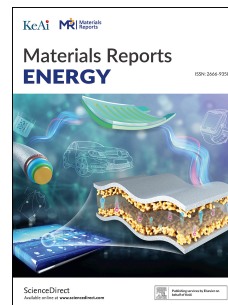# Journal Pre-proof

Advanced semiconductor catalyst designs for the photocatalytic reduction of CO_2

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Review

Advanced semiconductor catalyst designs for the photocatalytic reduction of CO$_2$

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Abstract:

Using clean solar energy to reduce CO_2 into value-added products not only consumes the over-emitted CO_2 that causes environmental problems, but also generates fuel chemicals to alleviate energy crises. The photocatalytic CO_2 reduction reaction (PCO_2RR) relies on the semiconductor photocatalysts that suffer from high recombination rate of the photo-generated carriers, low light harvesting capability, and low stability. This review explores the recent discoveries on the novel semiconductors for PCO_2RR, focusing on the rational catalyst design strategies (such as surface engineering, band engineering, hierarchical structure construction, single-atom catalysts, and biohybrid catalysts) that promote the catalytic performance of semiconductor catalysts on PCO_2RR. The advanced characterization techniques that contribute to understanding the intrinsic properties of the photocatalysts are also discussed. Lastly, the perspectives on future challenges and possible solutions for PCO_2RR are presented.

Keywords: Photoreduction of CO_2, Semiconductor catalysts, Photocatalyst modification, Heterojunction construction, Catalytic efficiency, Activity, Environmental and sustainable applications

Graphical abstract:
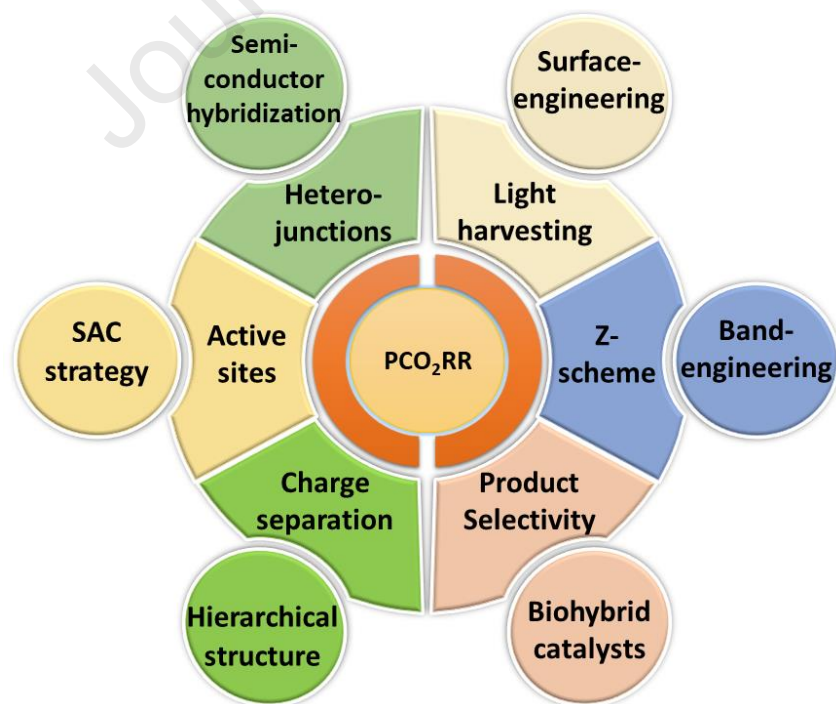
1. Introduction

Over the decades, the large consumption of fossil fuels due to anthropogenic activities has released heat and greenhouse gas into the atmosphere. The concentration of CO_2, one of the major greenhouse gases, in the atmosphere exceeds 410 parts per million (ppm), which is much higher than 280 ppm in the pre-industrial period.[1] The thermal radiation from the sunlight and the surface of the earth can be trapped by CO_2 molecules, augmenting the global temperature and aggravating the issue of global warming.[2] The over-emitted CO_2 is truly one of the top concerns for human society. The CO_2 reduction reactions (CO_2RR) that convert CO_2 molecules into value-added products such as CH_3OH, CH_4, CO, and $HCOOH$ give an alternative strategy to consuming CO_2 while mitigating the energy crises. In addition, realizing CO_2RR by clean energies such as solar energy offers an approach to alleviate both global warming and energy crisis issues in a green concept.[3] To fulfill this, photocatalytic CO_2 reduction reactions (PCO_2RR) has gained much attention because it utilizes semiconductor materials as photocatalysts to absorb sunlight as the driving force to reduce CO_2. Fig. 1a depicts the fundamentals of PCO_2RR on a semiconductor catalyst. Typically, the photocatalysis takes three main steps: i) the generation of the photo-generated carriers (e^-/h^+ paires) within the semiconductor photocatalyst through harvesting the incident light; ii) the transfer of the photo-generated electrons and holes to the surface of the photocatalyst; iii) the catalytic reactions (CO_2RR and the oxidation half-reaction) on the surface of the photocatalyst.[4] The photo-generated carriers (e^-/h^+ paires) are essential to PCO_2RR as they are the keys to the catalytic reactions. The photo-generated electrons in the conduction band (CB) participate in CO_2RR to reduce CO_2 molecules. The photo-generated holes in the valence band (VB) participate in the counter-reaction (oxidation half-reactions, such as water oxidation reaction). During the formation of the photo-generated carriers, the electrons

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and holes tend to recombine with each other through surface recombination and volume recombination, which prohibits catalytic efficiency. Besides, the potentials of the VB maximum and the CB minimum need to straddle the redox potentials of the oxidation half-reactions and CO_2RR, respectively.[5] **Equation (1)-(8)** shows some typical reaction steps involved in CO_2RR, along with the reactions for H_2 and O_2 productions (vs. Normal Hydrogen Electrode (NHE), in aqueous solution of pH=7).[3, 6]
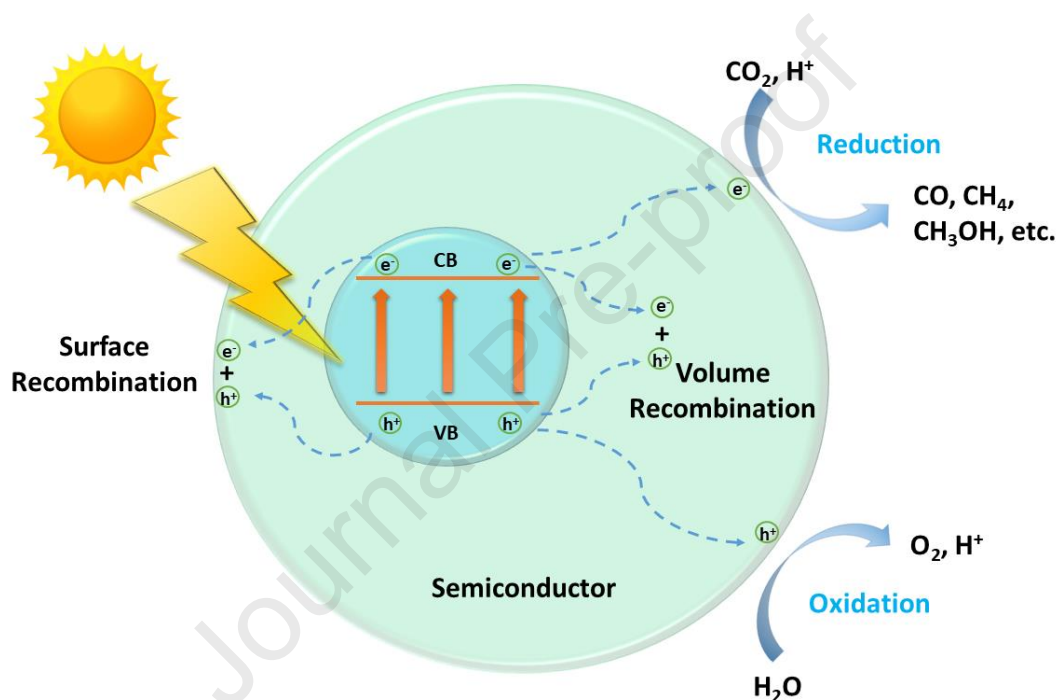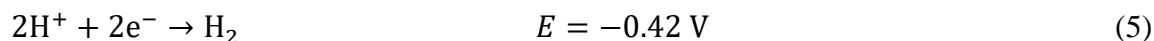

Fig. 1. Schematic of photocatalytic CO_2 reduction reactions (PCO2RR). Reproduced with permission from Ref. 7.

$$CO_2 + e^- \rightarrow CO_2^{\cdot-} \qquad\qquad E = -1.90\,\text{V} \qquad\qquad (1)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \qquad E = -0.61\,\text{V} \qquad\qquad (2)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E = -0.53\,\text{V} \qquad\qquad (3)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \qquad E = -0.48\,\text{V} \qquad\qquad (4)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad\qquad E = -0.42\,\text{V} \qquad\qquad (5)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E = -0.38 \text{ V} \qquad\qquad (6)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E = -0.24 \text{ V} \qquad\qquad (7)$$

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+ \qquad\qquad E = +0.82 \text{ V} \qquad\qquad (8)$$
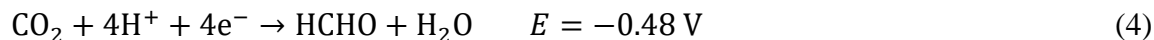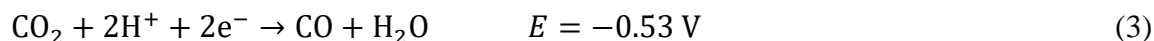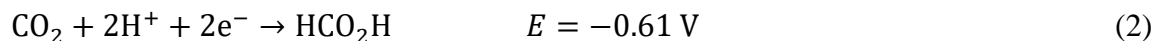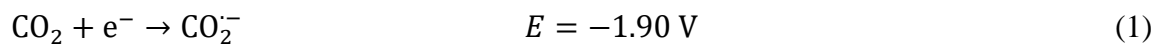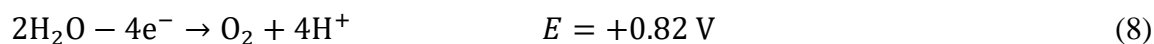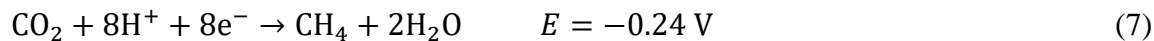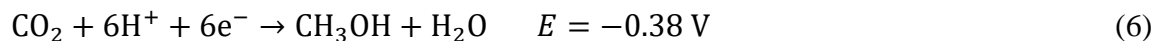
The semiconductor catalyst needs to meet not only the kinetic barriers but also the thermodynamic requirements to achieve a successful PCO$_2$RR. Moreover, the bandgap between CB and VB determines the wavelength range that the semiconductor can absorb from sunlight. When the value of the bandgap is larger than ca. 3.1 eV, the semiconductor catalyst can solely harvest ultra-violet illumination, which is only a small fraction of the sunlight. Increasing the light-harvesting ability of the photocatalysts requires the bandgap of the semiconductor materials to be relatively narrow. The single pure semiconductor catalyst alone usually cannot afford sufficient catalytic efficiency for PCO$_2$RR. Great efforts are made in the modification of the semiconductor catalysts (e.g. the refinement of crystallinity, defect engineering, heterojunction construction, etc.) to increase the catalytic performance (e.g. product selectivity and activity, light harvesting capability, stability) during PCO$_2$RR.[5] The goal is to design rational photocatalysts with I) the matching CB and VB potentials for CO$_2$RR and the oxidation half-reactions; II) the narrow bandgap to absorb sufficient sunlight; III) low recombination rate of the photo-generated carries; IV) sufficient and highly efficient active sites for CO$_2$RR and the oxidation half-reactions. This review concentrates on the most recent advanced photocatalyst designs for PCO$_2$RR, where the superiorities of semiconductor modification and integration are highlighted (Fig. 2). Hybridization strategies of photocatalysts such as surface engineering and band engineering are explained with some typical examples (e.g. co-catalyst designs, photosensitizer, heterojunction construction). Then, promising results from structural engineering and single-atom active site fabrications are exposed, along with the biohybrid

catalyst designs. Finally, the perspectives on the remaining challenges and future focuses are presented.
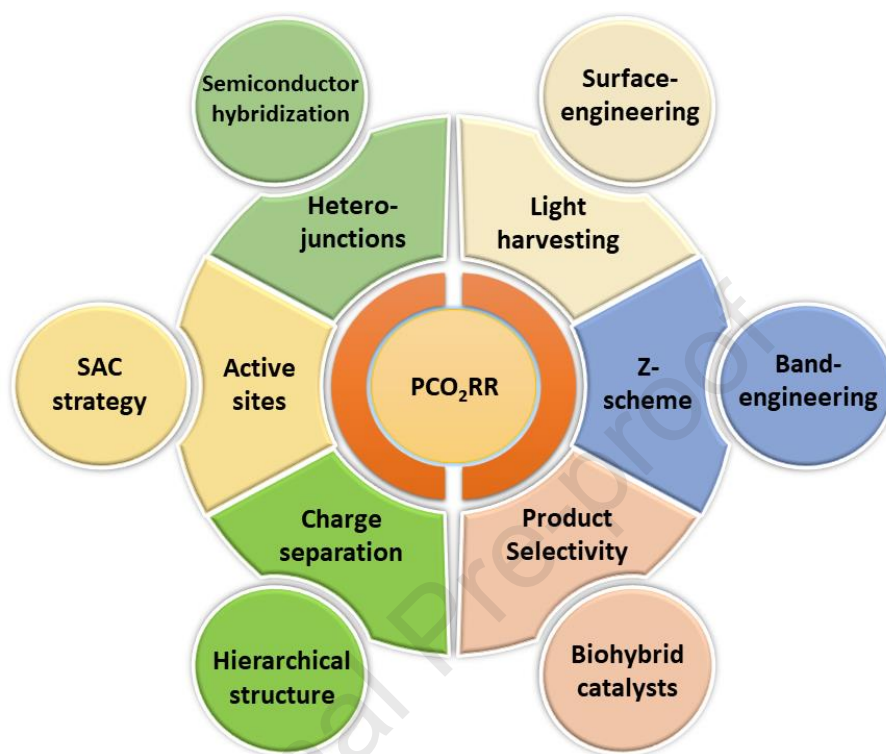
Fig. 2. Advanced semiconductor catalysts for PCO$_2$RR.

2. Hybridization of semiconductor catalysts for PCO$_2$RR

Currently, mainstream works focus on modifying the semiconductor photocatalysts by hybrid engineering such as surface modification and the integration of different semiconductors to form heterojunctions. Table 1 lists some typical hybrid photocatalysts for PCO$_2$RR.

2.1 Surface engineering

As the catalytic reaction takes place on the surface of the catalyst, its modification with active sites or support co-catalysts is a promising way to enhance the catalytic activities of the catalyst materials. For example, An et al. modified the Fe tetraphenyl porphyrin (FeTPP) catalyst with an

alkyne-functionalized supramolecular synthon to form an iron porphyrin box (PB) bearing 24 cationic groups (FePB-2(P)) that offered a synergy of porosity and charge effects. The modified FePB-2(P) exhibited a 41-times enhancement in catalytic performance, as compared to the original FeTPP, toward CO production in PCO$_2$RR.[8] The modification of the metal co-catalysts on the semiconductor surface can serve as not only the active sites to capture CO$_2$ molecules for the activation but also the electron trap to separate photo-generated carriers, demonstrating excellent PCO$_2$RR performance (e.g, Au-Cu alloy modified on TiO$_2$ substrates for CH$_4$ and C$_2$H$_4$ productions[9]; Ni cluster shell on NiO core for the CO generation[10]).

Surface engineering for light harvesting enhancement is another approach to increase photocatalytic efficiency. As photocatalysis utilizes solar energy to drive the catalytic reactions, the photocatalysts' efficiency of harvesting sunlight is vital in the practical aspect. Currently, many good semiconductor catalysts such as metal oxides exhibit wide bandgap, which limits light absorption within the ultra-violet range, only a small fraction of the incident solar radiation (less than 5%).[11] It makes those wide-bandgap photocatalysts less attractive in industrial applications, as sunlight mostly contains visible and infrared lights. The integration of semiconductor catalysts with light-response-efficient materials allows for the improved light-harvesting ability of the photocatalysts. Modifying semiconductor catalyst surfaces with photosensitizers is one of the approaches to achieve this goal. Wang et al. constructed a number of photosensitizers of homoleptic Al (III) for PCO$_2$RR with emission quantum yields from 10% to 40%.[12] Fig. 3a shows the molecular structures of the homoleptic Al (III) complexes. The light absorption band center can be tuned by changing the ligands attached to the Al (III) photosensitizers (Fig. 3b). Fig. 3d illustrates the PCO$_2$RR activities of different catalysts coupled with Al (III) photosensitizers. The catalyst of [Fe(qpy)(OH$_2$)$_2$](ClO$_4$)$_2$ (FeQPY; qpy =

2,2′:6′,2″:6″,2‴-quaterpyridine) affords the most durable and stable CO production among all the catalysts. Fig. 3c demonstrates the reaction scheme for the PCO$_2$RR with Al (III) photosensitizers/ FeQPY with 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]-imidazole (BIH) as the sacrificial electron donor. This noble-metal-free system achieves a CO selectivity of 99% and a TON value of 10250 under 450 nm light illumination in PCO$_2$RR (Fig. 3e). Das et al developed a porous organic polymer (POP) as a light harvester for improving PCO$_2$RR. The composite catalyst of In$_{2.77}$S$_4$ and POP was built by electrostatic interaction and exhibited a C$_2$H$_4$ product selectivity of 98.9% with a yield rate of 67.65 μmol g^{-1} h^{-1} under irradiation of visible light.[13]
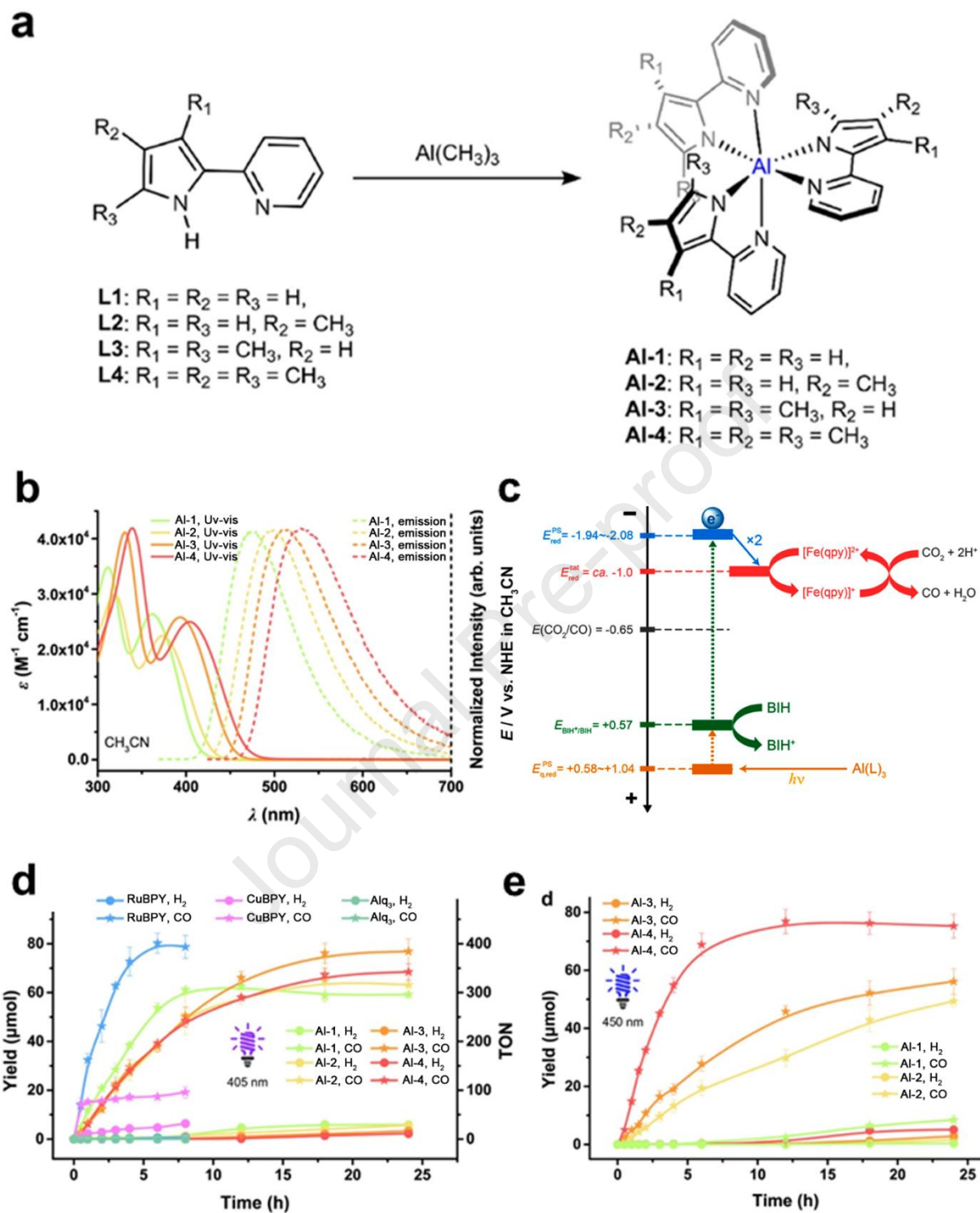
Fig. 3. (a) Synthetic diagram and molecular structures of different ligands applied for Al(III) PSs.

(b) UV–vis absorption spectra and the normalized emission (λ_{exc} = 355 nm) spectra of **Al-4** (red),

Al-3 (orange), **Al-2** (gold), and **Al-1** (lime) in purified CH_3CN solution at 293 K. (c) Simplified reaction and energy scheme for visible-light-induced CO production in PCO₂RR by Al(III)-PSs/**FeQPY** with BIH as sacrificial electron donor. Product yields of CO (star) and H_2 (circle) under irradiations of (d) 405 nm and (e) 450 nm with 0.05 mM **FeQPY** and 0.5 mM PS in CO₂-saturated, 0.3 M TEOA CH_3CN, and 50 mM BIH solutions. Reproduced with permission from Ref. 12.

To maximize the utilization of sunlight, scientists have discovered some promising semiconductor photocatalysts with narrow bandgap to harvest visible light, such as carbon nitride,[14-16] bismuth oxyhalides,[17, 18] CdS,[19] layered double hydroxides (LDHs),[4, 20, 21] etc. However, those visible light-response semiconductor materials suffer from severe recombination of the photo-generated carriers. The surface modification of the semiconductor catalyst with a metal co-catalyst such as Pd/TiO₂[22] and Ag-TiO₂[23], which can trap the photo-generated electron, emerges as a powerful strategy to separate the photo-generated carries and contributes to for an enhanced PCO₂RR performance. It is well applied to visible light-response photocatalysts as well. For instance, Yue et al. reported a Bi-MOF/BiOBr photocatalyst where Bi-MOF was in-situ mounted on the BiOBr for PCO₂RR with a CO yield rate of 21.96 μmol g^{-1} h^{-1}.[24]

Another approach is to integrate the semiconductor catalysts with metal co-catalysts. In this strategy, using plasmonic metals offer extra benefits for light harvesting. The nanocatalysts of plasmonic metal interact strongly with incident light, generating a localized surface plasmon resonance (LSPR). The LSPR effect can easily tune the light absorption wavelength from ultra-violet to near-infrared through adjusting the geometry structure of the plasmonic metal catalyst.[25, 26] For example, Cu/TiO₂ enables absorbance at 500–600 nm from the LSPR of Cu particles to

improve the CO production in PCO_2RR.[27] The LSPR effect of Au particles helps achieving the PCO_2RR under low-intensity irradiation at 420 nm.[26]

Based on the promising results provided by the assistance of the plasmonic metal Au in light harvesting and catalytic performance, modifying Au catalyst with other metal alloys has proven to enhance the employment of photons with low energy for PCO_2RR. Hu et al. fabricated plasmonic light harvesting Au rods and coupled them with a co-catalyst shell of CuPd alloy to achieve highly effective PCO_2RR to CH_4 production.[28] Fig. 4a demonstrates the structure of the Au/CuPd core-shell composite. Plasmonic catalysis often happens close to the surface of the catalyst (within the range of plasmon-induced local field). Pure Au nanorods are unlikely to collide with CO_2 molecules, resulting in its low CO_2 conversion efficiency (Fig. 4a, left). For Au/CuPd, the CuPd shell can capture CO_2 molecules to increase the CO_2 concentration on the surface of the catalyst, promoting the probability of further conversion and activation (Fig. 4a, right). The thickness of the shell and the Cu/Pd ratio can be easily adjusted by controlling the number of metal precursors during the synthesis. The optimized Au/CuPd catalyst can achieve a CH_4 yield rate of 15.6 $\mu mol\ g^{-1}\ h^{-1}$, which is almost 40 times higher than the one achieved by pure Au rods (Fig. 4b). The apparent quantum efficiencies are up to 0.1% at 800 nm (Fig. 4d). The optimized thickness of the CuPd shell is believed to maximize the number of active sites on the catalyst surface and strengthen the electron-phonon scattering effect, contributing to the best CH_4 production. Fig. 4c illustrates that C_2H_4 and C_2H_6 can also be detected after the long-term reaction test. This suggests the multiple proton-coupled electron transfer ability of the Au/CuPd core-shell catalyst. To avoid the scattering loss of incident light during PCO_2RR, a spherical-structured gas-solid reaction system is further applied (Fig. 4e). The novel spherical-structured reaction system can realize the re-incidence of scattered photons, which benefits the catalytic

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reaction system with a plasmonic effect. With the optimization of the partial pressure of CO_2 and the volume of H_2O in the system, the production rate of CH_4 can be further improved to 0.55 mmol g^{-1} h^{-1} (Fig. 4f). The spherical-structured reaction system affords a catalytic performance of around 35-folds to that of the conventional reaction system which only allows one single incident photon pass. Besides, the apparent quantum efficiency in the spherical-structured reaction system reaches 0.38% at 800 nm. It offers the opportunity to utilize the Au/CuPd core-shell catalyst in PCO_2RR under low-energy near-infrared irradiation.
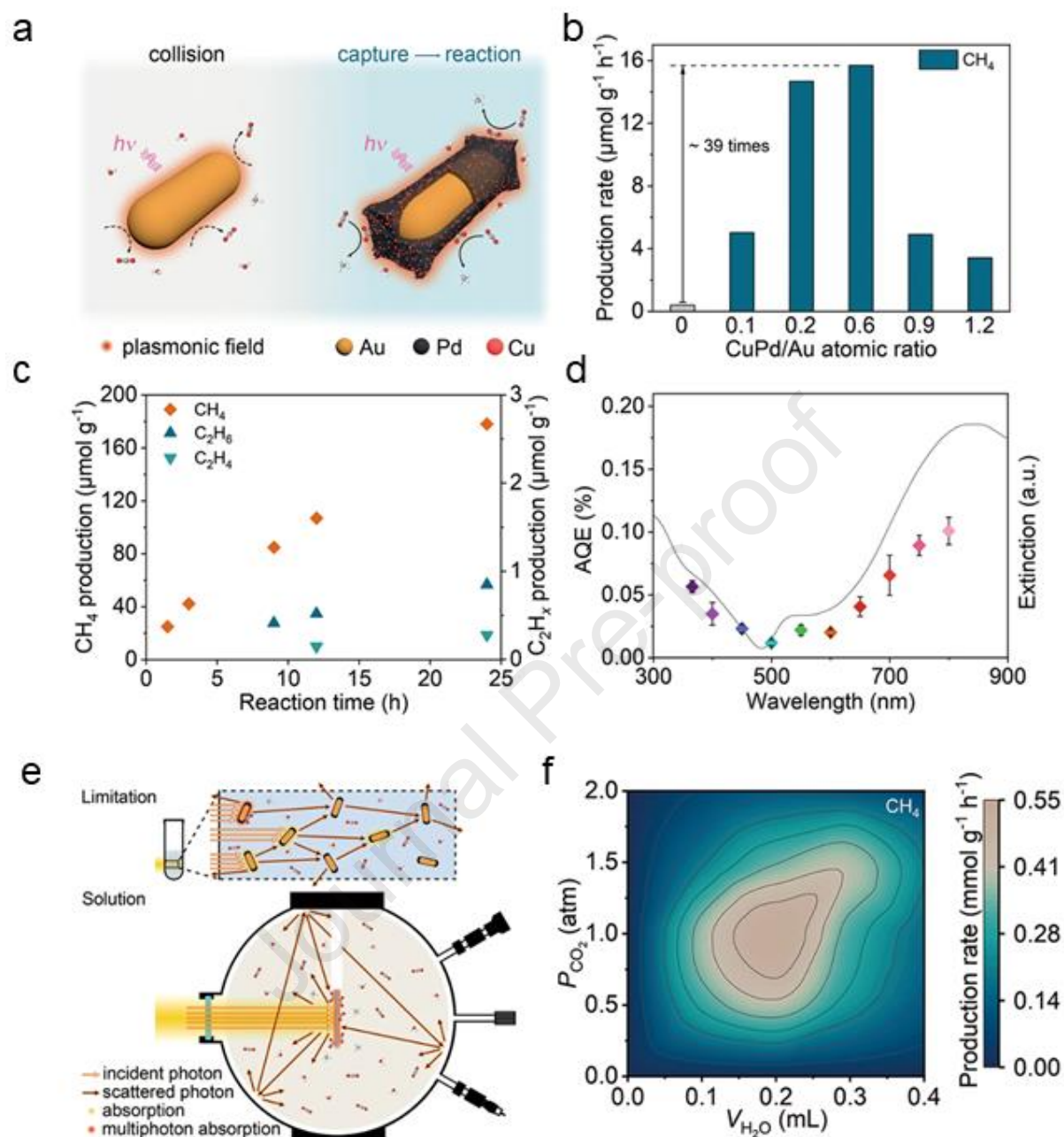
Fig. 4. (a) Schematic of CO_2 molecules being captured on the CuPd shell. (b) CH_4 production rates of Au/$CuPd_2$ with different thicknesses of the CuPd shell. (c) Time-dependent yield of CH_4 on Au/$CuPd_2$. (d) Calculated AQEs (dots) on Au/$CuPd_2$ under light illuminations with different monochromatic wavenumbers, compared to the UV-vis extinction spectrum (line). (e) Schematic of the gas-solid reaction, where full-spectrum light illuminates a spherical reactor. During

catalysis, the scattered photons are reflected on the surface of the catalyst, which leads to multi-absorption processes for efficient PCO$_2$RR. (f) CH$_4$ yield rates through plasmon-induced PCO$_2$RR in the gas-solid reactor on Au/CuPd$_2$ under different H$_2$O volumes and CO$_2$ pressures. Reproduced with permission from Ref. 28.

2.2 Band engineering

When applied in photocatalysis, single pure semiconductors often suffer from the issues of wide bandgap that limits the visible light harvesting, unmatched CB or VB potential positions to drive the catalytic reactions, etc. Integrating two semiconductors with different CB and VB potential positions to form a heterojunction becomes a useful approach to overcome these difficulties.
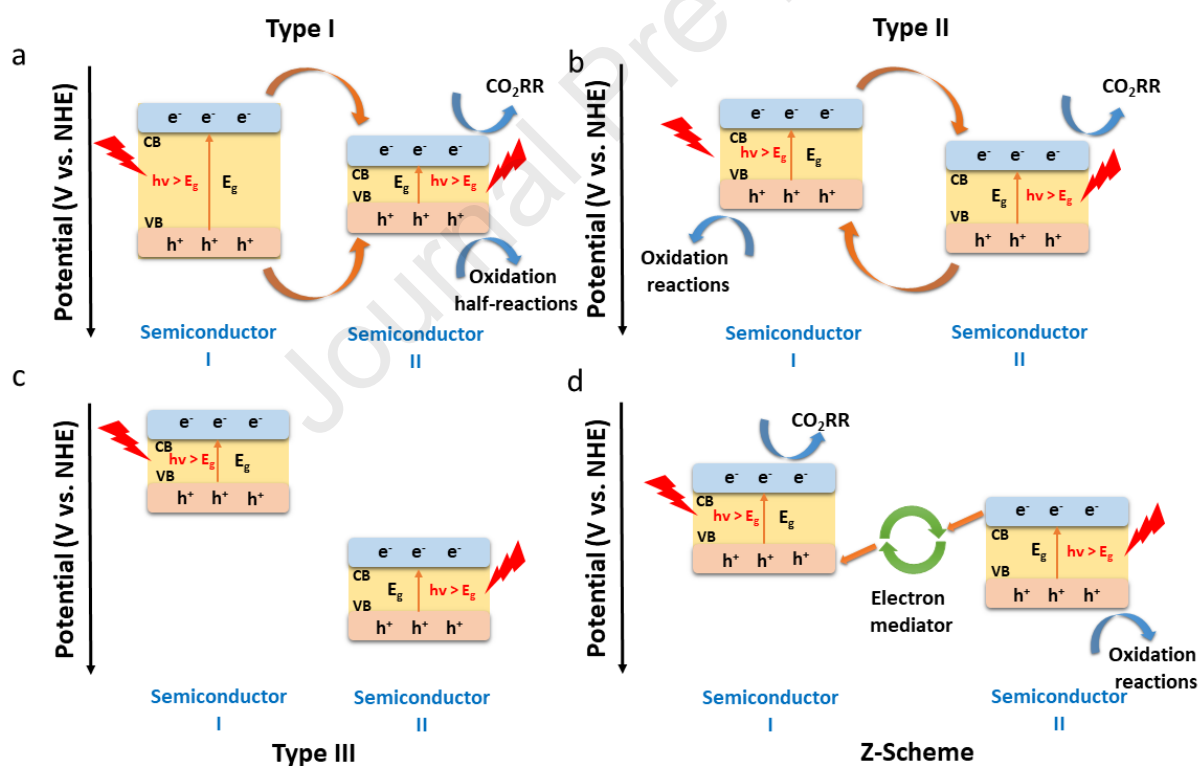

Fig. 5. Schematic of the band diagram on a semiconductor photocatalyst for CO$_2$RR and oxidation half-reactions: (a) Type I: straddling, (b) Type II: staggered, (c) Type III: broken gap, (d) Z-scheme. VB: valence band; CB: conduction band; h$^+$: hole; e$^-$: electron.

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There are three types of heterojunctions when integrating two different semiconductors. Type I is "straddling" where the CB and VB of one semiconductor are entirely contained in those of another semiconductor (Fig. 5a). In this type of heterojunction, both photo-generated electrons in CB and holes in VB of semiconductor I tend to transfer to the CB and VB of semiconductor II by the potential difference, respectively. It comes with two drawbacks. First, the CB and VB potentials of semiconductor II are less powerful to drive the catalytic redox reactions. Second, the accumulated photo-generated holes and electrons in semiconductor II exacerbate the recombination of the photo-generated carriers. Hence, the "straddling type" heterojunction is not ideal for photocatalysis.

Type II is "staggered" where the CB and VB of one semiconductor overlap with those of another semiconductor (Fig. 5b), generating a favourable heterojunction. Once semiconductor I have more negative CB and VB potential positions than semiconductor II, the photo-generated electrons tend to transfer from the CB of semiconductor I to the CB of semiconductor II while photo-induced holes tend to transfer from the VB of semiconductor II to the VB of semiconductor I. This new possible transfer pathway created by the "staggered type" heterojunction can separate the photo-generated electrons and holes in the semiconductors and significantly reduce the recombination rate of the photo-induced carriers in both semiconductor I and semiconductor II, boosting photocatalytic performance. The only drawback of this type of heterojunction is that the CB and VB that participate in the catalytic reactions are the less effective ones. Namely, the CB potential of semiconductor II is less negative than that of semiconductor I, and the VB of semiconductor I is less positive than that of semiconductor II.

Type III is a "broken gap" where the bandgaps of two semiconductors do not overlap (Fig. 5c). In this circumstance, the photo-generated electrons and holes between two semiconductors fail to

transfer.[29] Therefore, the type II heterojunction is of interest in photocatalysis. Many works focus on the fabrication of type II heterojunction to boost catalytic performance. For example, a heterojunction between $CsPbBr_3$ and graphitic carbon nitride (g-C_3N_4) is built based on the band position differences between g-C_3N_4 and $CsPbBr_3$. It provides a stable CO yield rate of 975.57 μmol g^{-1} h^{-1} in PCO₂RR for 76 hours.[30] Zhu et al. constructed the heterojunction in a heterostructure of $ZnIn_2S_4$-CdS for PCO₂RR.[31] The ultrafast transient absorption spectroscopy proves the accelerated charge transport in the heterostructure (Fig. 6 a and b). With the assistance of $Co(bpy)_3^{2+}$ as co-catalyst for CO₂RR and TEOA as the sacrificial compound to consume photo-generated holes (Fig. 6e), it exhibits the CO yield of around 33 µmol in the first hour (Fig. 6c) under visible light irradiation and retains its initial catalytic activity after 5 cycles (Fig. 6d) of the PCO₂RR measurements.
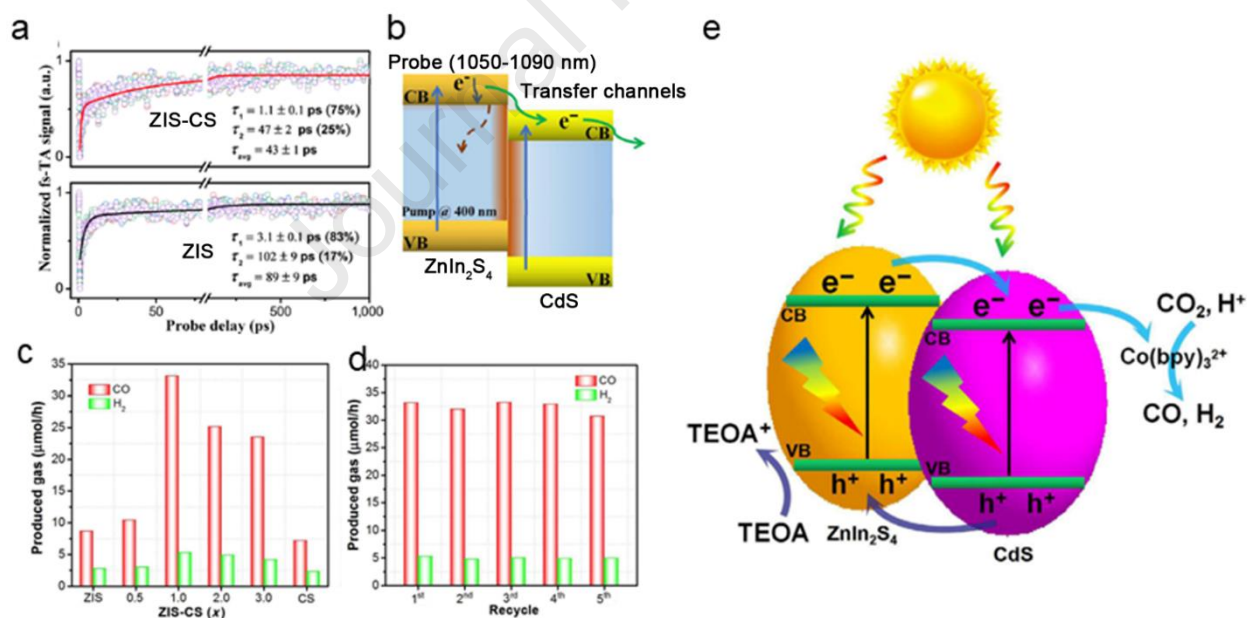

Fig. 6. (a) Global fitting and the ultrafast kinetics results (probing range: 1050–1090 nm with a 10 nm interval) for $ZnIn_2S_4$, and CdS QDs/$ZnIn_2S_4$. (b) Heterojunction schematic of $ZnIn_2S_4$-CdS. (c) PCO₂RR activities for $ZnIn_2S_4$, $ZnIn_2S_4$-CdS, and CdS. (d) Time-dependent PCO₂RR

performance on $ZnIn_2S_4$-CdS. (e) Possible charge carrier transfer mechanism of $ZnIn_2S_4$-CdS for PCO2RR under the irradiation of visible light. Reproduced with permission from Ref. 31.

As aforementioned, the type II heterojunction still shows limits concerning the CB and VB positions that participate in the catalytic reactions. Inspired by natural photosynthesis, an electron transfer pathway where the photo-induced electron in the CB of semiconductor II travels to the VB of semiconductor I to perform the recombination is proposed (Fig. 5d). It creates an electron transfer pathway with the shape of the letter Z, which is named "Z-scheme" in the heterojunction construction. The Z-scheme electron transfer pathway allows photo-generated carriers from the stronger CB and VB in the two semiconductors to participate in the catalytic reactions, which overcomes the difficulty raised in the type II heterojunction catalysts.

In another approach, the Z-scheme is constructed without building any additional bridge between two semiconductors, this is called the direct Z-scheme system.[6] The construction of the internal electric field in the heterojunction between two semiconductors proves to be an effective strategy to achieve the direct Z-scheme. Wang et al. built a 2D/2D Z-scheme heterostructure of Ni-$CsPbBr_3$/Bi_3O_4Br for PCO2RR.[32] Driven by the difference in the Fermi levels of the two semiconductors, the photo-generated electrons transfer from Ni-$CsPbBr_3$ to Bi_3O_4Br. It leads to increased charge densities at the interface, positive on the Ni-$CsPbBr_3$ side and negative on the Bi_3O_4Br side, respectively. The internal electric field formed in this space charge region creates the band-bending effect. Fig. 7a depicts the Z-scheme electron transfer pathway where the electrons are directed from the CB of Bi_3O_4Br to the VB of Ni-$CsPbBr_3$. Because of the bending effect, the shape of the electron pathway looks more like the letter "S" rather than "Z". Under this circumstance, the term "S-scheme" is preferred over "Z-scheme" to highlight the band-bending effect. The Ni-$CsPbBr_3$/Bi_3O_4Br with the S-scheme heterostructure demonstrates an

excellent 98.2% CO selectivity with a CO yield of 387.57 μmol g^{-1}, which is more than 10 times higher than that of CsPbBr$_3$ (Fig. 7b). Long et al. combined Fe$_2$O$_3$ and CdS to achieve the direct Z-scheme charge transfer pathway by a built-in internal electric field as well. The Z-scheme heterojunction of Fe$_2$O$_3$/CdS enables a CO yield of 9.3 μmol g^{-1} in the first hour during PCO$_2$RR, which is much better than the sum of those of pure Fe$_2$O$_3$ and CdS.[33] The unique Z-scheme favors not only the separation of photo-generated electron/hole pairs but also the redox capacity of the photo-generated electrons and holes involved in catalytic reactions such as CO$_2$RR.
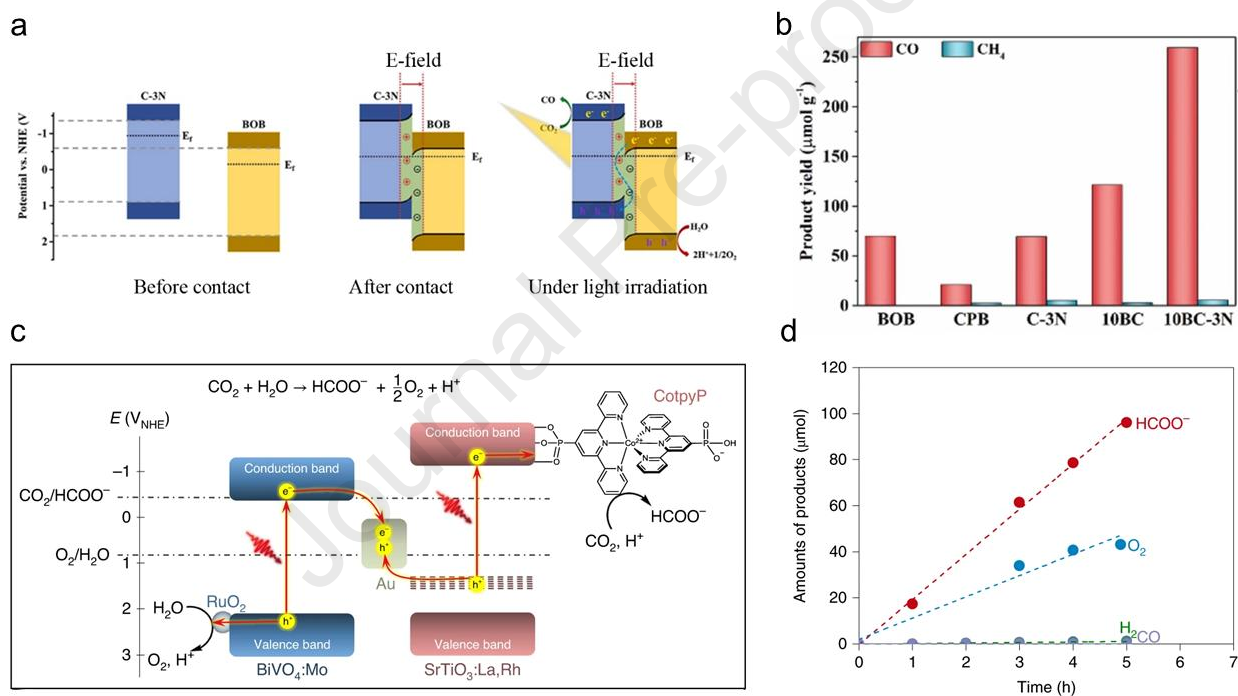
Fig. 7. (a) Schematic (individual, after contact, under the irradiation for CO$_2$RR with Z-scheme) of the band structures and the charge transfer pathways of C–3N and Bi$_3$O$_4$Br (BOB). (b) CO and CH$_4$ yield amount of C–3N, Bi$_3$O$_4$Br, and heterostructured catalysts. Reproduced with permission from Ref. 32. (c) Energy diagram of PCO$_2$RR coupled with water oxidation over SrTiO$_3$:La, Rh|Au|RuO$_2$-BiVO$_4$:Mo. The reduction potentials are given versus the NHE at pH 6.7. (d) Time course of the PCO$_2$RR and water oxidation over SrTiO$_3$:La, Rh|Au|RuO$_2$-

$BiVO_4$:Mo. The reaction conditions: CO_2-saturated 0.1M $KHCO_3$ aqueous solution, at 298 K. Reproduced with permission from Ref. 34.

Alternatively, when the Z-scheme is constructed with the help of the additional bridge between two semiconductors, it is called the indirect Z-scheme system. For example, Wang et al. delicately fabricated lanthanum (La)- and rhodium (Rh)-doped $SrTiO_3$ ($SrTiO_3$:La, Rh) and the light absorber of Co(II) bis(terpyridine) modified molybdenum (Mo)-doped $BiVO_4$ ($BiVO_4$:Mo) and the RuO_2 catalysts on a gold layer ($SrTiO_3$:La, Rh|Au|RuO_2-$BiVO_4$:Mo) for the PCO_2RR (Fig. 7c). The Au layer in $SrTiO_3$:La, Rh|Au|RuO_2-$BiVO_4$:Mo is believed to bridge the CB of RuO_2-$BiVO_4$:Mo and the VB of $SrTiO_3$:La, Rh, which constructs an effective indirect Z-scheme for the PCO_2RR to $HCOO^-$ and the H_2O oxidation reaction. It affords an $HCOO^-$ selectivity of 97% with a production rate of around 20 $\mu mol\ g^{-1}\ h^{-1}$ (Fig. 7d).[34]

3. Hierarchical structure construction of the catalysts for PCO_2RR

The catalyst structure plays an essential role during photocatalysis, benefiting the spatial separation of the photo-generated carriers for improved catalytic performance. Taking 2D catalysts as an example, the ultra-thin 2D nanosheets facilitate the transfer of the photo-generated electron/hole pairs to the surface of the catalyst, promoting catalytic activity. For instance, ultrathin 2D NiMgV-layered double hydroxide nanosheets afford excellent CO and CH_4 productions in PCO_2RR.[35] Liang et al. constructed a 2D dislocated bilayer MOF that allowed 100% product selectivity of CO in PCO_2RR.[36] However, 2D structured materials often suffer from agglomeration, leading to the prolongation of the carriers' transfer and a decreased active area of the catalysts, which jeopardizes the catalytic performance. Wang et al. morphologically modified CuInZnS by introducing negatively charged $Ti_3C_2T_x$ to interfere with the nucleation and growth processes of CuInZnS. It creates a defect regulation in CuInZnS and results in thinner 2D

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nanosheets of CuInZnS with a bigger specific surface area and larger pore size than those of the pristine CuInZnS. The hybrid 2D $Ti_3C_2T_x$-CuInZnS exhibits a CO production rate of 42.8 μmol g^{-1} h^{-1} in PCO_2RR.[37] With the proper synthetic routes, escalated hierarchical structures such as leaf/flower/litchi-like nanostructures can be fabricated through 2D nanostructures.[38] As aforementioned, Zhu et al. constructed the heterojunction in a heterostructure of $ZnIn_2S_4$-CdS for PCO_2RR.[31] The authors also took advantage of the hierarchical structure construction by anchoring 0D CdS quantum dots on the 3D $ZnIn_2S_4$ nanoflowers, which contributes to better charge transfer and separation during PCO_2RR. Other than the stacked 2D nanosheets/nanofibers to construct hierarchical structures, the 3D core-shell structure is also a hot topic in this field. Li et al. reported a 3D core-shell heterostructure made of c-TiO_2@a$TiO_{2-x}(OH)_y$ with HO-Ti-[O]-Ti surface frustrated Lewis pairs (SFLPs) on the shell in PCO_2RR.[39] Fig. 8a illustrates that the SFLPs dissociate dihydrogen, forming hydrides and charge-balancing protonated hydroxyl groups at unsaturated Ti sites on the surface of the catalyst to promote the PCO_2RR performance. The crystalline-amorphous heterostructure prolongs the lifetime of the electron/hole carriers (Fig. 8b). It allows a CO production rate of 5.3 mmol g^{-1} h^{-1} which is 350 times of the original c-TiO_2 catalyst.

Wei et al. developed a hollow multi-shelled structure (HoMS) of CeO_2@CeO_2/TiO_2 for CH_4 production in PCO_2RR. The high-angle annular dark field scanning TEM (HAADF-STEM) and X-ray energy dispersive spectral (EDS) mapping images in Figs. 8 e and f present the multi-shelled structure of CeO_2@CeO_2/TiO_2. The quadruple inner shells are made of CeO_2, which reduces CO_2 into CO accumulated within the multi-shelled structure. The amorphous outer shell is made of TiO_2, which further converts the accumulated CO into CH_4 (Fig. 8g). The tandem CO_2-CO-CH_4 reaction of the HoMS CeO_2@CeO_2/TiO_2 affords the CO and CH_4 production rates

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of 97.6 μmol g^{-1} h^{-1} and 15 μmol g^{-1} h^{-1}, respectively (Fig. 8 c and d). The HoMS structure can be destroyed by grinding $CeO_2@CeO_2/TiO_2$ into debris, causing a dramatic catalytic performance decrease (CH_4 production rate of 3.4 μmol g^{-1} h^{-1}). The control experiment highlights the significance of the hierarchical structure for the tandem reaction in PCO_2RR.[40] It reveals that the rational structure construction strategy of hybrid catalysts can further promote catalytic performance by combining different functional semiconductors to achieve a complex reaction of PCO_2RR for high-value-added products.
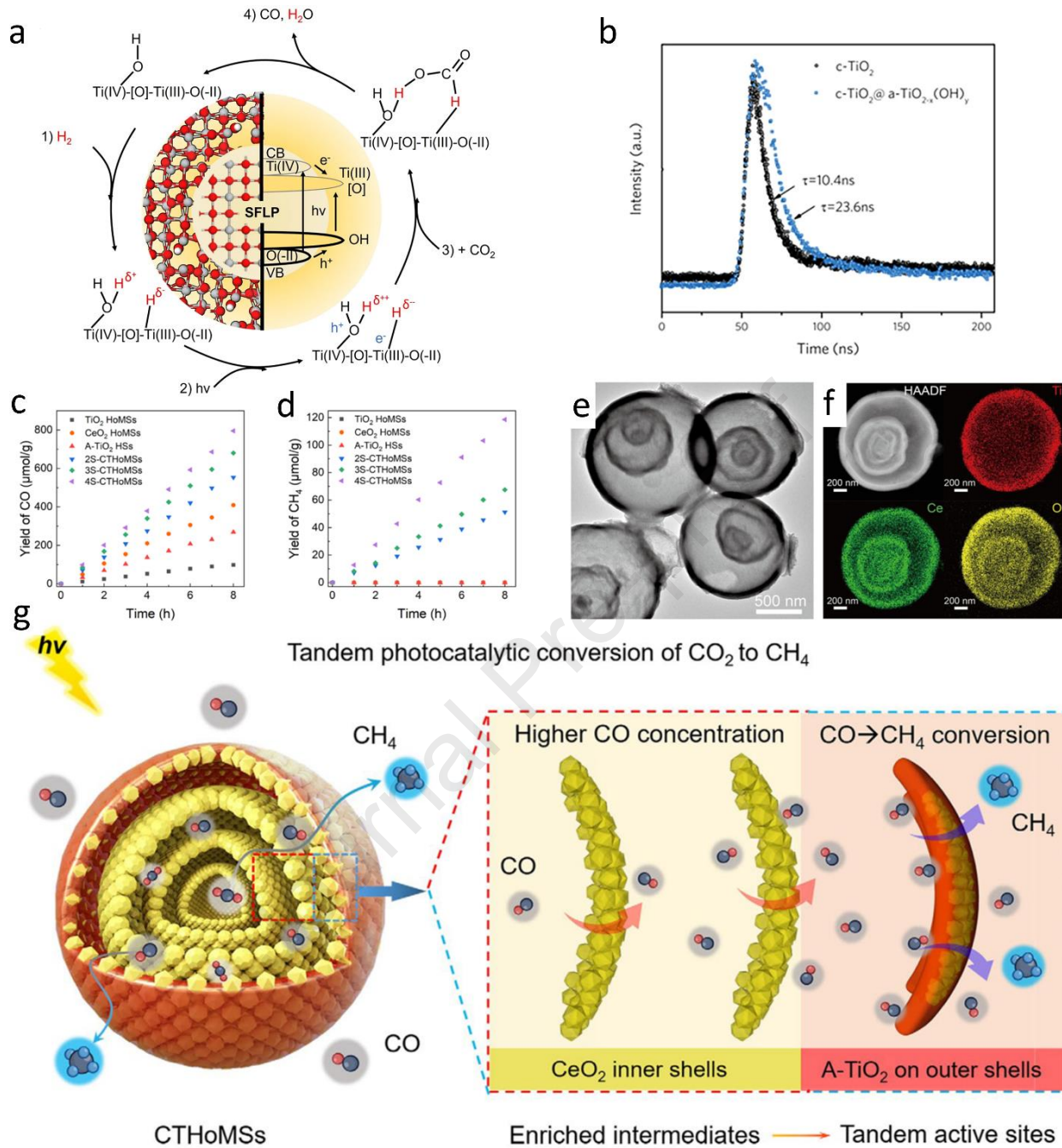
Fig. 8. (a) Illustration of the physicochemical properties of CO_2-to-CO by SFLPs in c-TiO_2@a-$TiO_{2-x}(OH)_y$. (b) Time-resolved photoluminescence spectroscopy decay curves of c-TiO_2 and c-TiO_2@a-$TiO_{2-x}(OH)_y$. Reproduced with permission from Ref. 39. (c) CO yield and d) the CH_4 yield of the corresponding samples under AM 1.5 G illumination for 8 h. (e) HAADF-STEM

images and (f) The EDS mapping images of quadruple-shelled $CeO_2@CeO_2/TiO_2$. (g) Schematic of the hetero-shell structure and the tandem PCO_2RR to CH_4 in $CeO_2@CeO_2/TiO_2$. Reproduced with permission from Ref. 40.

The production of C_{2+} is difficult for CO_2RR. Cu-based materials are the most known metal catalysts to facilitate the C-C coupling for the formation of C_{2+} products.[41] Many Cu-based photocatalysts show catalytic activities towards the production of C_{2+} products, such as In-Cu SA/PCN for CH_3CH_2OH production,[42] P/Cu SAs@CN for C_2H_6 production[43] and NiCo SA-TiO_2 for the CH_3COOH production.[44] With the assistance of the hierarchical structure engineering strategy, Cu-based photocatalysts demonstrate promising activity toward C_{2+} production in PCO_2RR. Chakraborty et al. applied the operando surface reconstruction of Wurtzite phase $CuGaS_2$ to form a 2D CuO layer-modified $CuGaS_2$, which led to a C_2H_4 production of 20.6 μmol g^{-1} h^{-1} with a selectivity of 75.1% in PCO_2RR.[45] Jia et al. grew p-type Cu_2O selectively on an Au bipyramid with the assistance of CTAB, fabricating a hetero-structure of dumbbell top which spatially separate Au and CuO active catalysts in an hybrid photocatalyst Au/CuO. Taking advantage of both the structural engineering and the LSPR effect, dumbbell-shaped Au/CuO affords much higher C_{2+} productions under near-infrared irradiation than under visible light irradiation.[46]

4. **Single-atom catalyst (SAC) strategy for PCO_2RR**.

Nowadays, atomically dispersed catalysts and single-atom catalysts (SACs) have gained much attention for their maximum active site utilization and superior catalytic performance.[47, 48] SACs have commonly supported metal catalysts that consist of isolated monometallic moieties (single metal atoms surrounded by neighboring atoms within the support), which offer well-defined active sites in the catalysts.[49, 50] Integrating the state-of-art highly active SACs with

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semiconductor substrates holds great promise in the catalytic performance enhancement of PCO$_2$RR. Anchoring the metal atoms on the substrate catalysts is currently one of the most common strategies to construct SAs such as Au, Ag, and Pt SAs on graphene.[51] Ou et al. fabricated Au SAs on red P support (Au$_1$/RP) with low electronegativity to absorb CO$_2$ for PCO$_2$RR.[52] RP is a single-element constituent, which provides a uniform coordination environment for Au SAs. Fig. 9 a-e depicts that Au SAs are evenly distributed on the RP support. Au$_1$/RP affords a C$_2$H$_6$ production rate of 1.32 μmol g^{-1} h^{-1} with a selectivity of 96% (Fig. 9f). The turnover frequency (TOF) also reaches 7.39 h^{-1}, which is pretty high among many photocatalysts (Fig. 9g). The CO$_2$ adsorption analysis (Fig. 9h) and the in-situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS, Fig. 9i) confirm that Au$_1$/RP provides better CO$_2$ adsorption and activation than those of pure RP. It is suggested that the P atoms around the Au SAs are electron rich and capable of serving as active sites for CO$_2$ activation. In the meantime, the Au SAs can decrease the C-C coupling energy barrier for C$_2$H$_6$ production in PCO$_2$RR (Fig. 9j).
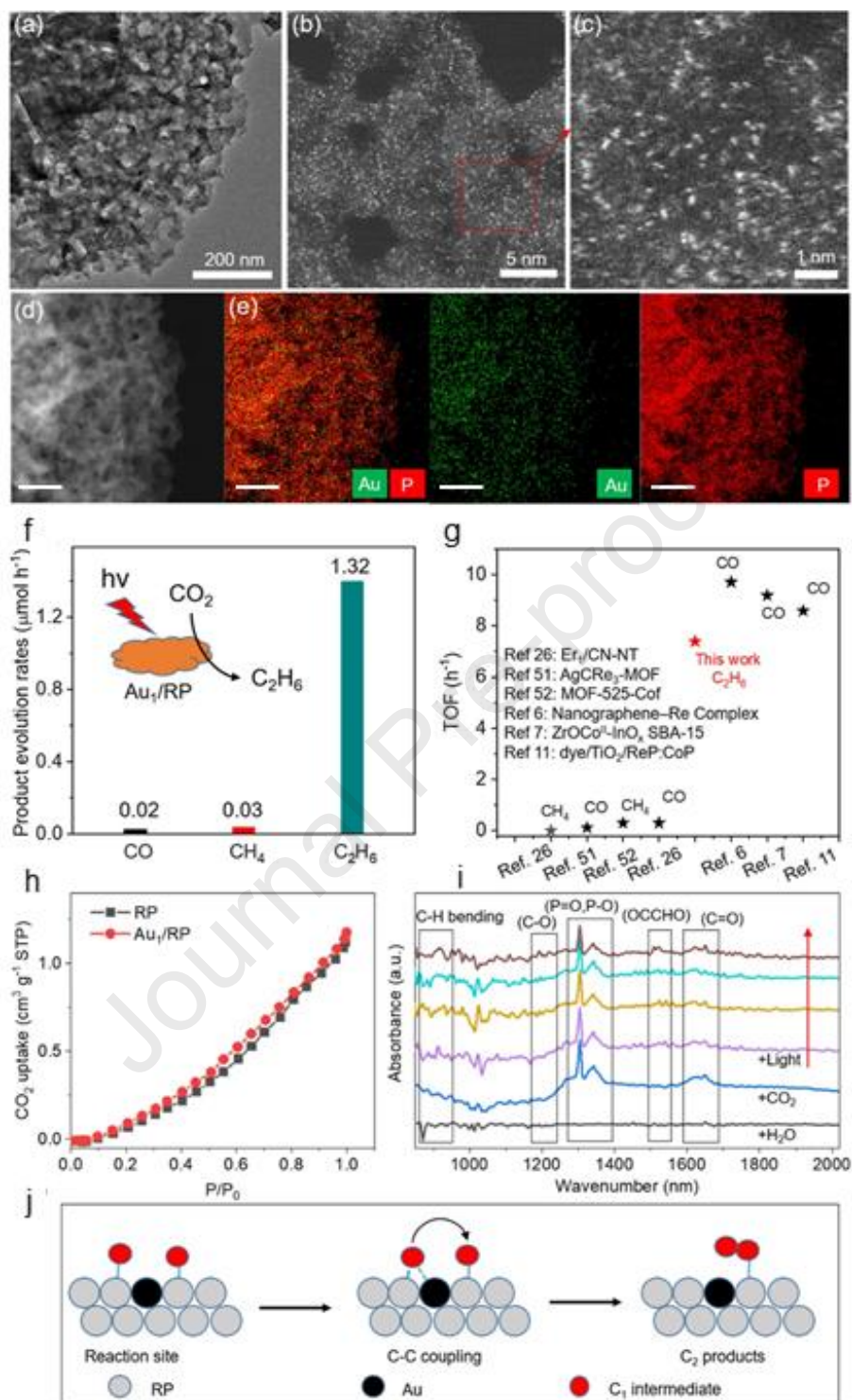
Fig. 9. (a) TEM image of Au$_1$/RP. (b) HAADF-STEM image and (c) enlarged image of Au$_1$/RP. (d) HAADF-STEM image of Au$_1$/RP (scale bar: 100 nm). (e) EDS mapping images of P and Au of Au$_1$/RP (scale bar: 100 nm). (f) PCO$_2$RR performance evaluation. (g) TOF values for

PCO$_2$RR of Au$_1$/RP with the recently reported values in literature. (h) CO$_2$ adsorption of RP and Au$_1$/RP. (i) In-situ DRIFTS spectra of Au$_1$/RP for PCO$_2$RR. (J) Schematic of Au$_1$/RP for C–C coupling. Reproduced with permission from Ref. 52.

Metal organic frameworks (MOFs) are popular precursors and templates in the CO$_2$RR catalyst fabrication, as well as in the SACs synthesis.[53-55] The metal node and organic ligand structure of MOFs facilitate the formation of SAs with a post-treatment of pyrolysis.[56, 57] Using MOFs as the precursors is a solid strategy to fabricate SAC-combined semiconductor catalysts. Other than the MOF strategy, the facile thermal polymerization strategy is also successful in SACs fabrication. Shi et al. reported a Cu-In dual-metal SAC by the polymerization strategy for PCO$_2$RR.[58] As demonstrated in Fig. 10a, the metal ion salt, urea, and MIL-68 are used as precursors to fabricate the polymer. Followed by the calcination, Cu-In dual site SACs are prepared. TEM results in Fig. 10 b-d show that Cu and In are evenly distributed on the CN nanosheets with isolated atom spots. The X-ray absorption spectroscopy reveals that the coordination environments of Cu and In in CuInCN are dominated by Cu-N and In-N rather than Cu-Cu and In-In, which confirms the single Cu and In atoms in the CuInCN catalyst (Fig. 10 e-p). The Cu-In dual site SAC affords the superior CO yield rate of 1.2 mmol g^{-1} h^{-1} that is almost ten times of the one of the original CN catalyst under visible light irradiation while maintaining the catalytic activities after 6 runs of the tests (Fig. 10 q and r).
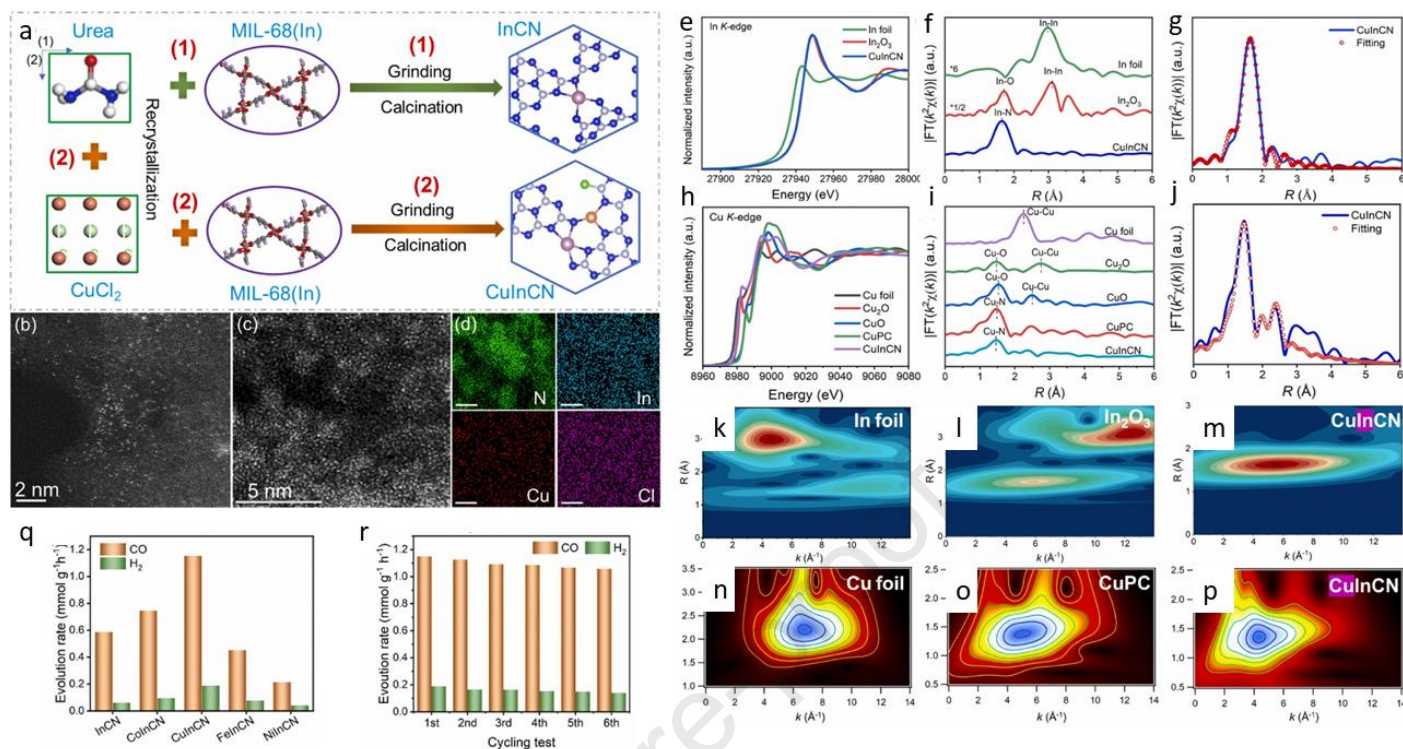
Fig. 10. (a) Schematic of the synthetic process for CuInCN and InCN (green: Cl atom, orange: Cu atom, pale purple: In atom, red: O atom, blue: N atom, light gray: C atom, white: H atom). HAADF-STEM images of (b) InCN and (c) CuInCN. (d) EDS mapping images of CuInCN (scale bar: 2 μm). (e) In K-edge XANES of CuInCN. (f) EXAFS spectra. (g) EXAFS fitting curves. (h) Cu K-edge XANES of CuInCN. (i) XAFS spectra. (j) EXAFS fitting curves. In K-edge Wavelet transforms contour plots of (k) In foil, (l) In₂O₃, (m) CuInCN. Cu K-edge transforms contour plots of (n) Cu foil, (o) CuPC, (p) CuInCN. (q) PCO₂RR productions on CuInCN with different Cu loadings. (r) Repeat reaction test with the reaction time of 3 h. Reproduced with permission from Ref. 58.

Besides, many novel synthetic strategies were discovered over recent years. For instance, Wang et al. applied a co-dissolution strategy to dissolve $[PtV_9O_{28}]^{7-}$ into $[V_{10}O_{28}]^{6-}$ to obtain the Pt single-atom catalyst that allowed a CH_4 production rate of 247.6 μmol g^{-1} h^{-1}, much higher than

that of Pt particles.[59] The numerous possibilities for the SAC synthesis of different elements hold

great potential for refining the PCO$_2$RR catalysts for better catalytic activities.

5.   Biohybrid catalysts for PCO$_2$RR

For abiotic photocatalysts, the effective transfer of the photo-generated electrons into chemical

bonds for CO$_2$RR is challenging. Biohybrid catalysts offer alternative means for CO$_2$RR for the

production of biofuels and biochemicals with higher product selectivity by integrating catalyst

materials with biological cells.[60-66] Many successful biohybrid semiconductor photocatalysts

have been developed for PCO$_2$RR. For example, moorella thermoacetica-based biohybrid

photocatalysts are efficient for the production of acetic acid from CO$_2$, such as the self-

photosensitization of moorella thermoacetica/CdS nanoparticles (Fig. 11 a and b) [67] and moorella

thermoacetica/Au nanoclusters (Fig. 11 c and d).[68] Moreover, light-harvesting artificial cells

containing cyanobacteria afford to fix CO$_2$ into glucose.[69]
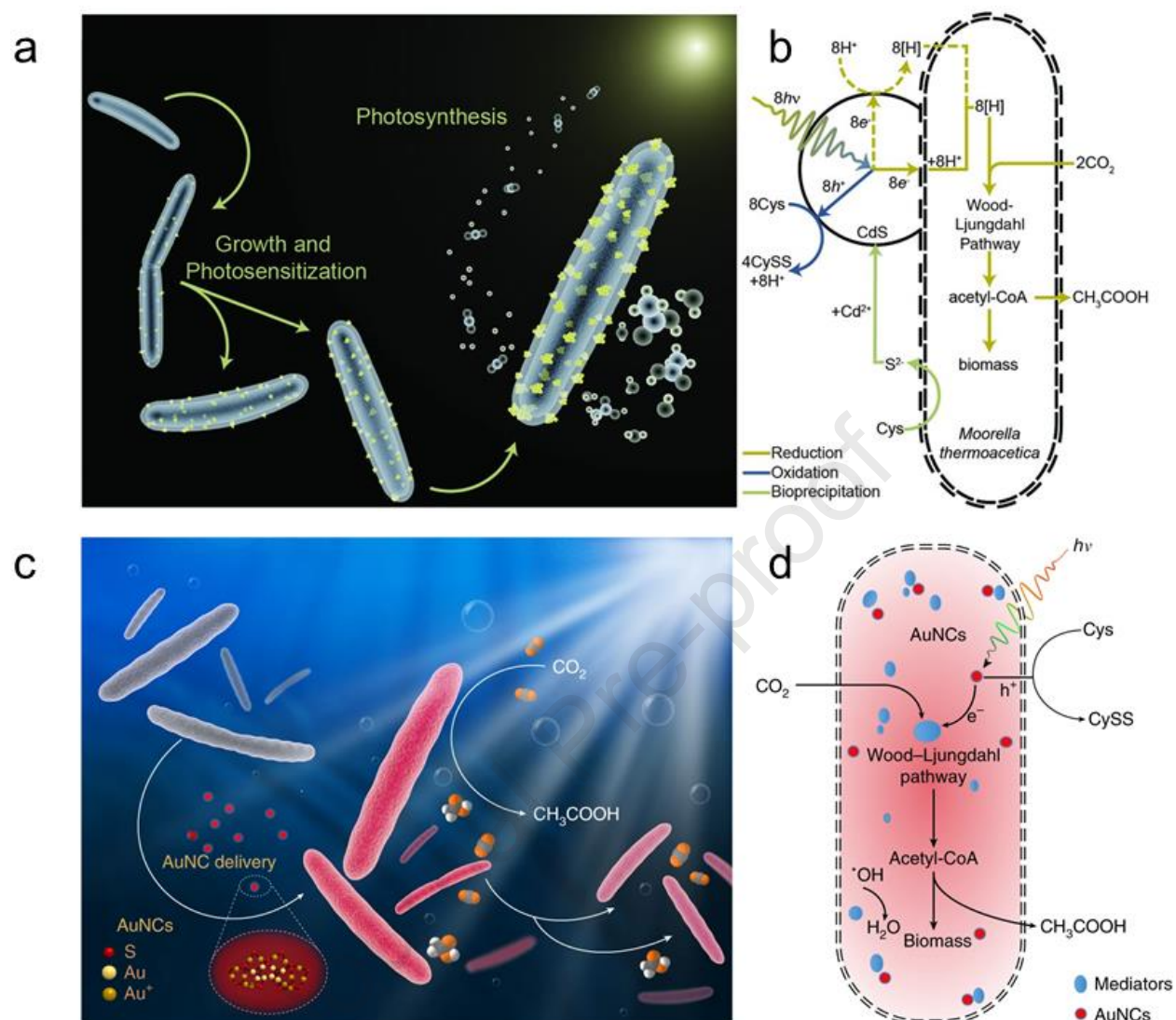
Fig. 11. (a) Illustration of the moorella thermoacetica–CdS bio-hybrid PCO_2RR system, yellow dots: CdS nanoparticles. CO_2 (center right) is converted to acetic acid (right). (b) Schematic of the moorella thermoacetica–CdS bio-hybrid PCO_2RR system. [H] generates outside the cell (marked in dashed line) or generated by the direct electron transport to the cell (marked in solid line). Reproduced with permission from Ref. 67. (c) Illustration of the moorella thermoacetica/AuNCs bio-hybrid PCO_2RR system. $Au_{22}(SG)_{18}$ nanoclusters are delivered into bare moorella thermoacetica (grey) during the catalyst synthesis to form moorella thermoacetica/AuNCs with red emission. Insert: the simulated chemical structure of

$Au_{22}(SG)_{18}$ nanoclusters. (Au atoms in the core: light yellow spheres; Au atoms in the staple motifs: dark yellow; S atoms in the shell: red; Oxygen atoms: orange; Carbon atoms: grey; hydrogen atoms: white.) (d) Schematic of the bacterium. The photo-generated electrons in AuNCs under irradiation are utilized by the enzymatic mediators inside the cytoplasm, which pass on to the Wood–Ljungdahl pathway. Reproduced with permission from Ref. 68.

Other than bacteria, protein can also be used in biohybrid semiconductor systems for PCO_2RR. Saif et al. designed a –NH_2 group functionalized 1D protein-encapsulated CeO_2 nanorods (PCNRs) for CO and CH_4 productions in PCO_2RR.[70] As depicted in Fig. 12a, the bovine serum albumin (BSA) is applied as an efficient biotemplate to synthesize PCNRs. With TEOA as the electron donor to consume the holes and the assistance of RhB, PCNRs demonstrate excellent activity toward H_2 production (Fig. 12b). When carried out in a CO_2 gas environment, PCNRs show catalytic activities towards CH_4 and CO productions under light irradiation of 400 nm $< \lambda <$ 780 nm (Fig. 12c) with great suppression of H_2 production. Fig. 12d and e reveal that PCNRs exhibit CO and CH_4 production rates of 5.0 and 3.3 µmol h^{-1} g^{-1}, which are 50 and 83 times higher than those of non-biohybrid CeO_2, respectively. The authors believe that the protein hybrid PCNRs significantly enhance the material stability and facilitate the transfer of photo-generated holes to promote the separation process of photo-generated carriers.
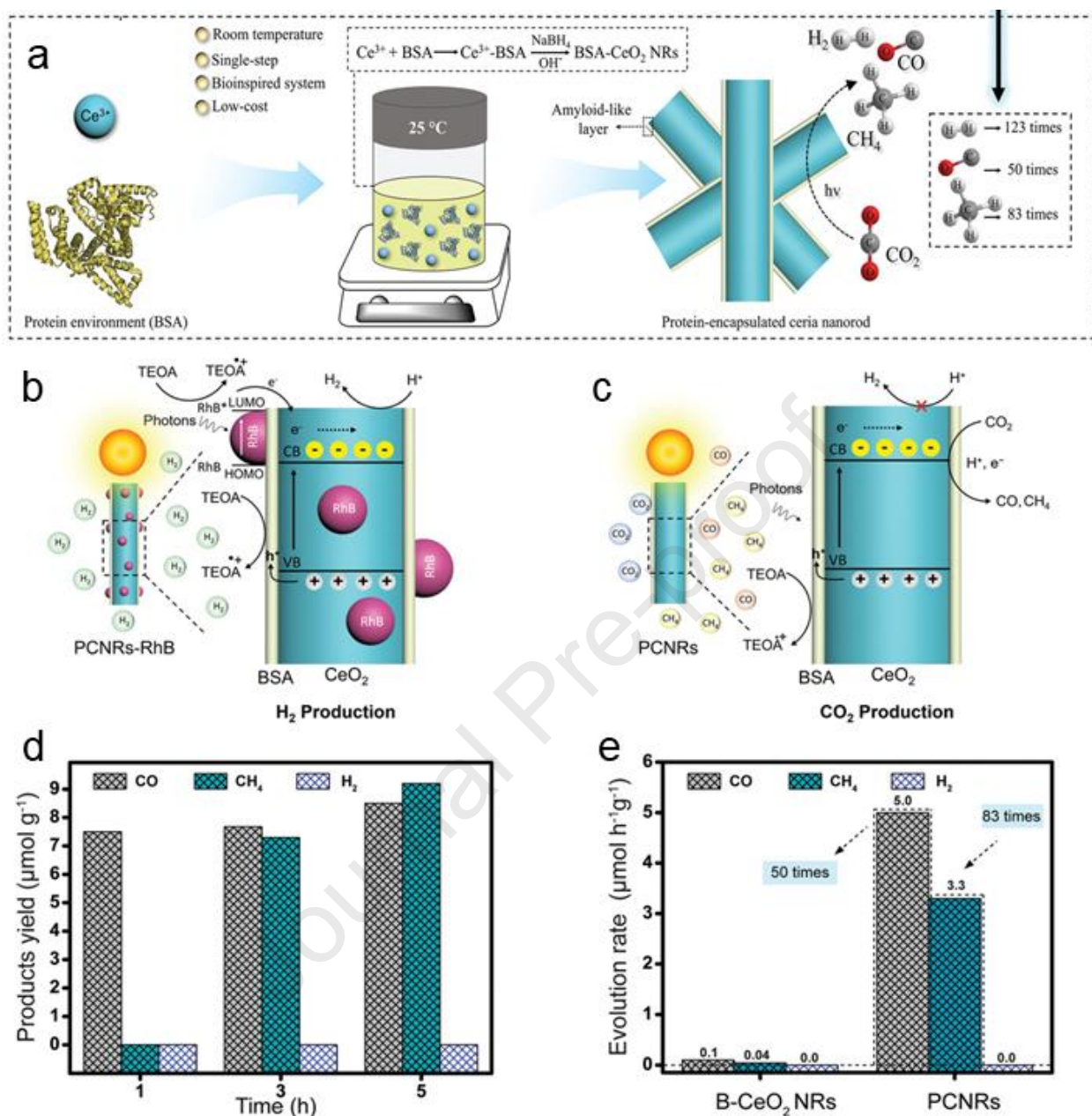
Fig. 12. (a) Schematic of the synthetic procedure of the catalyst. (b) H_2 generation reaction mechanism on the PCNRs. TEOA serves as the electron donor to consume the photo-generated hole. (c) PCO$_2$RR mechanism. (d) CO, CH_4, and H_2 yields during PCO$_2$RR on PCNRs. (e) CO, CH_4, and H_2 production rates on PCNRs and B-CeO$_2$ NRs. Reproduced with permission from Ref. 70.

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Researchers should still pay attention to some key points, concerning the future design of biohybrid photocatalysts. First, semiconductor materials that are compatible with bio cells need to be rationally constructed to protect microbial cells from deactivation while sufficiently harvesting visible light to provide enough electrons for CO_2RR. Second, the interface of the biotic–abiotic should be tailored for quick charge transfer, accelerating the separation rate of electron/hole pairs for better catalytic performance. Finally, the integrated bio-material should be able to efficiently utilize photo-generated electrons to produce fuel chemicals from PCO_2RR.[60]

Table 1. Photocatalytic performance of some typical hybrid catalysts.

Catalyst	Light source	Reduction Product (selectivity)	Production rate (μmol g^{-1} h^{-1})	Stability	Other parameters	Ref.
Metal oxides						
CoO$_x$/N-C-ZnO	AM 1.5G light	CO	CO: 2.6	5 h	CO$_2$ + H$_2$O; Apparent quantum yield: 1.49% at 420 nm	71
NiO/hexaniobate-Ni cluster	Simulated solar light (150 W)	CO	CO: 730		CO$_2$ + H$_2$O	72
Ag-TiO$_2$/GDL	UV light ($\lambda < 400$ nm)	CO (~66%), CH$_4$ (~33%)	CO+ CH$_4$: 305.7	60 h	CO$_2$ + H$_2$O	23
CeO$_2$@CeO$_2$/TiO$_2$	AM 1.5G light	CO (~87%), CH$_4$ (~13%)	CO: 97.6 CH$_4$: 15.0	8 h	CO$_2$ + H$_2$O and triethanolamine (TEOA)	40
Au$_{0.2}$Cu$_{0.8}$/TiO$_2$	AM 1.5G light	CH$_4$ (~90%), C$_2$H$_4$ (~10%)	CH$_4$: 3578.9 CH$_4$: 369.8	8 h	CO$_2$ + H$_2$O	9
Pd-HPP-TiO$_2$	300 W Xe lamp	CO (~41%), CH$_4$ (~59%)	CO: 34.0 CH$_4$: 48.0	20 h	CO$_2$/O$_2$ mixed gas, or air	22
Cu$_2$O-111-Cu^0	300 W Xe lamp	CH$_4$ (~97%), C$_2$H$_4$, CO, H$_2$	CH$_4$: 78.4	8 h	CO$_2$ + H$_2$O	73
Alloys						
Au/CuPd	400 mW cm^{-2} full-spectrum light	CH$_4$ (100%)	CH$_4$: 15.6	30	CO$_2$ + H$_2$O Apparent quantum efficiency: 0.38% at 800 nm	28
Bi-based						
BiOCl-V$_{Bi}$	300 W Xe lamp	CO	CO: 21.99	30 h	In air	74
Ni@MOF/BiVO$_4$	300 W Xe lamp	CO (99.2%), H$_2$	CO: 178.0	28 h	CO$_2$ + H$_2$O	75
SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo	AM 1.5G light	HCOO$^-$ (97%)	HCOO$^-$: ~20.0	24 h	CO$_2$-saturated 0.1 M KHCO$_3$ aqueous solution + CO$_2$; Turnover number (TON):	34

						427
			CdS-based			
α-Fe₂O₃/CdS	AM 1.5G light	CO	CO: 9.3	6 h	$CO_2 + H_2O$	33
ZnIn₂S₄-CdS	visible light ($\lambda > 420$ nm)	CO (~85%), H₂	CO: 2182.5	20 h	$CO_2 + H_2O$, TEOA, MeCN, CoCl₂, and 2,2-bipyridine; TON = 43.65	31
			Layered double hydroxides			
NiAl-LDH	visible light ($\lambda > 600$ nm)	CO (29.7%), CH₄ (70.3%)	CO: 43.0 CH₄: 103.0	4 h	$CO_2 + H_2O$, acetonitrile (ACN), TEOA, and Ru(bpy)₃Cl₂·6H₂O;	20
Pd/CoAl-LDH	visible light ($\lambda > 400$ nm)	CO (50%), H₂ (50%)	CO: 1680.0	4 h	$CO_2 + H_2O$, TEOA, and Ru(bpy)₃Cl₂·6H₂O;	21
			Carbonaceous			
CN/MRF	visible light ($\lambda > 420$ nm)	CH₃OH	CH₃OH: 0.99	5 h	$CO_2 + H_2O$, 80 °C; Quantum efficiency: 5.5% at 380 nm	76
Co₂P@BP/g-C₃N₄	300 W Xe lamp	CO (96%), CH₄	CO: 16.21	20 h	CO₂ + acetonitrile, H₂O, and TEOA	77
Cu₁N₃@PCN	visible light ($\lambda > 420$ nm)	CO	CO: 49.8	25 h	$CO_2 + H_2O$	78
Fe SA/COF	visible light ($\lambda > 420$ nm)	CO (96.4%), H₂	CO: 980.3	20 h	CO₂ + acetonitrile, H₂O, and TEOA	79
HOF-Ni/GO	visible light ($\lambda > 420$ nm)	CO (96.3%), H₂	CO: 24323.0	8 h	$CO_2 + H_2O$, MeCN, TIPA, and Ru(bpy)₃Cl₂·6H₂O;	80
Au/N-graphene	300 W Xe lamp	CO (95%)	CO: 111360	36 h	$CO_2 + H_2O$	51
			Perovskite			
Cs₂NaBiCl₆	300 W Xe lamp	CO (96.4%), CH₄ (3.6%)	CO: 30.22 CH₄: 1.12	50 h	Gas ($CO_2 + H_2O$)	81
Ni-CsPbBr₃/Bi₃O₄Br	visible light ($\lambda > 420$ nm)	CO (98.2%), CH₄ (1.8%)	CO: 96.9 CH₄: 1.7	20 h	Gas (air + H_2O)	32

6. Characterization techniques in PCO₂RR

After the design of highly efficient catalysts, many characterization techniques are required to understand the properties and uniqueness of the photocatalyst material for excellent catalytic efficiency. X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), UV-Vis spectroscopy, and X-ray absorption spectroscopy (XAS) are common techniques for exploring the element valence, crystallization, bandgap value, and coordination environment information of the materials. Scanning electron microscopes (SEM), transmission electron microscopy (TEM), and energy dispersive spectroscopy (EDS) can directly provide visual images of morphologies and element distributions of catalyst materials. The combination of different characterization techniques is important to confirm one's assumption. For example, the analysis of XAS and XPS helps to confirm the N/O ratio in N-Ti-O/V[O] for the production of C_{2+} products on TiO_2 catalysts.[82] For revealing the reaction mechanism of CO_2RR, the density functional theory (DFT) simulations emerge as one of the most useful tools to demystify the structure-activity relationship and catalytic mechanism for complex catalytic systems such as hybrid catalysts.[83-86] In the meantime, in-situ characterizations, such as in-situ XRD, in-situ XAS, and in-situ Raman spectroscopy, are powerful experimental approaches to trace the evolution of the catalyst structures and reaction intermediates during the catalytic reaction of CO_2RR.[87-90] Apart from Raman spectroscopy, in-situ Fourier transform infrared absorption spectroscopy (FTIR) can also provide evidence of reaction intermediates, uncovering the reaction pathway of CO_2RR.[91, 92] Wu et al. prepared an oxygen vacancy (V_o)-rich MoO_{2-x} for PCO₂RR.[93] The V_o-rich MoO_{2-x} exhibits a CH_4 production rate of 5.8 and 12.2 μmol g⁻¹ h⁻¹ under NIR and full light irradiation in PCO₂RR, which is around 10- and 7-fold to those of the V_o-poor MoO_{2-x},

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respectively (Fig. 13a). Besides, the V_o-rich MoO_{2-x} performs PCO$_2$RR directly under an air atmosphere with a CO production rate of 6.5 μmol g^{-1} h^{-1} under NIR irradiation (Fig. 13b). V_o-rich MoO_{2-x} also demonstrates good stability in PCO$_2$RR activity under NIR irradiation in concentrated CO_2 after 4 runs (Fig. 13c). In-situ FTIR is applied to reveal the reaction mechanism of PCO$_2$RR over the MoO_{2-x} catalysts. Fig. 13d shows that carbonate species and *CO_2^- appear in the dark, suggesting the absorption and activation of CO_2 on the V_o-rich MoO_{2-x} surface. Additional peaks of *COOH (1593 cm^{-1}), *CH_3O (1170 and 1100 cm^{-1}), and *CHO (1082 cm^{-1}) appear and are gradually strengthened with the increase of illumination time under NIR (Fig. 13e). These intermediates are essential to the production of CH_4 in CO_2RR. When illuminated under full spectrum light, the IR peak intensities of the intermediates further increased (Fig. 13f). It reveals the efficient light response of V_o-rich MoO_{2-x} and the possible reaction pathway ($CO_2 \rightarrow$ *$CO_2 \rightarrow$*COOH$\rightarrow$ *CO$\rightarrow$CO or *CHO$\rightarrow$*$CH_2O \rightarrow$*$CH_3O \rightarrow CH_4$) for PCO$_2$RR.
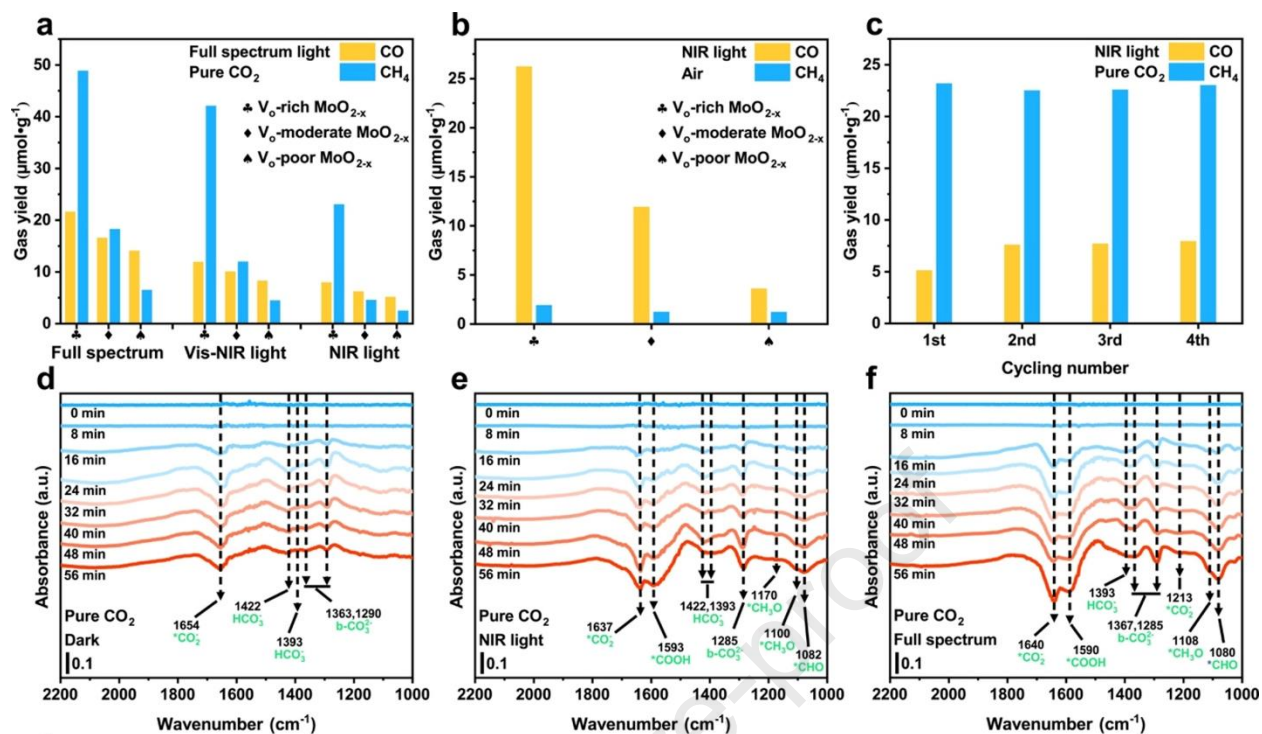
Fig. 13. PCO$_2$RR performance on MoO$_{2-x}$ under (a) whole light illumination in pure CO$_2$, (b) NIR illumination in air, and (c) repeat tests of PCO$_2$RR under NIR illumination in pure CO$_2$. In-situ FTIR experiments on V$_o$-rich MoO$_{2-x}$ (d) under the dark, (e) under NIR illumination, and (f) under whole light illumination in pure CO$_2$. Reproduced with permission from Ref. 93.

With the advancing of characterization techniques, powerful characteristic techniques are exploited for revealing the compositional effects in hybrid catalysts for PCO$_2$RR. Chen et al. recently applied spatiotemporally resolved surface photovoltage measurements (SPVM) on the facet and defect-engineered Cu$_2$O catalysts (Fig. 14a) to map the holistic charge transfer processes at the single-particle level on the femtosecond timescale.[94] Fig. 14b depicts that the {001} facet has more accumulated photo-generated electrons than the {111} facet of the Cu$_2$O octahedron, owing to the high Cu vacancies (V$_{Cu}$) on the {001} facet. Fig. 14c demonstrates that the anisotropic charge transfer is optimized with a truncated octahedral configuration, suggesting the contribution of the inter-facet built-in electric field to the anisotropic charge transfer. SPVM

in Fig. 14d further illustrates that the moderate hydrogen-compensated V_{Cu} (H-V_{Cu}) results in an efficient spatial separation of the photo-generated carriers on {111} and {001} facets. On the contrary, the extreme incorporation of H-V_{Cu} leads to the quench of the photo-generated electron/hole pairs (Fig. 14e). The photoemission electron images in Fig. 14f visualize the dynamics of anisotropic electron transfer for single Cu_2O particle, indicating that the ultrafast inter-facet electron transfer contributes significantly to the anisotropic electron distribution. Au being selectively deposited on the {001} facet of Cu_2O can also be successfully probed by SPVM (Fig. 14 g-i). It is confirmed that the H_2 evolution performance is associated with the anisotropic charge transfer of Cu_2O (Fig. 14j). This powerful SPVM technique brings meaningful insights into the photo-carrier transfer dynamics, which can be transplanted to PCO$_2$RR. With more advanced characterization techniques developed and applied to the PCO$_2$RR catalysts, the rational design of the next-generation photocatalyst for excellent catalytic performance can be precisely and systematically guided.
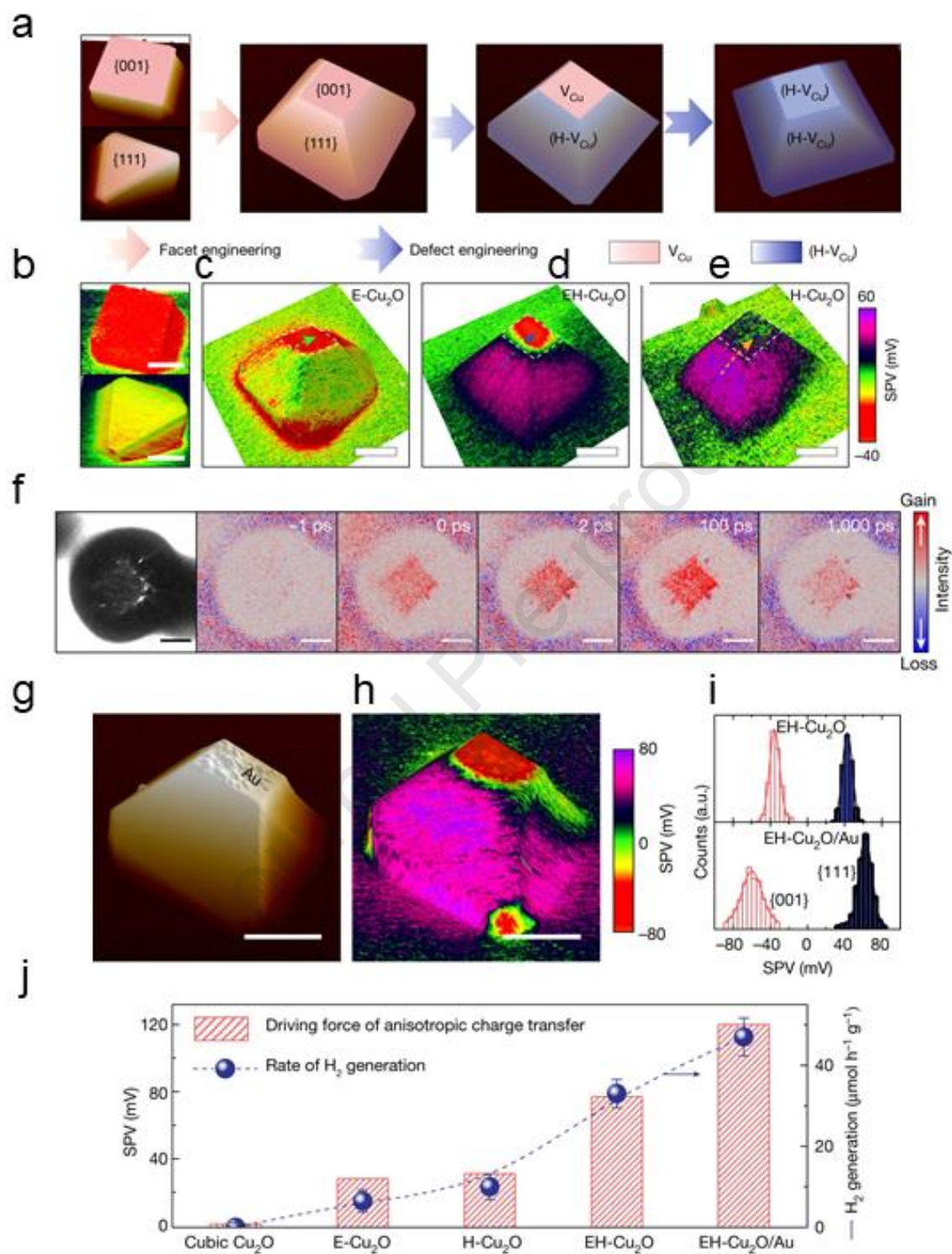
Fig. 14. (a) Schematic of the anisotropic facets and defects engineering on Cu₂O particles. (b)

SPVM images of octahedral (bottom) and cubic (top) Cu₂O particles. SPVM images of truncated

octahedral Cu_2O particles of (c) without incorporation of (H-VCu) defects, (d) with moderate incorporation of (H-VCu) defects, and (e) with extreme incorporation of (H-VCu) defects. Time-resolved photoemission electron microscopy of E-Cu2: (f) PEEM image and a series of TR-PEEM images of EH-Cu_2O O at different pump–probe delay times, as labeled. Scale bars: 2 µm. (g) AMF image and (h) corresponding SPVM image of EH-Cu_2O O/Au. (i) Comparison of the statistical SPV signals on the {001} and {111} facets of EH-Cu_2O with Au particles selectively deposited on the {001} facet (marked as EH-Cu_2O/Au. (j) Driving forces of the anisotropic charge transfer and the PCO2RR performance. Reproduced with permission from Ref. 94.

7. Perspectives

To sum up, semiconductor photocatalysts often suffer from unsatisfying catalytic performance (e.g. with production rate at the level of µmol g^{-1} h^{-1}) in PCO2RR, owing to the poor light harvesting ability, the low separation rate of the photo-induced carriers, and stability issues. Designing novel semiconductor materials with highly efficient catalytic performance for PCO2RR that address these issues is a priority. The hybridization of semiconductor catalysts through different approaches such as surface modification and band engineering strategies can integrate the advantages of the different semiconductor catalysts and co-catalysts to prohibit the recombination of the photo-generated electron/hole pairs and promote the light response of the semiconductor catalysts for PCO2RR. The hierarchical structure construction of semiconductor catalysts also contributes to the separation of the photo-generated electron/hole pairs and sometimes can even achieve a spatially coordinated tandem reaction to produce C_{2+} products from PCO2RR. Active sites are essential to catalysis. Anchoring highly catalytically effective SACs on semiconductor catalysts holds great promise for the augmentation of catalytic activities

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in PCO_2RR. To improve product selectivity, integrating biological materials that are highly selective in photosynthesis with semiconductor catalysts has been proven to be an effective solution. Moreover, by using advanced characterization techniques for in-situ probing, the underlying mechanism of the reaction pathway and catalyst structure evolution can be demystified for next-generation PCO_2RR catalyst design. Other than the proposed solutions discussed above, current research on PCO_2RR still needs to focus on the following perspectives:

- The duration of the catalytic performance is always a big issue in PCO_2RR. Most photocatalysts present a catalytic activity duration of dozens of hours, which is excessively low for industrial requirements (more than thousands of hours).[95, 96] The fabrication of highly active semiconductor materials for CO_2RR without accumulating residues of poisoning intermediates is forever a priority. Besides, the addition of the protective layer on the surface of photocatalysts to mitigate the decay of the catalyst structure during PCO_2RR could be a possible solution to enhance the catalyst stability.[7]

- In addition, the combination of photocatalysis with other catalytic methods such as electrochemical catalysis and thermal catalysis (e.g. photo-electrocatalysis) holds great potential to improve both the catalytic activities and product selectivity in CO_2RR.[97, 98] CO_2 capture and storage (CCS) takes a vital part in the mitigation of over-emitted CO_2 because it is energy-consuming.[99] Sorbent porous materials such as metal oxides,[100-102] zeolites and amine-functionalized silicas,[103] covalent organic frameworks (COFs),[104-106] MOFs,[107-109] and porous carbons[110] are effective toward CO_2 captures. Many of these sorbent materials also demonstrate photocatalytic activity towards CO_2RR. Hence, coupling CO_2-capture with PCO_2RR can be a practical means in the further market for better efficiency.[111-115]

- To finally achieve a practical application, a rational catalysis setup needs to be designed for high catalytic efficiency and scale-up production. Many promising CO_2RR systems have been developed for electrolysis, such as gas phase flow cells, solid oxide electrolysis cells (SOECs), etc.[116-118] For the photocatalysis-related setup upgrade, there are also some interesting discoveries, e.g., the back-illuminated photoelectrochemical flow cell for the increased solar-to-fuel conversion efficiency,[119] the aerobic environment for the improved PCO_2RR in a less restricted reaction condition.[120]

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Declaration of competing interest

There is no conflict of interest to declare.

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