZIF shed light on the development of photothermal catalysis. Inspired by the delivered high catalytic performance from polymorphic anatase and rutile titanium dioxide, rhombohedral $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ polymorph was prepared for photocatalytic CO_2 hydrogenation to CH_3OH and CO (Fig. 7e) [84]. The resultant rhombohedral polymorph demonstrated a promoted selectivity to CH_3OH over CO with high catalytic activity and superior structural stability. The *operando* spectroscopic technique and theoretical calculation indicated that the Lewis acidity and basicity was optimized by the polymorph engineering, thus promoting CO_2 activation and H_2 dissociation. The light illumination was also

highly related to CO and CH_3OH formation pathways (Figs. 7f and g).

6. C_2+ productions

Xie's group reported that constructing asymmetric Metal₁-O-Metal₂ triple-atom sites in O-vacancy-rich Zn_2GeO_4 nanobelts was an effective strategy to promote the C–C coupling process in CO_2 reduction for C_2 fuels production by photoheat induced molecular vibration enhancement (Fig. 8a) [10]. The reactivity of Zn–O–Ge triatomic sites was preliminarily verified through quasi *in situ* Raman spectra and DFT calculation. The enhancement of C–C coupling process should be derived from the difference in the charge distributions of adjacent C_1 intermediates induced by asymmet-

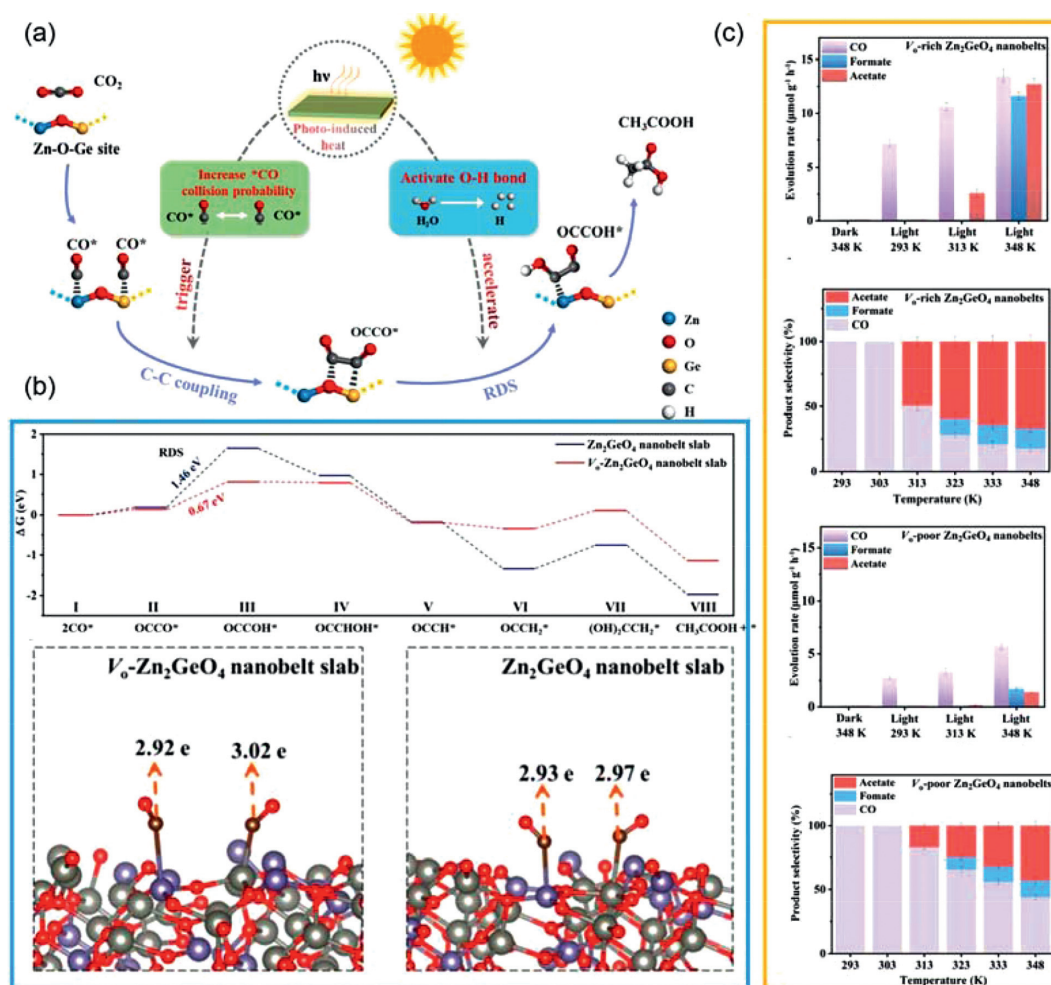


Fig. 8. (a) The role of photothermal effect in CO₂ reduction to CH₃COOH. (b) DFT calculations of free energy (up) and atomic configurations (down) of two adsorbed CO molecules on O-vacancy-rich Zn₂GeO₄ nanobelts (left) and Zn₂GeO₄ (right). (c) Summary of photothermal catalytic performance of O-vacancy-rich Zn₂GeO₄ nanobelts for atmospheric CO₂ reduction. Reproduced with permission [10]. Copyright 2021, American Chemical Society.

ric triple-atom sites (Fig. 8b). The abundance of O vacancy is suggested to be favorable to the rate-determining hydrogenation step by lowering the energy barrier from 1.46 eV to 0.67 eV. The role of light-induced heat was also been systematically investigated through *in situ* Fourier transform infrared (FT-IR) spectroscopy and isotopic experiments. Photothermal effect in the catalyst cannot only initiate the C–C coupling but also speed up OCCO* hydrogenation processes. The asymmetric Metal₁–O–Metal₂ triple-atom sites in O-vacancy-rich Zn₂GeO₄ nanobelts lead to a high conversion (29.95%), a high acetate selectivity (66.9%), and a high output (12.7 μmol g⁻¹ h⁻¹) under 0.1 W/cm² illumination and simulated air atmosphere (Fig. 8c) [10].

At present, the main products of solar-driven CO₂ hydrogenation are C₁ products, such as CH₄ and CO. Transformation of CO₂ into high-value-added C₂ compounds, i.e., light alkanes of hydrocarbon fuels is more attractive but challenging. Inspired by the fact that single Fe catalysts can catalyze CO₂ conversion to CO through reverse water gas shift (RWGS) reaction while Co species is active in Fischer-Tropsch synthesis (FTs) through C–C coupling process, CoFe-based catalysts were prepared for CO₂ hydrogenation through H₂-reduction of CoFeAl-LDH nanosheets under different temperature from 300 °C to 700 °C (Fig. 9a) [25]. Interestingly, CoFe-650 catalyst composed of CoFe alloy nanostructure exhibited high CO₂ conversion (78.6%) and selectivity to C₂₊ hydrocarbon (35.2%) under UV-vis irradiation (Fig. 9b). The selectivity of the product was

verified to be closely related to the reduction temperature of the catalyst. The states of Co and Fe in CoFe-x catalysts witnessed a transformation from FeO_x/CoO_x cationic form to FeCo metallic state. CoFe-300 to 400 catalysts showed a nearly 100% selectivity to CO. The selectivity to CH₄ was increased in CoFe-450 to 550 catalysts. DFT calculations were used to explore the adsorption behavior of CO intermediate and the C–C coupling ability in CoFe-x catalysts. CoFe bimetallic alloy in CoFe-650 catalyst can lower the adsorption barrier of CH-CH₂ for C–C coupling in CO₂ hydrogenation (Fig. 9c) [25]. This work provided an insight for CO₂ hydrogenation to high-value C₂₊ hydrocarbon by harnessing abundant solar-energy.

The application of sodium-promoted metallic cobalt nanoparticles@carbon layers nanocomposite (Na-Co@C) for the photothermal CO₂ hydrogenation (Fig. 10a) [85]. Interestingly, the selectivity to C₂ and C₃ products was as high as 16.5% and 12.5%, respectively, for Na-Co@C, with a nearly 100% selectivity to hydrocarbons and high CO₂ conversion of >97% (Figs. 10b and c). On the contrary, the dominant production was CH₄ under conventional thermal catalytic conditions. The reference Co@C nanocomposite also demonstrated a high selectivity of >96% to CH₄ without the Na promoter. Control experiments verified the participation of photo-generated charges from Co@C nanocomposite. Near ambient-pressure X-ray photoelectron indicated that the carbon layers in Na-Co@C was in an electron-rich state under the light

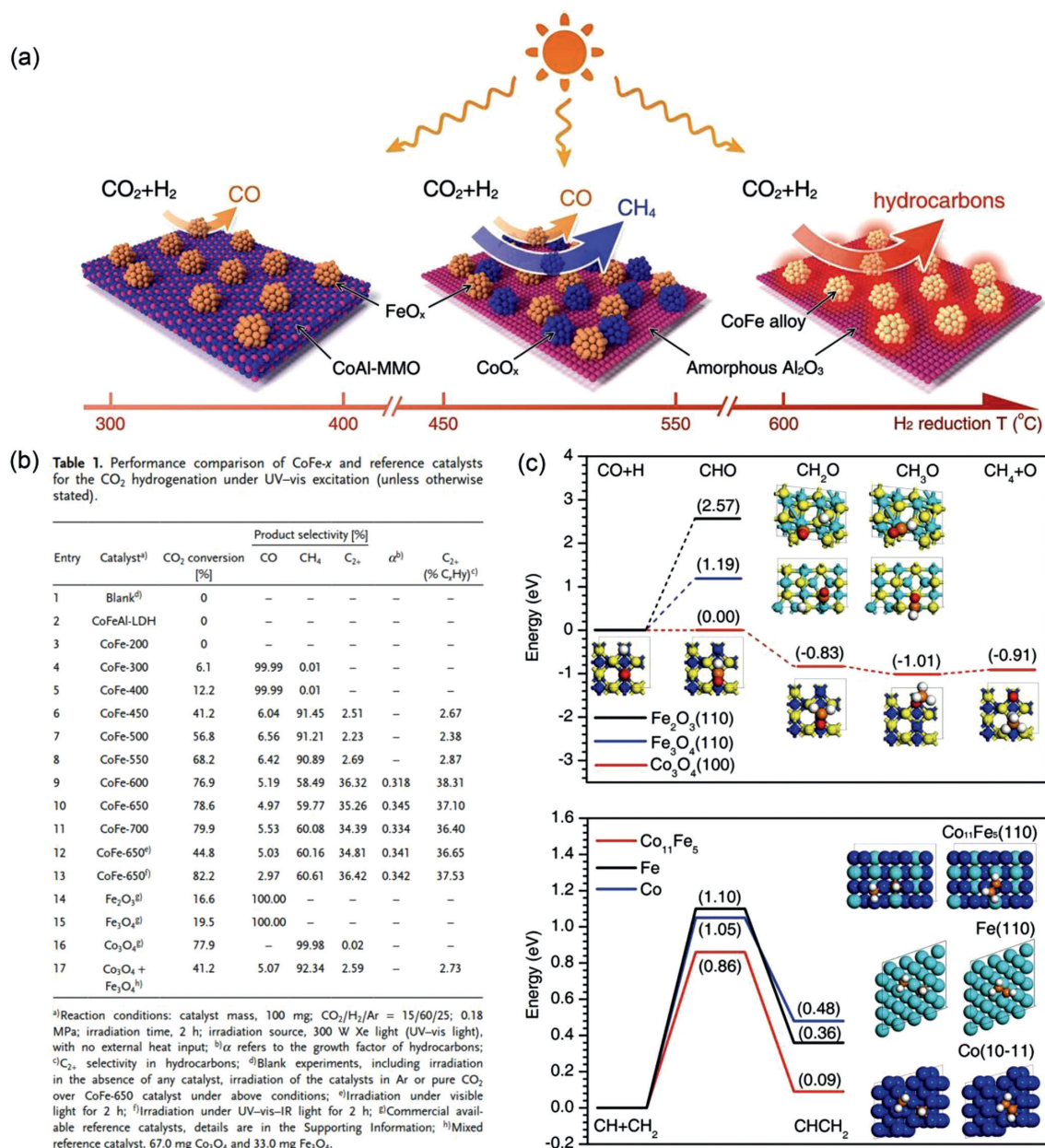


Fig. 9. (a) Illustration of the relationship between preparation temperature and production selectivity in CO₂ hydrogenation selectivity of CoFe-x (x is temperature) catalysts. (b) Comparison of catalytic activity in CoFe-x and reference catalysts. (c) DFT calculations for clarifying CO and CH₄ selectivity in CoFe-300 and CoFe-550 (up) and the C₂₊ hydrocarbons through C-C coupling path in CoFe-650. Reproduced with permission [25]. Copyright 2018, Wiley-VCH.

irradiation activation. The introduction of light irradiation into CO₂ hydrogenation reaction was confirmed to manipulate the types of intermediate species on the surface of Na-Co@C, thereby resulting in versatile reaction routes. The carbon layers in Na-Co@C were suggested to stabilize CO species and then facilitate the ethanol production through CO insertion pathway. The existence of sodium was suggested to facilitate the C-C formation. Without the addition of sodium, enol should be the dominant species and the CH₄ was formed with high selectivity through simply breaking C-OH bonds (Figs. 10d-f) [85].

7. Summary, challenges and perspectives

In this review, we provided a systematic and detailed blueprint for photothermal catalysis in CO₂ conversion. The formation mechanisms of photothermal effects were categorized. Three types

of photothermal catalysis were demonstrated according to the functioning modes of thermochemical and photochemical contributions. The design criteria for photothermal catalysts were illustrated based on the in-depth understanding of photothermal catalysis routes. A comprehensive introduction of different photothermal catalysts for CO₂ conversion through reverse water gas shift-RWGS, methane synthesis, dry reforming, Sabatier reaction, methanol synthesis, C₂ production synthesis were provided to help the targeted design of catalysts. Photothermal catalysis as an emerging research area has demonstrated great potential to alleviate and/or abandon traditional thermal energy inputs in a wide range of catalytic processes including but not limited to CO₂ conversion. Finally, we also take a cautious look at the opportunities and challenges in the hope of inspiring the future development and application of photothermal catalysis.

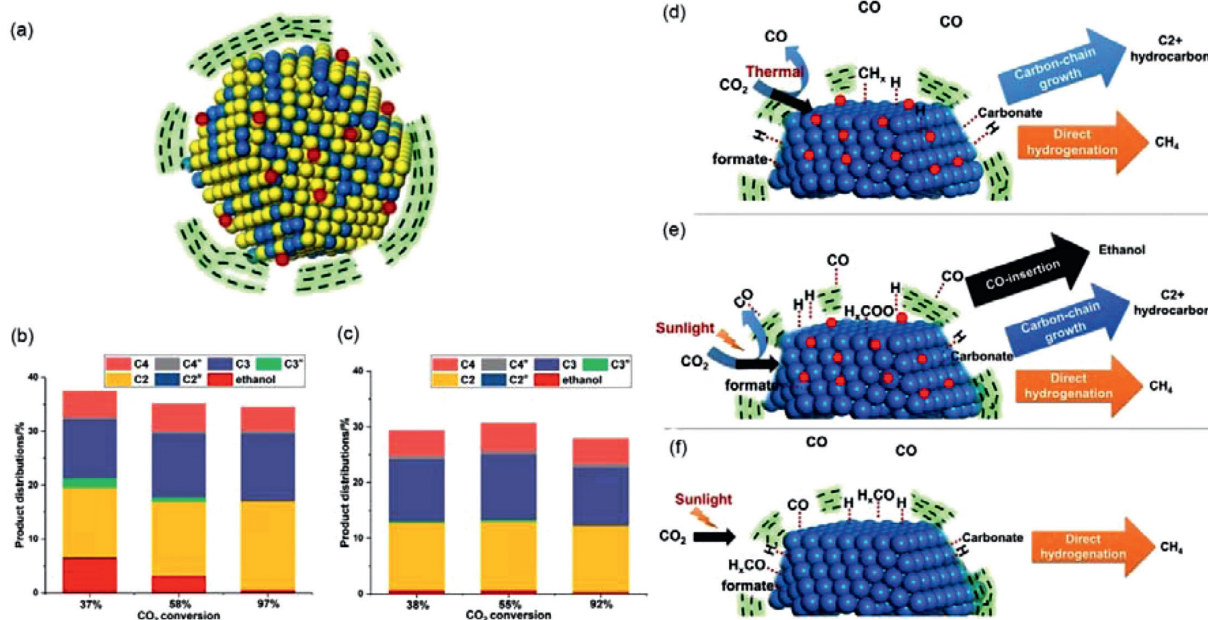


Fig. 10. (a) Illustration of Na-Co@C nanocomposite (Co, yellow; CoO_x, blue; sodium, red; carbon layer, shaded dashed lines). Selectivity to C₂₊ hydrocarbons under (b) photothermal or (c) thermal conditions. The reaction pathways of (d) CH₄ and C₂₊ hydrocarbons over Na-Co@C under thermal conditions, (e) C₂₊ hydrocarbon over Na-Co@C under photothermal conditions, (f) CH₄ over Co@C under photothermal conditions. Reproduced with permission [85]. Copyright 2018, Elsevier B.V.

7.1. New materials, structure and composition

Although photothermal catalysis has come a long way, the current conversion efficiency from light to heat is still low. New photothermal materials should maximize the utilization and conversion of full solar spectrum, especially for the relatively large share of visible light. The manipulation of composition and structure is the key to achieving new photothermal materials [86]. The physical and chemical properties of active sites including types, sizes, morphologies, energy band, interface engineering, hybrid system, etc. should be well considered, which have great impact on the activity and selectivity in CO₂ conversion through modulating the adsorption and desorption behaviors of reactants/intermediates/products. The structure design (porosity, pore structure, pore size [87,88], chiral structures [89,90], hollow structures [91–94], core-shell structures [95,96], sub-1 nm structures [58,97–104]) of new photothermal materials is also of great significance in regulating the synergy of thermochemical and photochemical pathways, which can greatly affect the conversion efficiency of light to heat, thermal diffusion, and mass transfer [105]. More specifically, we anticipate that new photothermal materials should be including but not limited to black/violet phosphorus [106,107] with a tunable band gap in the range of 0.3 eV to 2 eV, metal-organic frameworks (MOFs) with tunable node and ligand [26,108], Xenes/binary-enes [109] with abundant composition and electronic properties, and their hybrid structures, which will further enhance photothermal catalytic performance.

7.2. C₂₊ fuels production

Despite the considerable progress made in the development of photothermal catalytic CO₂ reduction, the present productions are mainly concentrated in C₁ fuels, such as CO, CH₄ and CH₃OH. The photothermal conversion of CO₂ to C₂ products (CH₃COOH, C₂H₅OH, C₂H₄, C₂H₆, etc.) with higher energy density and broader application prospect has attracted extensive attention but is rarely reported. However, the formation of C₂ products definitely involved multielectron transfer and C–C coupling reaction pathways with

typical thermodynamically intractable and kinetically retarded features [110]. Therefore, designing effective photothermal catalytic systems to achieve high selectivity towards C₂ products is of great significance and challenge.

7.3. Standardization of photothermal catalytic tests

The emerging photothermal catalysis has aroused great interest in heterogeneous catalysis. However, the reaction conditions during the process of photothermal catalytic reactions, such as light source information, temperature, pressure, flow rate of reaction gas, proportion of reactants, usage of catalyst, reactor types and so on, vary from person to person. As a result, the present production rate varies considerably from millimolar to micromolar, making it difficult to compare the final results with each other. Thus the standardization of photothermal catalytic tests should be highly emphasized. The identification of surface macroscopic temperature and local temperatures (T_{local}) is very important to uncover the conversion efficiency of light to heat. Currently, the surface macroscopic temperature profiles of different catalyst films were measured by a direct-contact thermocouple, which exhibited a small difference in temperature. The determination of local temperatures (T_{local}) is challenging and rarely reported [5]. A recent report indicated that the T_{local} can be evaluated by analyzing equilibrium constants, in which of course the reaction should be conducted to reach equilibrium first. Theoretical calculations and simulations are suggested to assist systematic characterization in order to reveal photochemical and/or thermochemical pathways. Advances in experiment and theory will guide the design of catalysts, thereby facilitating the development of highly efficient photothermal catalytic systems. For industrial applications, in addition to the aforementioned issues of conversion and selectivity, the production cost and the long-term stability of the reaction system should be carefully considered.

7.4. In-depth understanding of photothermal catalysis

Ex situ, *in situ* and *operando* characterizations of photothermal catalysis are of great significance for the understanding of cat-

alytic mechanism (thermal/light-assisted pathways) and thus for the design of catalyst. *In situ* and *operando* characterization techniques are highly desired for further understanding photothermal catalytic processes by exploring the bond sensitivity of catalyst-surface adsorbate to light or heat [37,111]. The deactivation process in photothermal catalysis also should be ascertained. Normally, the chemical composition, the physical property, the nanostructure and the electronic band structure of photothermal catalyst can be well characterized by using most of the characterization means in traditional photocatalyst and thermal catalyst. Specially, ultraviolet-visible-near infrared diffuse reflectance spectrophotometer (UV-vis-NIR) spectrometry and IR camera play fundamental and important roles in determining the ability of catalyst in light absorption and photothermal conversion. In addition, electron energy-loss spectrum (EELS) can be used to achieve the three-dimensional visualization of the LSPR components throughout silver nanocube by reconstructing LSPR 3D images [112]. *In situ* and *operando* (operating or working) characterizations are very important in analyzing a catalyst and its performance under model or actual reaction condition. To date, various techniques, such as microscopic, scattering, and spectroscopic fields, have been widely developed for photothermal catalysis. *In situ* X-ray absorption spectroscopy (XAS) can monitor the stability of photothermal catalyst. *In situ* DRIFTS and Raman spectra are important to monitor the reaction intermediates. *In situ* transient absorption (TA) spectroscopy and X-ray photoelectron spectroscopy (XPS) can be used to explore the charge generation and transfer. Isotopic experiment is also necessary to track the carbon species considering the reaction systems, e.g., catalyst, environment, reactants, exist potential carbon sources. Based on the systematical consideration of the actual catalytic system, the rational application of *in situ* techniques will help to reveal the photothermal mechanisms.

Declaration of competing interest

The authors declare no declarations of interest.

Acknowledgments

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