

Incorporating Catalytic Units into Nanomaterials: Rational Design of Multipurpose Catalysts for CO₂ Valorization

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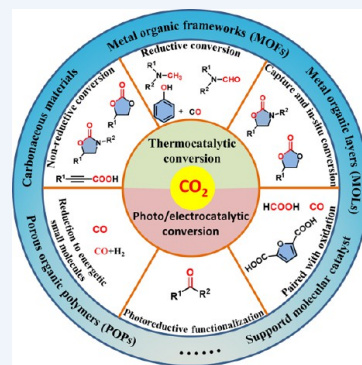
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CONSPECTUS: CO₂ conversion to valuable chemicals is effective at reducing CO₂ emissions. We previously proposed valorization strategies and developed efficient catalysts to address thermodynamic stability and kinetic inertness issues related to CO₂ conversion. Earlier, we developed molecular capture reagents and catalysts to integrate CO₂ capture and conversion, i.e., in situ transformation. Based on the mechanistic understanding of CO₂ capture, activation, and transformation at a molecular level, we set out to develop heterogeneous catalysts by incorporating catalytic units into nanomaterials via the immobilization of active molecular catalysts onto nanomaterials and designing nanomaterials with intrinsic catalytic sites.

In thermocatalytic CO₂ conversion, carbonaceous and metal–organic framework (MOF)-based catalysts were developed for nonreductive and reductive CO₂ conversion. Novel Cu- and Zn-based MOFs and carbon-supported Cu catalysts were prepared and successfully applied to the cycloaddition, carboxylation, and carboxylative cyclization reactions with CO₂, generating cyclic carbonates, carboxyl acids, and oxazolidinones as respective target products. Reductive conversion of CO₂, especially reductive functionalization with CO₂, is a promising transformation strategy to produce valuable chemicals, alleviating chemical production that relies on petrochemistry. We explored the hierarchical reductive functionalization of CO₂ using organocatalysts and proposed strategies to regulate the CO₂ reduction level, triggering heterogeneous catalyst investigation. Introducing multiple active sites into nanomaterials opens possibilities to develop novel CO₂ transformation strategies. CO₂ capture and in situ conversion were realized with an N-doped carbon-supported Zn complex and MOF materials as CO₂ adsorbents and catalysts. These nanomaterial-based catalysts feature high stability and excellent efficiency and act as shape-selective catalysts in some cases due to their unique pore structure.

Nanomaterial-based catalysts are also appealing candidates for photocatalytic CO₂ reduction (PCO₂RR) and electrocatalytic CO₂ reduction (ECO₂RR), so we developed a series of hybrid photo-/electrocatalysts by incorporating active metal complexes into different matrixes such as porous organic polymers (POPs), metal–organic layers (MOLs), micelles, and conducting polymers. By introducing Re-bipyridine and Fe-porphyrin complexes into POPs and regulating the structure of the polymer chain, catalyst stability and efficiency increased in PCO₂RR. PCO₂RR in aqueous solution was realized by designing the Re-bipyridine-containing amphiphilic polymer to form micelles in aqueous solution and act as nanoreactors. We prepared MOLs with two different metallic centers, i.e., the Ni-bipyridine site and Ni-O node, to improve the efficiency for PCO₂RR due to the synergistic effect of these metal centers. Sulfhydrylphenoxyl-decorated cobalt phthalocyanine (CoPc) cross-linked polypyrrole was prepared and used as a cathode, achieving the electrocatalytic transformation of diluted CO₂ benefiting from the CO₂ adsorption capability of polypyrrole. We fabricated immobilized 4-(*t*-butyl)-phenoxy cobalt phthalocyanine and Bi-MOF as cathodes to promote the paired electrolysis of CO₂ and 5-hydroxymethylfurfural (HMF) and obtained CO₂ reductive products and 2,5-furandicarboxylic acid (FDCA) efficiently.

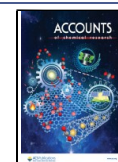


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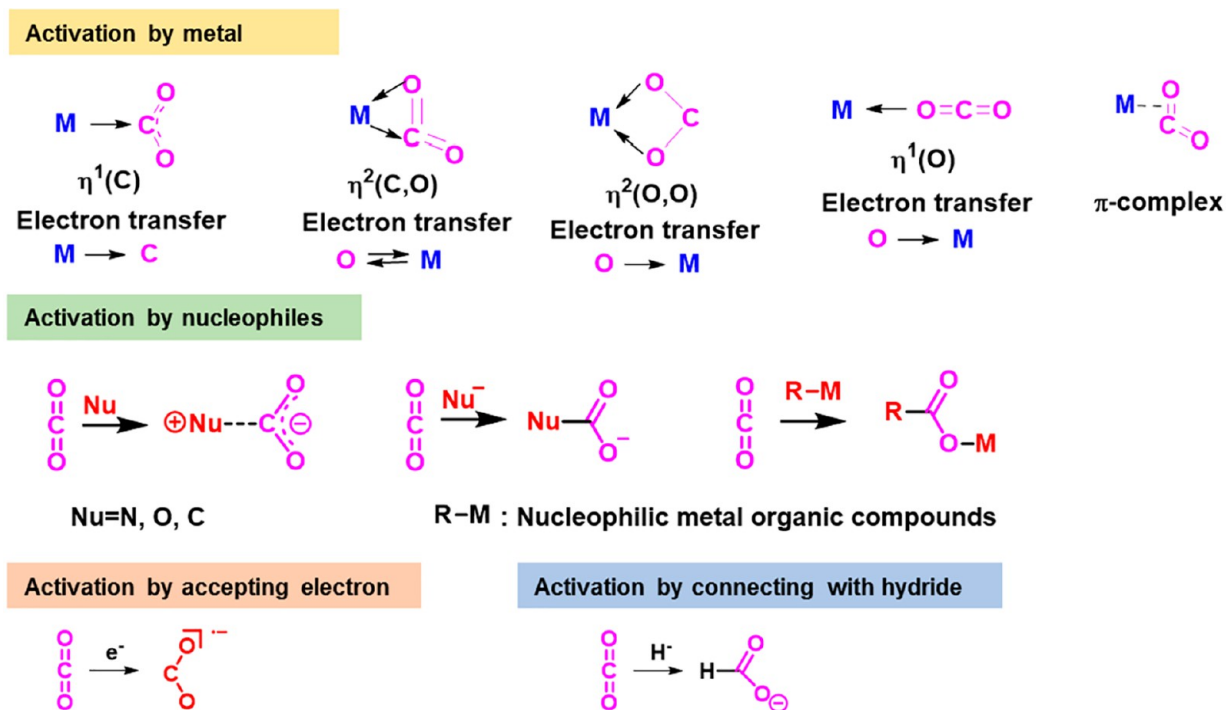


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Figure 1. Common methods of CO₂ activation.

achieve equimolar CO₂ capture and in situ transformation to oxazolidinones with either aziridine or propargyl amine in poly(ethylene glycol) (PEG₁₅₀).

- Liu, X.-F.; Li, X.-Y.; Qiao, C.; Fu, H.-C.; He, L.-N. Betaine Catalysis for Hierarchical Reduction of CO₂ with Amines and Hydrosilane To Form Formamides, Aminoalcohols, and Methylamines. *Angew. Chem., Int. Ed.* **2017**, *56*, 7425–7429.² In this work, betaine was proven to be an efficient catalyst to realize the hierarchically reductive functionalization of CO₂ with amines and hydrosilane, showing the feasibility of regulating products with species containing the carbamate anion.
- Cao, C.-S.; Xia, S.-M.; Song, Z.-J.; Xu, H.; Shi, Y.; He, L.-N.; Cheng, P.; Zhao, B. Highly Efficient Conversion of Propargylic Amines and CO₂ Catalyzed by Noble-Metal-Free [Zn₁₁₆] Nanocages. *Angew. Chem., Int. Ed.* **2020**, *59*, 8586–8593.³ In this report, the noble-metal-free MOFs catalyst with a giant and lantern-like [Zn₁₁₆] nanocage in the zinc-tetrazole 3D framework was synthesized and applied to the cyclization of propargylic amines with CO₂, affording various 2-oxazolidinones exclusively under mild conditions.
- Ren, F.-Y.; Chen, K.; Qiu, L.-Q.; Chen, J.-M.; Darendbourg, D. J.; He, L.-N. Amphiphilic Polycarbonate Micellar Rhenium Catalysts for Efficient Photocatalytic CO₂ Reduction in Aqueous Media. *Angew. Chem., Int. Ed.* **2022**, *61*, e202200751.⁴ The amphiphilic polycarbonate nanomicelles containing Re-bipyridine units were synthesized to act as a “nano-reactor” for PCO₂RR in the aqueous solution, which can inhibit the competitive hydrogen evolution reaction and catalyst deactivation.

1. INTRODUCTION

CO₂ accumulation and its detrimental environmental impacts have become issues of public concern.⁵ To address the carbon emission issues, various strategies have been proposed, among

which carbon capture and utilization (CCU), one of the negative carbon technologies, is regarded as an important initiative. In particular, converting such captured CO₂ to valuable products without desorption can avoid energy consumption in CO₂ desorption. Furthermore, the captured CO₂ can be considered to be the activated CO₂ species and thus promotes the subsequent transformation under mild conditions.³

CO₂ is a thermodynamically stable molecule with a standard formation enthalpy of 393.5 kJ mol^{−1}.⁶ Simultaneously, the linear symmetric structure makes CO₂ a kinetically inert molecule. The above features imply that the CO₂ transformation relies on efficient CO₂ activation and high energy input (from the substrate with high free energy or external light and/or electrical energy). Accordingly, the activation of CO₂ through thermo-, photo-, or electrocatalytic processes is a prerequisite to CO₂ valorization.

The CO₂ molecule can, in general, be activated by metal and nucleophilic reagents, generating activated species with a bent structure or charge redistribution. Eventually, electron and/or hydride transfer to CO₂ can improve the reactivity as depicted in Figure 1.⁷ Hitherto, homogeneous catalytic systems have been widely explored in CO₂ conversion via forming the aforementioned active CO₂ species; therefore, a plethora of thermocatalytic and photo-/electrocatalytic CO₂ transformation protocols have been developed. Then based on the understanding of the catalytic mechanism in homogeneous catalytic systems, heterogeneous catalysts have been gradually developed to overcome the thermal instability and non-recyclability issues encountered in homogeneous catalytic systems. Heterogeneous catalysts can be fabricated through different strategies, among which the immobilization of a molecular catalyst onto nanomaterial via covalent bonding or intermolecular interaction is widely adopted due to its operational simplicity. In addition, designing nanomaterials with intrinsic catalytic sites proves to be another robust method.⁸

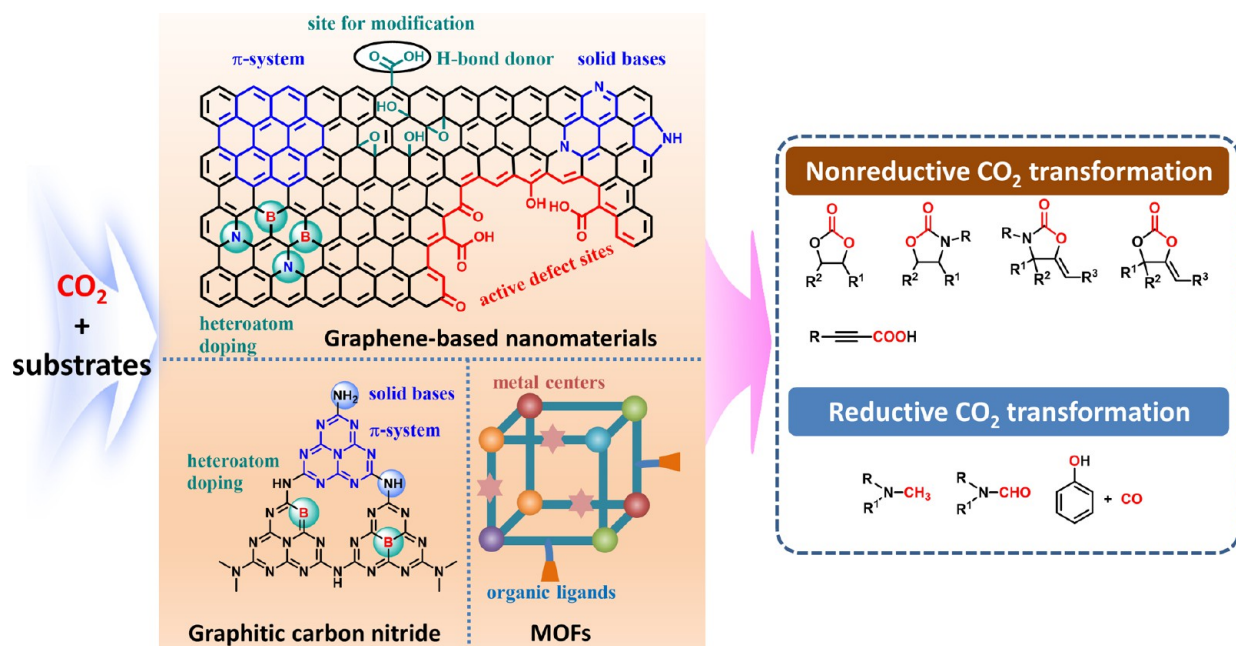


Figure 2. Carbonaceous materials and MOFs for the thermocatalytic conversion of CO₂ to chemicals.

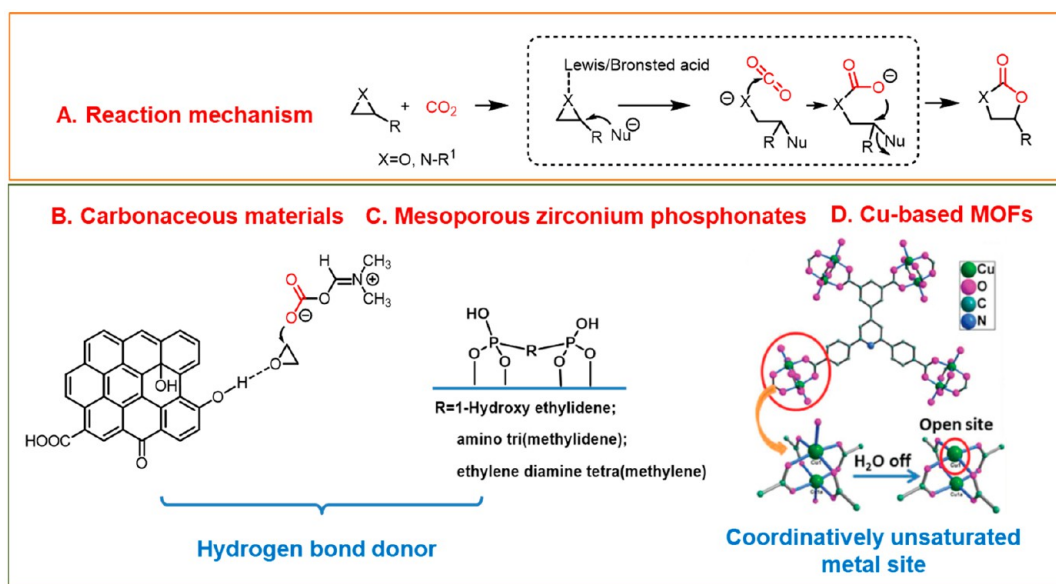


Figure 3. Nanomaterials used in the cycloaddition reaction of CO₂ with epoxide/aziridine. Reproduced with permission from ref 18, copyright (2016) Wiley-VCH.

Recently, precisely controlling the atomic, molecular, and nanolevel structure, morphology, and chemical composition of catalysts and thus realizing the directional conversion of CO₂ has evoked intensive interest. In this Account, we select our own results and typical works of other peers as examples to showcase the latest advancements in CO₂ valorization with nanomaterials, following the logical order of establishing a CO₂ conversion strategy with molecular catalysts, gaining insight into the reaction mechanism at the molecular level, and rationally designing nanomaterials, namely, from molecular catalysis to heterogeneous catalysis through molecular engineering. We hope that this Account will promote a comprehensive understanding of CO₂ transformation over nanomaterials and inspire the development of novel CO₂ transformation protocols based on tailored nanomaterials.

2. THERMOCATALYTIC CO₂ CONVERSION

In thermocatalytic CO₂ valorization, high-energy substrates are necessary, considering their thermodynamic stability. According to the variation of the CO₂ valence state, the conversion protocols can be divided into nonreductive and reductive ones, among which the nanomaterials containing multiple catalytic sites, especially carbonaceous materials and metal–organic frameworks (MOFs), provide a versatile platform to activate both CO₂ and substrates (Figure 2).^{9,10}

2.1. Nonreductive CO₂ Transformation

In nonreductive CO₂ transformation, the entire CO₂ is incorporated into the product in the form of a carboxyl, ester, or carbamate group, and the valence state of the carbon atom remains unchanged. In this scenario, increasing the nucleophil-

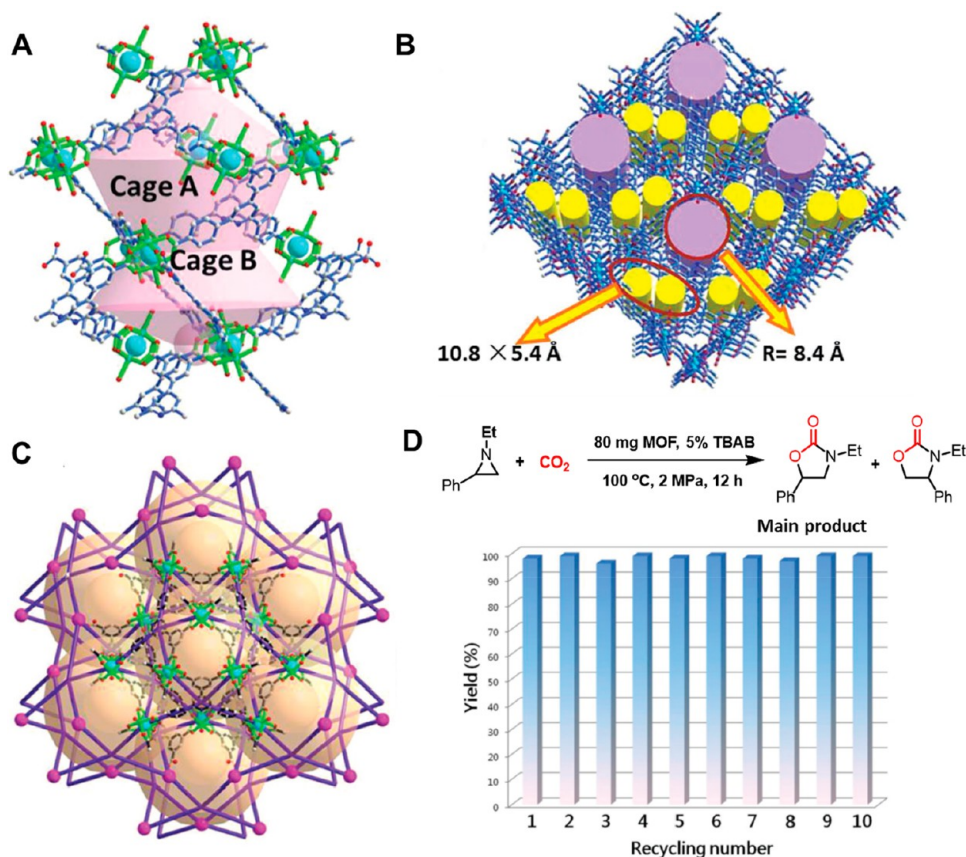


Figure 4. Structure of MOF assembled by [Cu₃₀] nanocages and its utilization in a cycloaddition reaction with CO₂. (A) Nanosized [Cu₃₀] cage. (B) Perspective view of the framework along the *c* direction. (C) 3D framework and 1D channels along the *b* direction. (D) Recycle tests for the cycloaddition reaction of CO₂ with 1-ethyl-2-phenylaziridine. Reproduced with permission from ref 18, copyright (2016) Wiley-VCH.

icity of the substrate or enhancing the electrophilicity of CO₂ is vital to facilitating the transformation.

2.1.1. Cycloaddition Reaction of Epoxide/Aziridine and CO₂. Cycloaddition reactions employing epoxide/aziridine and CO₂ are widely used in cyclic carbonate/oxazolidinone synthesis.¹¹ To promote this transformation, a Lewis or Brønsted acid and nucleophilic reagents are necessary to promote the ring opening of epoxide/aziridine, forming nucleophilic and electrophilic sites for coupling with CO₂. In our investigation, Zn-, Ca-, and Cu-based molecular catalysts with strong Lewis acidity and an organic small molecule with a hydrogen bonding donor can activate epoxide/aziridine.^{12–15} Simultaneously, nucleophilic halide ions and carbonate and carbamate anions are also necessary to facilitate the ring opening as presented in Figure 3A.^{12–15}

Based on the reaction mechanism, Qu's group applied graphene oxide with sufficient carboxyl and hydroxyl groups on the surface to the cycloaddition reaction of epoxide and CO₂ in *N,N*-dimethylformamide (DMF) solvent (Figure 3B).¹⁶ It is proposed that the exposed carboxyl and hydroxyl groups can activate the epoxide by forming a hydrogen bond. Concurrently, the solvent DMF can form the adduct with CO₂ and then act as a nucleophile to facilitate the ring opening of the epoxide.

In addition to the carbonaceous materials, the other material with a hydrogen bonding donor can also catalyze the cycloaddition reaction with CO₂. In view of this, we synthesized three mesoporous zirconium organophosphonates using 1-hydroxyethylidene-1,1'-diphosphonic acid (HEDP), amino tri(methylene phosphonic acid) (ATMP), and the sodium salt

of ethylene diamine tetra(methylene phosphonic acid) (EDTMPs) as the coupling molecules. Its porous structure and the existence of phosphoric acid groups and hydroxyl or amino groups connected to organic moieties may facilitate the activation of both aziridine and CO₂ (Figure 3C).¹⁷ When applied to the cycloaddition reaction of aziridine with CO₂, the resulting mesoporous zirconium organophosphonates deliver 85–90% yields of oxazolidinones in a solvent-free system without introducing any cocatalysts or halogen species.

MOFs are also promising catalyst candidates for use in the cycloaddition reaction. In one of our works, we designed and synthesized a novel organic ligand 5-(2,6-bis(4-carboxyphenyl)-pyridin-4-yl)isophthalic acid (H₄BCP) with low symmetry and applied it to MOF synthesis with Cu salt. As a result, an MOF with uniquely nanosized [Cu₃₀] cages composed of 15Cu₂(O₂CR)₄ paddlewheel units was obtained (Figure 3D and Figure 4).¹⁸ When utilized in the cycloaddition of CO₂ with aziridines in combination with tetrabutylammonium bromide (TBAB), this MOF material can afford up to 99% yield of the oxazolidinones in a solvent-free system with regioselectivity exceeding 90:10. Furthermore, the framework of this MOF material is found to be satisfyingly stable, thus this heterogeneous catalyst can be reused at least 10 times without any obvious activity loss. It is proposed that the in situ-formed Lewis acidic unsaturated coordinative Cu²⁺ sites via H₂O leaving in the Cu₂(O₂CR)₄ paddlewheel units serve as catalytic active sites to activate aziridines.

2.1.2. Carboxylation with CO₂. The carboxylation of an acidic C–H bond such as a terminal alkyne is also a typical

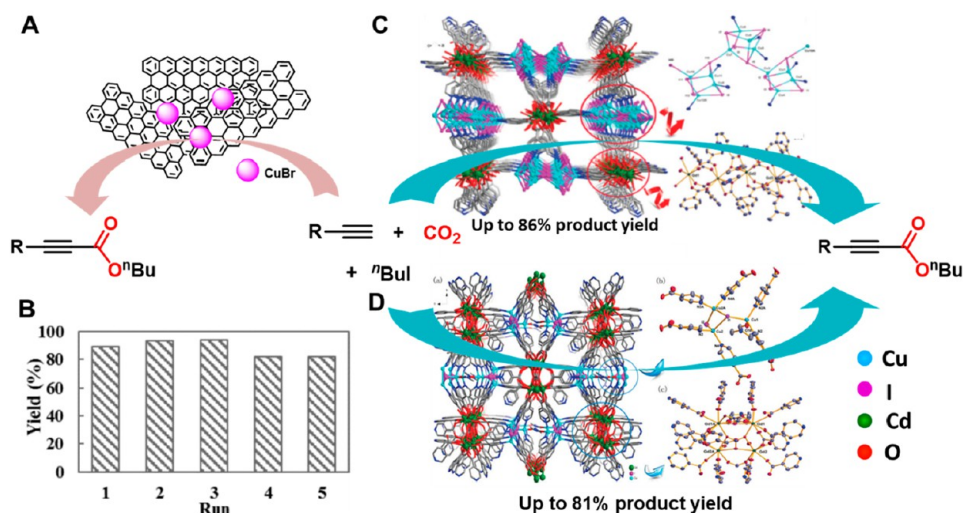


Figure 5. Nanomaterials used in terminal alkyne carboxylation. (A) Activated carbon-supported CuBr. (B) Recovery and reuse of the CuBr@C catalyst. (C) Three-dimensional structure of the heterometallic MOF with the $[\text{Cu}_{12}\text{I}_{12}]$ cluster and $[\text{Gd}_3(\text{IN})_9(\text{DMF})_4]$ cluster. (D) Three-dimensional structure of the heterometallic MOF-containing $[\text{Gd}_4(\text{CO}_3)_2(\text{IN})_9]$ cluster, $[\text{Cu}_3\text{I}_2]$ cluster, and $[\text{CuI}]$ units. Reproduced with permission from ref 21, copyright (2015) American Chemical Society.

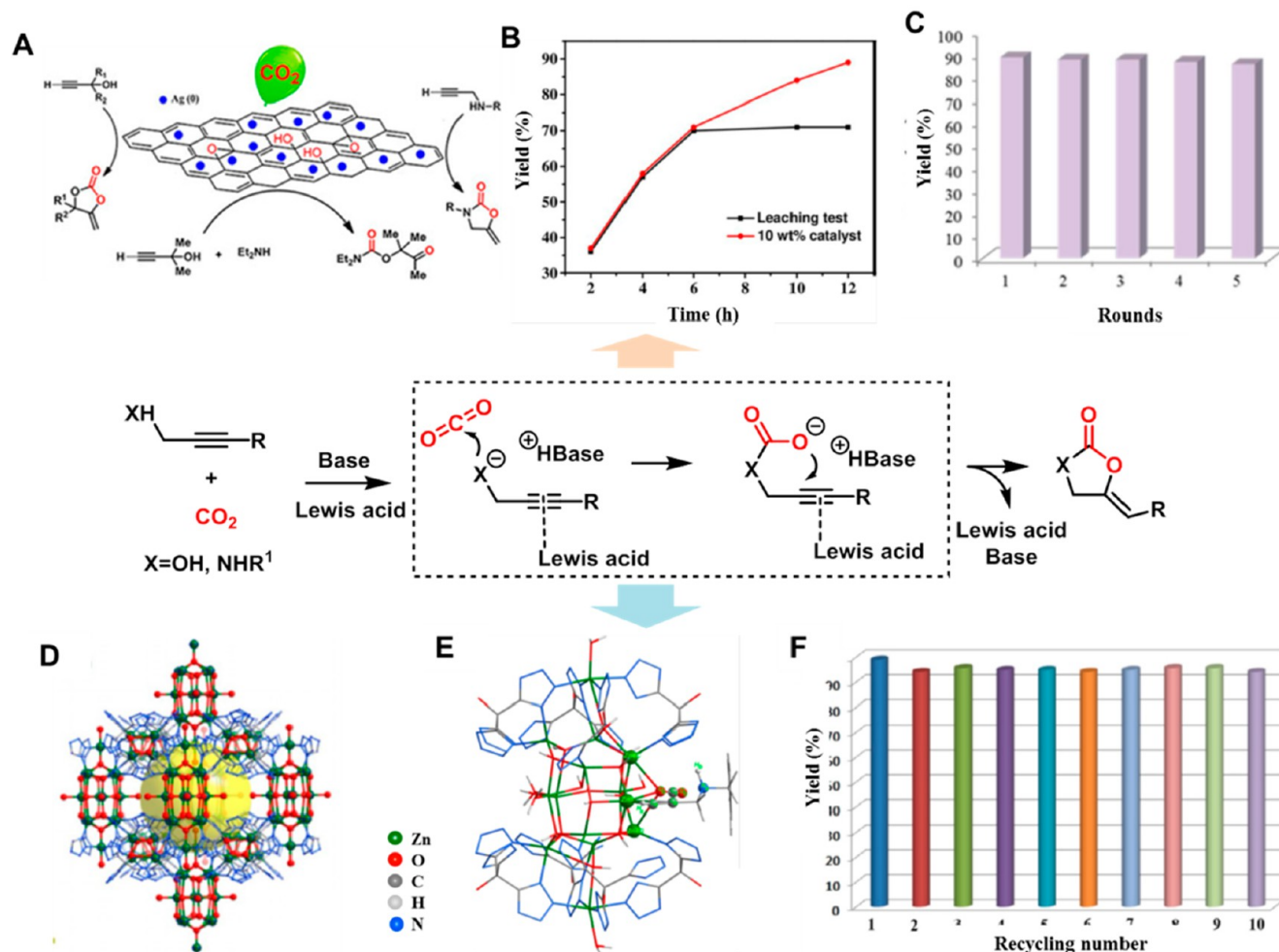


Figure 6. Nanomaterials employed in carboxylative cyclization with CO_2 . (A) Nano-Ag particles supported on reduced graphene oxide. (B) Leaching test of Ag@rGO. (C) Reusability of Ag@rGO. (D) Ball-and-stick view of the $[\text{Zn}_{116}]$ cage. (E) Geometric structure of the transit state in the reaction. (F) Reusability of Zn-based MOF. Reproduced with permission from ref 26, copyright (2020) Wiley-VCH and ref 3, copyright (2020) Wiley-VCH.

reaction of CO₂, in which the substrate activation is crucial. In this kind of transformation, we found that the combination of a Cu- or Ag-based catalyst and base can act as an efficient catalyst in ethylene carbonate solvent, in which base is used to abstract the proton and the metal catalyst stabilizes the formed nucleophile via forming a C–M bond.^{19,20} To develop the heterogeneous catalytic protocol, we immobilized CuBr on the activated carbon to increase the catalytic site number and achieve catalyst recycling.²¹ With Cs₂CO₃ as the cocatalyst, up to 90% yield of alkynyl carboxylic acids can be obtained under 1 bar of CO₂ (Figure 5A). It should be mentioned that the supported catalyst can be reused and the recovered catalyst presents a higher yield of product in the second and third runs attributed to the partial reduction of Cu(II) species (Figure 5B).

MOF is also an attractive catalyst for the carboxylation of a terminal alkyne with CO₂. Considering the solvent and thermal stabilities of heterometallic MOFs and the effectiveness of CuI for the carboxylation reaction of terminal alkyne, we further prepared the [Cu_xI_y] clusters containing heterometallic MOFs by altering the Gd precursors (Gd(NO₃)₃·6H₂O and Gd₂O₃) and their molar ratios to CuI using isonicotinic acid as an organic ligand. Consequently, two novel heterometallic 3D MOFs consisting of both a Gd cluster and [Cu₁₂I₁₂] and [Cu₃I₂] clusters, respectively, were obtained (Figure 5C and 5D).²² It is revealed that the Cu(I) atoms in the above Cu clusters are four-coordinate, and the coordination unsaturated sites render the activation of alkynes, thus facilitating the carboxylation of terminal alkyne and affording a moderate yield of carboxylation products under mild conditions.

2.1.3. Carboxylative Cyclization with CO₂. Carboxylative cyclization with CO₂ represents another important CO₂ transformation protocol in which the substrates containing a nucleophilic site such as amine, hydroxyl, or acidic C–H and an electrophilic site such as the C–C double or triple bond are usually involved. To catalyze this transformation, a Lewis acid and base are necessary to activate the unsaturated bond and nucleophilic site, respectively. Our previous studies show that the Lewis acidic Ag or Zn salts are effective in activating the carbon–carbon triple bonds owing to their π -coordination with the alkyne, thus exhibiting superior catalytic activity.^{23–25}

Inspired by the effectiveness of the Ag-based catalyst, we further prepared the reduced graphene oxide-supported Ag nanoparticles and explored their activity in the carboxylative cyclization of propargyl amine or propargyl alcohol with CO₂ (Figure 6A).²⁶ With a catalytic amount of ionic liquid [N₄₄₄₄][Triz] as a base, the cyclic carbonate or oxazolidinone products can be accessed in 82–99% yield under 1 bar of CO₂. Moreover, these supported Ag nanoparticles can also be used in the cascade reaction of the carboxylative cyclization of propargyl alcohol and subsequent nucleophilic ring-opening reaction with amine, generating β -oxopropylcarbamate in 86% yield. The leaching test excluded the possibility of catalyst dissolution and showed the heterogeneous catalysis features. Furthermore, the heterogeneous catalyst can be reused without obvious activity decay (Figure 6B and 6C). It is deduced that the reduced graphene oxide can not only inhibit the agglomeration of the nanoparticles but also alter the electronic structure of the Ag nanoparticles and thus increase their Lewis acidity.

The excellent performance of the Zn-based complex in catalyzing the carboxylative cyclization with CO₂ encourages us to pursue a Zn-based MOF as a catalyst. As a result, a zinc-tetrazole 3D MOF with the giant and lantern-like [Zn₁₁₆] nanocages was synthesized using Zn(NO₃)₂·6H₂O and the in

situ-generated ligand tri(1H-tetrazol-5-yl)methanol (Figure 6D).³ This MOF features thermostability, solvent stability, and pH stability as well as Lewis acidity. Notably, the porous framework of this MOF possesses a CO₂ uptake of 27.00 cm³ g^{−1} at ambient pressure at 25 °C, which makes it especially suitable for CO₂ conversion. The calculation results show that this material can activate propargylamine and CO₂ concurrently (Figure 6E). Consequently, it presents high catalytic activity for the carboxylative cyclization of propargylic amines and CO₂ with TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) as the cocatalyst, giving up to 99% yield of oxazolidinone products under mild conditions with excellent reusability (Figure 6F).

2.2. Reductive Transformation of CO₂

Reductive CO₂ transformation implies a decrease in the CO₂ oxidation state and has gained sustained attention due to its ability to access fuels and various important chemicals, among which the reductive functionalization of CO₂, i.e., CO₂ reduction accompanied by new C–X bond formation, breaks through the limitation of the CO₂ valence state; therefore, CO₂ can be used as a methylation, methylenation, or formylation reagent for a suitable nucleophile.^{27,28}

Our group concentrates on catalyst development and product regulation for the reductive functionalization of CO₂ with amine using hydrosilane as a reductant. It is found that the slightly polar Si–H bond in hydrosilanes can be activated by silicophilic species such as the carboxylate anion by forming a hypervalent silicon intermediate.^{29,30} In particular, we found that the organocatalyst, i.e., betaine with a carboxylate anion, can achieve a hierarchical reduction of CO₂ with amines, affording formamides, aminals, and methylamines, by adjusting the amount of CO₂, pressure, and reaction temperature.⁴

Inspired by this finding, N-doped porous carbon containing pyridinic N and pyrrolic N is applied to the reductive functionalization of CO₂ with amine, considering that the silicophilic carbamate anion can be formed by capturing CO₂ (Figure 7A). For example, Cao et al. applied N-doped porous carbon from the pyrolysis of chitosan and NaNH₂ to the reductive functionalization of CO₂ with amines, affording formamide at moderate to excellent yield with PhSiH₃ as a

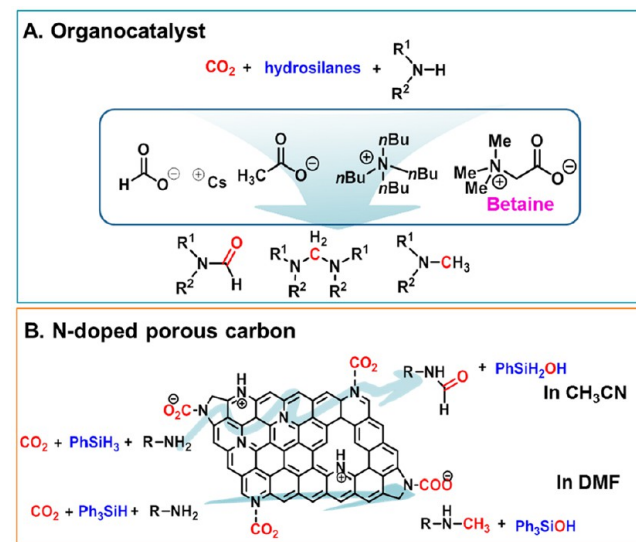
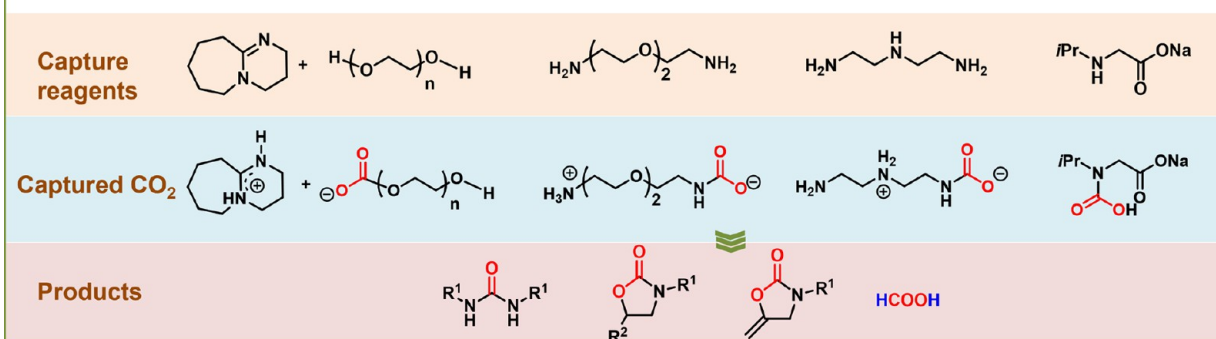
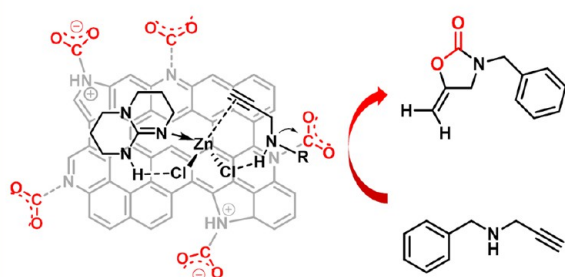


Figure 7. Reductive CO₂ functionalization with carbon-based nano-materials.

A. CO₂ capture and *in-situ* conversion using molecular capture reagents



B. N-doped carbon as CO₂ adsorbent and catalyst support



C. Porous MOF-poly(ionic liquid) composite material

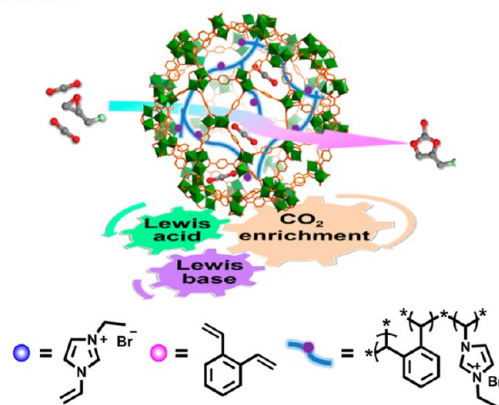


Figure 8. Application of nanomaterials to CO₂ capture and in situ transformation. Reproduced with permission from ref 37, copyright (2018) American Chemical Society.

reductant and CH₃CN as a solvent.³¹ In another example (Figure 7B), N-doped porous carbon derived from a mixture of urea and tannic acid was prepared and utilized as a catalyst for the reductive functionalization of CO₂ with amines by Liu et al., and methylamines are produced with Ph₃SiH as the reductant and DMF as the solvent.³²

2.3. Novel CO₂ Conversion Strategies

CO₂ capture and in situ catalysis, i.e., using the captured CO₂ as the surrogate of gaseous CO₂ to participate in the subsequent catalysis, are considered to function as a novel CO₂ conversion strategy to avoid the energy-intensive CO₂ desorption step for absorbent recovery; therefore, this is becoming a vibrant research area. More importantly, adsorbed CO₂ is usually present as a bent structure instead of its original linear structure, which can be considered to be the activated form and presumably facilitates the subsequent transformation smoothly under mild conditions even at atmospheric pressure. We have proposed such an in situ CO₂ conversion protocol, i.e., the integration of absorption with subsequent conversion by developing CO₂ capture reagents as illustrated in Figure 8A.^{1,33–35} Benefitting from the tailored active sites and heterogeneous characteristics, nanomaterials are promising candidates facilitating CO₂ capture and in situ transformation.

Biomass-based N-rich porous carbon provides a platform to perform CO₂ capture and in situ conversion due to its ability to absorb and activate CO₂ by N-containing groups and to immobilize molecular catalysts via a van der Waals interaction.

Based on this, our group prepared N-rich porous carbon by pyrolysis and the activation of bean dregs. This material can be used to support Zn-based catalysts and capture CO₂, which then serve as the CO₂ source and catalyst to promote the carboxylative cyclization of propargylamine facilitated by organic base TBD, giving an excellent yield of oxazolidinone product (Figure 8B).³⁶ Remarkably, the N-rich porous carbon supported with the Zn catalyst can be recovered and reused without obvious activity decay.

In particular, MOFs are widely used in CO₂ capture and in situ conversion. Recently, Jiang et al. prepared the MOF-poly(ionic liquid) composite material by incorporating imidazolium-based poly(ionic liquid)s (PILs) into the pores of MIL-101 via in situ polymerization of encapsulated monomers (Figure 8C).³⁷ The resultant composite material possesses Lewis acid and base sites as well as good CO₂ capture capability, which can work synergistically to facilitate the cycloaddition of diluted CO₂ with epoxides, forming cyclic carbonates in excellent yield.

3. PHOTO-/ELECTROCATALYTIC CO₂ REDUCTIVE CONVERSION

The photo-/electrocatalytic CO₂ reductive conversion utilizes the electrons from photoexcitation or an external electric field to realize CO₂ reduction, and this field has become increasingly popular due to its ability to use renewable solar energy under mild conditions. In PCO₂RR and ECO₂RR, CO₂ can be reduced to energetic small molecules such as CO, CH₃OH, CH₄, C₂H₄, CH₃CH₂OH, etc. (Figure 9A). Then the CO₂ reductive

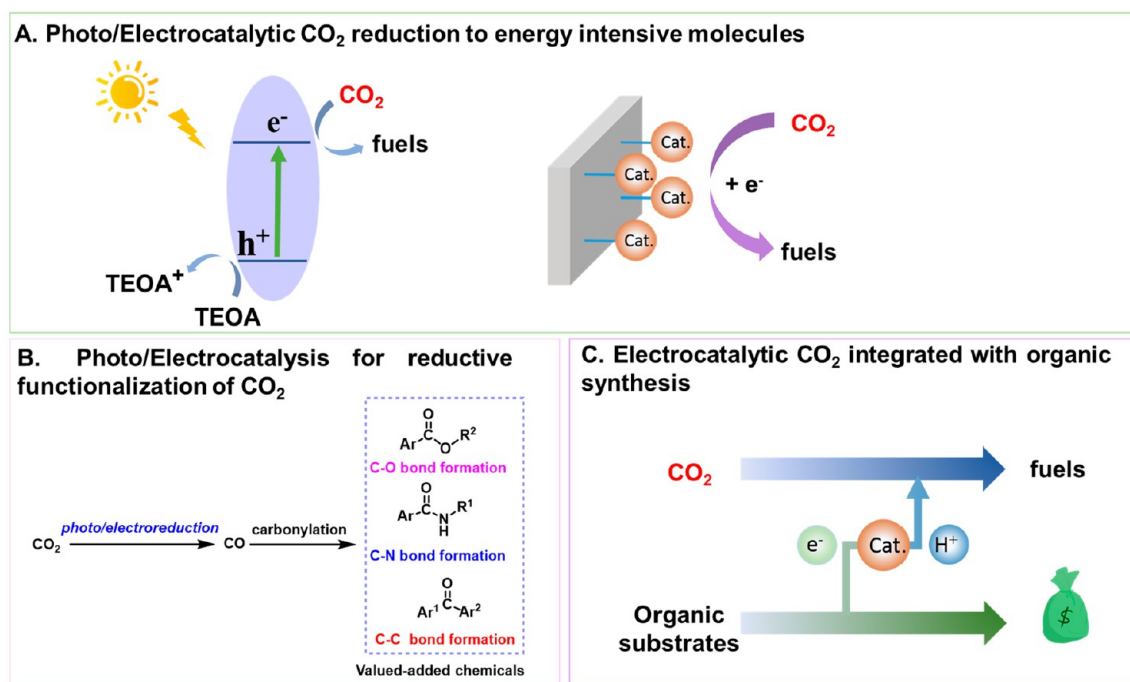


Figure 9. Photo-/electrocatalytic CO₂ reductive conversion strategies.

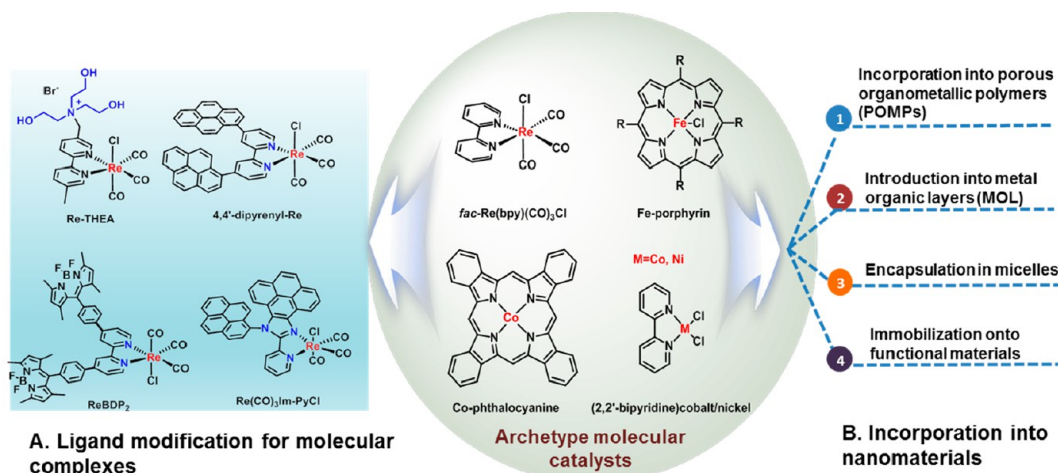


Figure 10. Strategies of developing efficient catalysts for photo-/electrocatalytic CO₂ reductive conversion.

product, e.g., CO or formate, can be further transformed to valuable chemicals in situ or ex situ, and this strategy is called photo-/electrocatalytic reductive functionalization of CO₂ (Figure 9B). Recently, the coupling of PCO₂RR/ECO₂RR with organic compound oxidation has attracted much concern because of its ability to avoid expensive sacrificial agents necessary in photocatalytic CO₂ reduction and replace the sluggish O₂ evolution reaction in electrocatalytic CO₂ reduction (Figure 9C). Moreover, valuable oxidative products can be obtained concomitantly with CO₂ reduction by deliberately selecting the substrate.

In the aforementioned photo-/electrocatalytic CO₂ reduction strategies, molecular complexes as listed in Figure 10 have attracted much concern due to their well-defined structure and explicable reaction mechanism.^{38–40} However, these molecular complexes encounter limited energy efficiency and stability issues.

3.1. Photo-/Electrocatalytic CO₂ Reduction to Energy-Intensive Molecules

Based on the effectiveness of complex *fac*-Re(bpy)(CO)₃Cl on the photocatalytic reduction of CO₂ to CO, our group put effort into modifying its ligand skeleton or attaching specific functional groups to its second shell. As a result, the visible light absorption ability, electron transfer efficiency, and excited (triplet) state lifetime are enhanced, improving the performance of the photocatalyst (Figure 10A).^{41–44}

The positive effect of the structure modification to *fac*-Re(bpy)(CO)₃Cl motivates us to incorporate this catalytically active unit into the nanomaterials and regulate the chemical environment near the catalytic centers. According to the strategies depicted in Figure 10B, we prepared two kinds of porous organometallic polymers (POMPs) containing a Re-bipyridine complex. One is obtained by copolymerizing the Re-bipyridine complex with the ionic liquid (POMP-IL) (Figure 11A–11C), in which the distribution of the Re-bipyridine

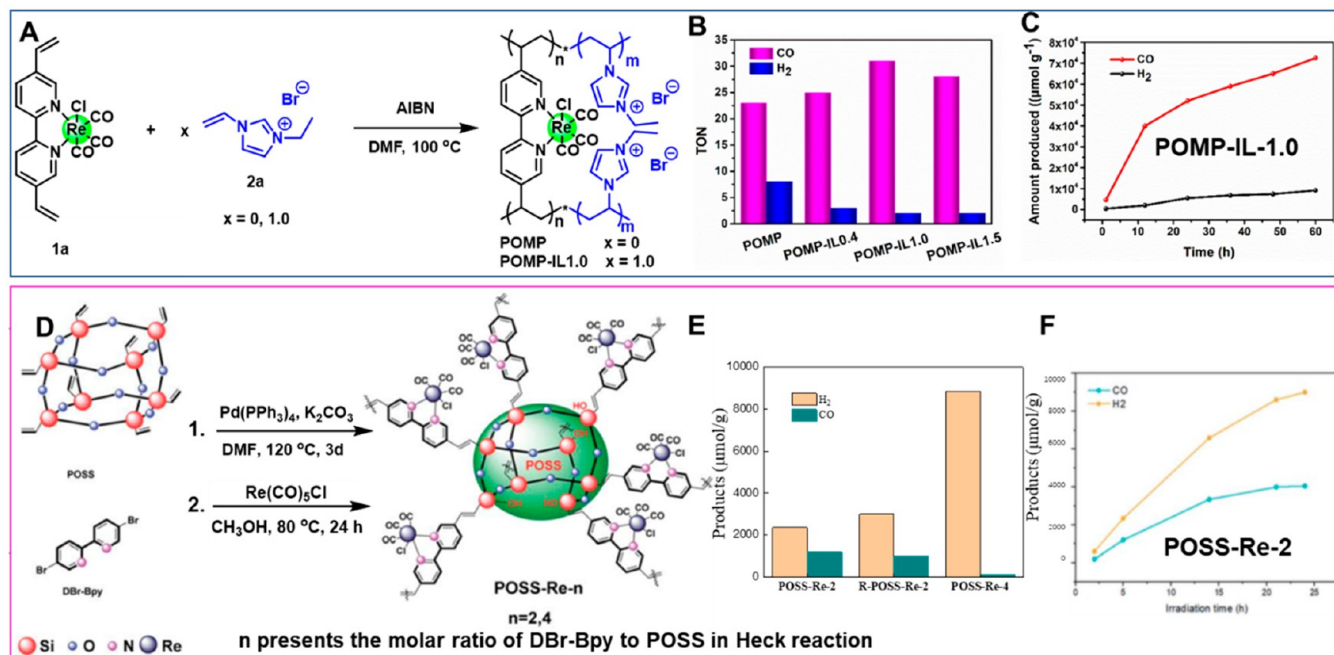


Figure 11. (A) Synthesis route of POMP-IL. (B) Effect of the IL amount on catalytic activity. (C) Time curve of CO/H₂ formation over POMP-IL.1.0. (D) Synthetic route of POMP-Re. (E) Catalytic performances over POSS-Re-n. (F) Time curve of the formation of CO/H₂ over POSS-Re-2.

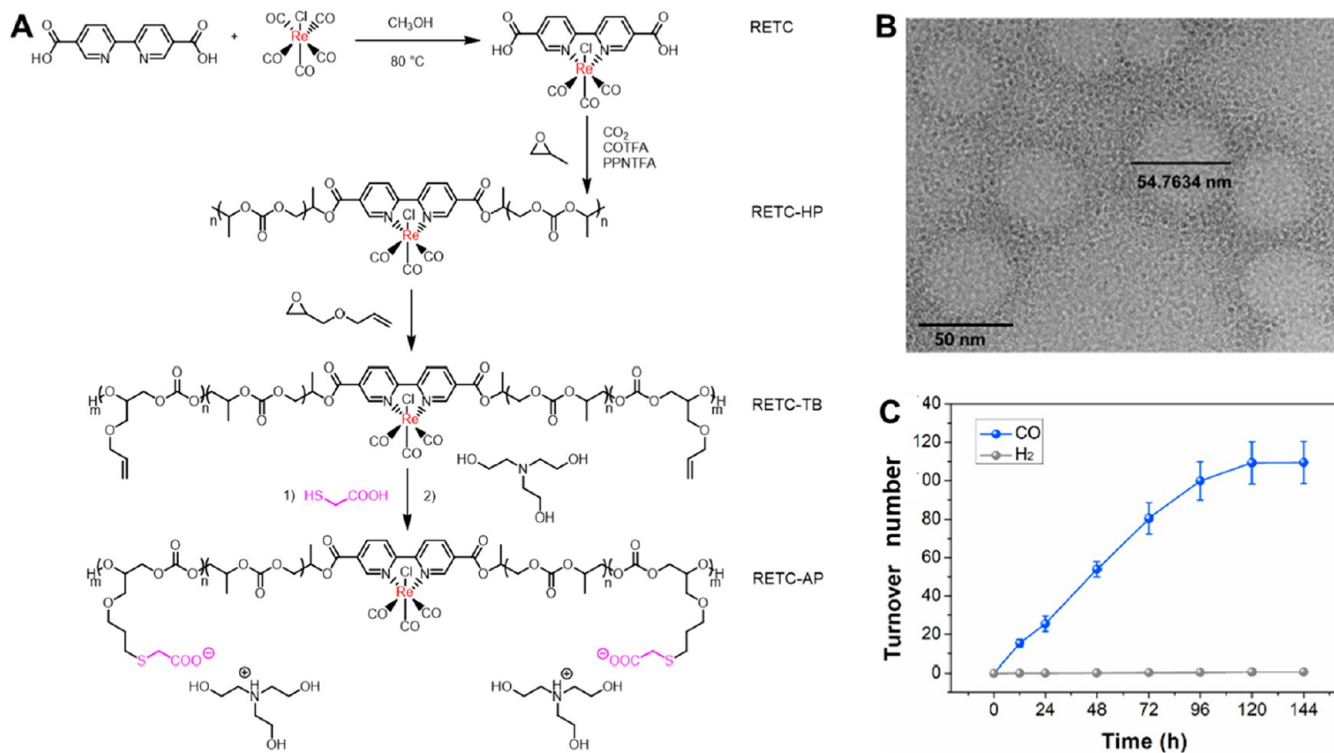


Figure 12. (A) Synthesis route to the Re(dcbpy)-based amphiphilic micellar catalysts. (B) TEM images of RETC-AP in aqueous solution. (C) PCO₂RR catalyzed by RETC-AP over time under xenon lamp irradiation in aqueous solution. Reproduced with permission from ref 4, copyright (2022) Wiley-VCH.

complex is regulated by altering the ratio of the two polymer monomers.⁴⁵ The other is synthesized via the Heck reaction between different molar ratios of 5,5'-dibromo-2,2'-bipyridine (DBr-Bpy) and polyhedral octavinylsilsesquioxane (POSS) units and postmetalation with the Re complex (Figure 11D–11F).⁴⁶ Albeit with the same catalytic centers, these two

kinds of materials present different performance when applied to the PCO₂RR, showing the importance of the local chemical environment. For POMP-IL, the catalytic activity and selectivity to CO increases with the content of IL, and optimal values are obtained when equimolar Re-bipyridine and IL precursors are used in POMP-IL preparation. For POMP-ILs containing the Re-

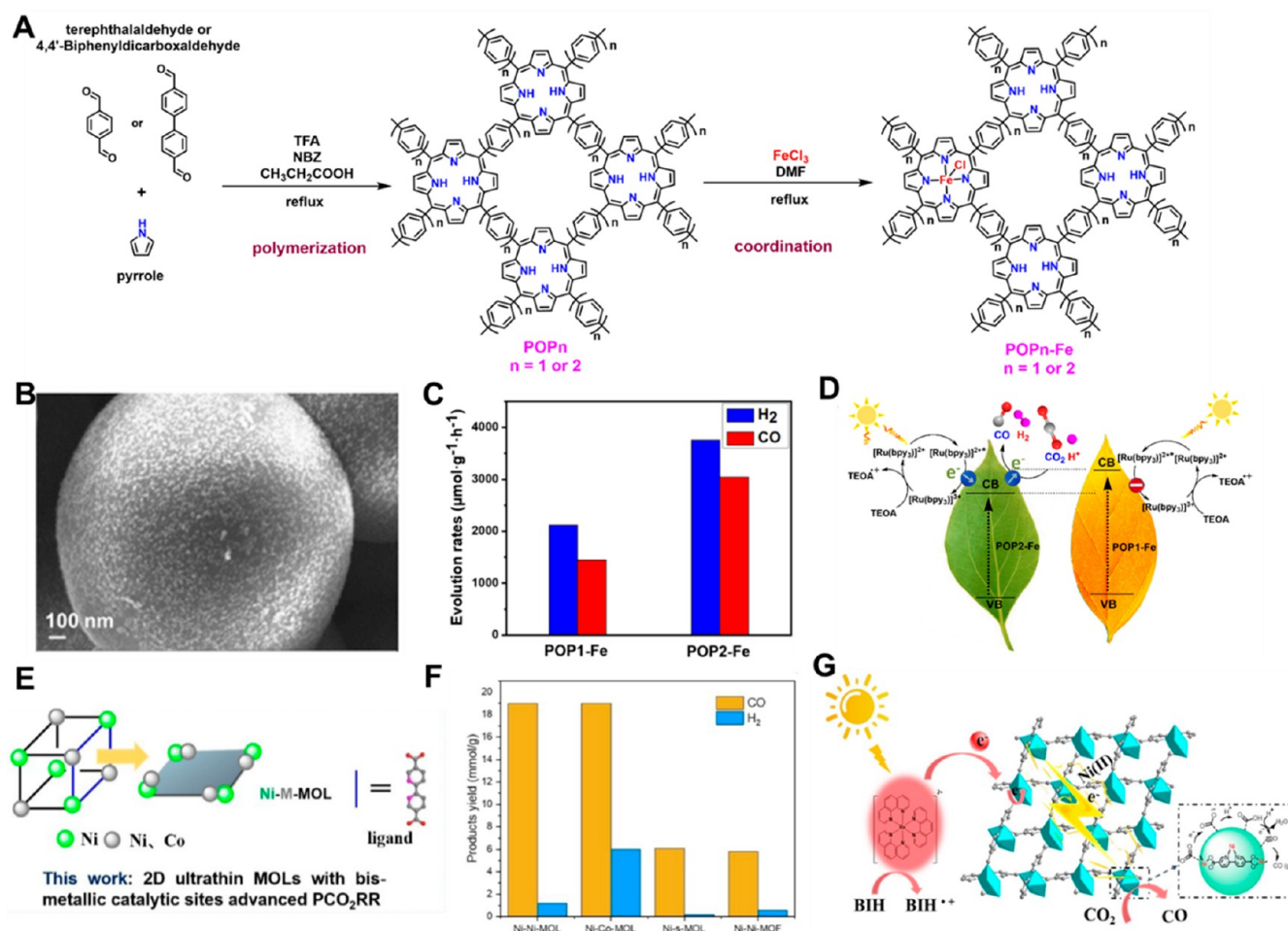


Figure 13. (A) Synthesis of Fe-porphyrin-based POP (TFA, trifluoroacetic acid; NBZ, nitrobenzene). (B) SEM images of POP2-Fe. (C) Photocatalytic syngas production performance of POPn-Fe. (D) Proposed mechanism for the photocatalytic CO₂RR. (E) Schematic illustration of 2D Ni-Ni-MOL formation. (F) Catalytic performance over 2D Ni-Ni-MOL. (G) Proposed photocatalytic mechanism for Ni-Ni-MOL. Reproduced with permission from ref 50, copyright (2021) American Chemical Society and ref 51, copyright (2022) Wiley-VCH.

bipyridine complex and POSS units, syngas is obtained, and adjusting the molar ratio of DBr-Bpy to POSS or reducing the C–C double bonds between the Re-bipyridine and POSS units (R-POSS-Re-2) can alter the composition of synthetic gas. Besides, these two kinds of materials can work robustly even after a long time of irradiation.

Although proven to be effective catalysts for PCO₂RR, the *fac*-Re(bpy)(CO)₃Cl complex is often used in anhydrous organic solvents because of the challenges associated with poor catalyst solubility, competing hydrogen evolution reactions, and the low solubility of CO₂ in water. To address the above issues and at last realize the artificial photosynthesis in an aqueous solution, we synthesized a triblock amphiphilic polymer containing the Re-bipyridine complex in its backbone under the collaboration with D. J. Darensbourg's group (Figure 12A). When the molar ratio of propylene oxide (PO) and allyl glycidyl ether (AGE) is 1:1, the resulting amphiphilic polymer can form stable and uniform spherical micelles in deionized water containing triethanolamine via self-assembly, where the Re-bipyridine unit is located in the hydrophobic portion of the nanostructured micelle (Figure 12B).⁴ In PCO₂RR, the hydrophilic outer layer can promote the stability and uniform dispersion of the micelles, while the hydrophobic long polycarbonate chains can not only suppress the dimerization deactivation of the Re species but also provide a

high local CO₂ concentration around the catalytic center. Furthermore, the insulation of the Re complex from water can inhibit the hydrogen evolution reaction. Consequently, the micellar catalysts showed higher efficiency (TON_{CO} up to 110), durability, and CO selectivity (99%) compared to the Re(dcbpy)(CO)₃Cl molecular catalyst, without the need for an additional photosensitizer (Figure 12C).

Developing efficient catalysts based on earth-abundant metals^{47–49} for PCO₂RR is also attractive and challenging, among which Fe-porphyrin complexes are proven to be appealing catalysts for this purpose. To improve the stability and catalytic activity of Fe-porphyrin complexes, we synthesized two Fe-porphyrin-based POP materials as depicted in Figure 13A.⁵⁰ The as-synthesized POP-Fe nanomaterials have spherical structures with ferric and chlorine atoms uniformly distributed on the surface (Figure 13B). In PCO₂RR, these two materials can generate CO and H₂ simultaneously in DMF solvent with Ru(bpy)₃Cl₂ as a photosensitizer, and the linkers between the catalytic centers can particularly affect the CO/H₂ selectivity (Figure 13C). In comparison with POP1-Fe, POP2-Fe shows relatively high activity in the production of both CO and H₂, probably due to its suitable redox potential to accept electrons from the excited photosensitizer and then transfer them to CO₂ as presented in Figure 13D.

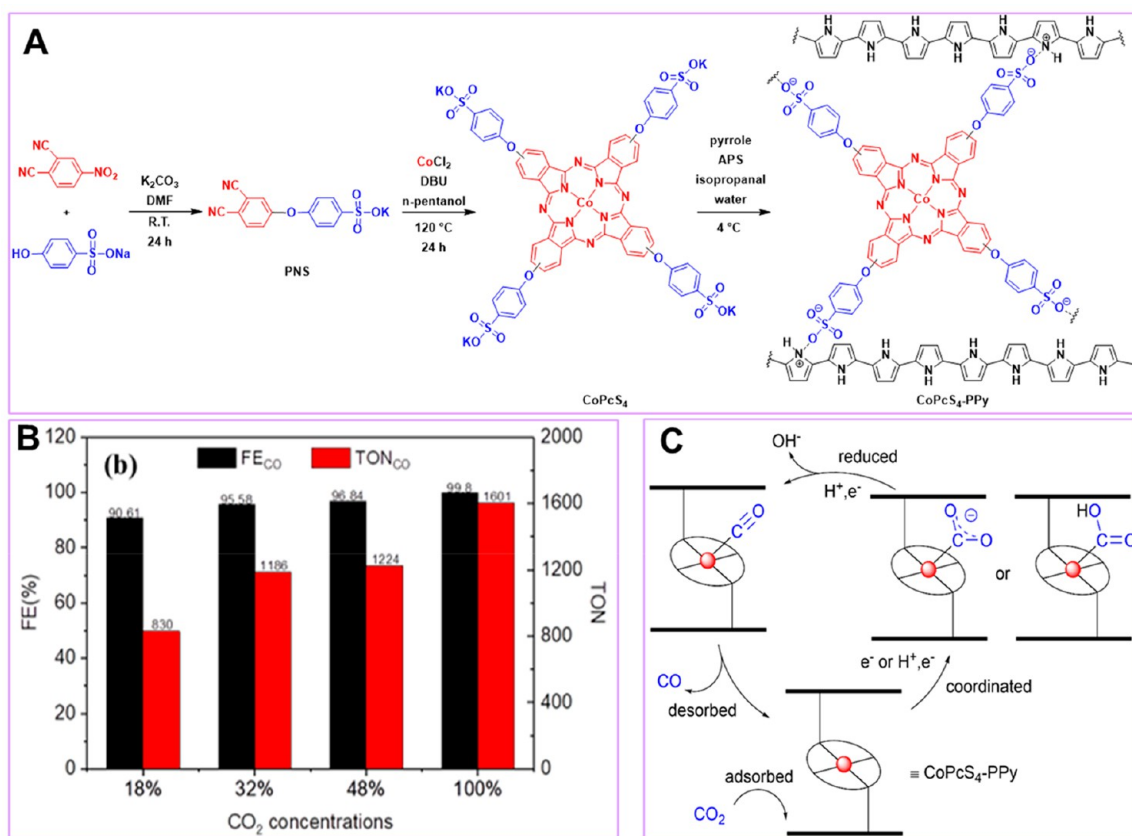


Figure 14. (A) Synthesis of CoPcS₄-PPy. (B) Faradaic efficiency and TON_{CO} at -0.9 V for 1 h in 0.1 M KHCO₃ aqueous electrolyte. (C) Proposed mechanism for ECO₂RR to CO catalyzed by CoPcS₄-PPy-CC. Reproduced with permission from ref 52, copyright (2022) Wiley-VCH.

In another work, the 2D ultrathin metal–organic layers (MOLs) with two different kinds of metal-based catalytic centers, i.e., Ni–Ni–MOL and Ni–Co–MOL, are prepared from bidentate ligand 2,2′-bipyridine-5,5′-dicarboxylate and Ni(II) or Ni(II) and Co(II) (Figure 13E).⁵¹ For comparison, Ni–Ni–MOF and Ni–s–MOL are also prepared with 2,2′-bipyridine-5,5′-dicarboxylate and naphthalene-2,6-dicarboxylic acid as ligands, respectively. It is detected that Ni–Ni–MOL and Ni–Co–MOL possess higher metal content than the bulky Ni–Ni–MOF, and, as expected, they present high efficiency in PCO₂RR with Ru(phen)₃(PF₆)₂ (phen = 1,10-phenanthroline) as the photosensitizer in aqueous solution, where Ni–Ni–MOL shows higher selectivity to CO (Figure 13F). The mechanism investigation reveals that the ultrathin layer structure contributes to the enhanced electron transfer efficiency, and the different nickel-based catalytic centers (Ni–O metal node and the Ni–bipyridine unit) at a reasonable distance can work synergistically to give high performance in PCO₂RR (Figure 13G).

The development of a multifunctional electrocatalyst for ECO₂RR is becoming a hotly pursued research area. In this regard, the sulfonylphenoxy-decorated cobalt phthalocyanine (CoPcS₄) is synthesized and then immobilized onto the carbon cloth electrode surface via in situ polymerization of pyrrole, generating sulfonylphenoxy-decorated CoPc cross-linked polypyrrole on the electrode surface (CoPcS₄-PPy-CC) (Figure 14A).⁵² The strong electronic interactions between polypyrrole and sulfonylphenoxy-decorated CoPc can prevent the aggregation of CoPc. Moreover, by utilizing the impressive electronic transfer efficiency and CO₂ capture and activation capabilities of polypyrrole, this catalyst has demonstrated a faradaic efficiency

(FE) for CO of over 90%, even with diluted CO₂. (Figure 14B). By contrast, the homogeneous CoPcS₄ can promote H₂ evolution only under the same conditions, demonstrating the crucial role of polypyrrole in ECO₂RR. It is assumed that the polypyrrole can absorb CO₂ and facilitate subsequent CO₂ coordination with reduced Co(I), and then electron transfer and proton coupling occur to form CO, followed by CO desorption and catalytic species regeneration (Figure 14C).

3.2. Photo-/Electrocatalysis for the Reductive Functionalization of CO₂

With our ongoing exploration of the photo/electrocatalytic CO₂ reduction to CO and inspired by the success of CO₂ electroreduction coupled to the carbonylation reaction,^{53,54} we proposed the strategy of the photoreductive functionalization of CO₂ based on the integration of CO₂ photoreduction and the cascade transformation of such reductive products. Accordingly, we developed a protocol composed of photocatalytic CO₂ reduction to CO and the Pd-catalyzed carbonylation reaction, in which a pipeline was used to transport the in situ-generated CO from the CO₂ reduction reactor to the carbonylation reactor. As a result, biaryl ketones, amides, esters, and even pharmaceuticals such as fenofibrate are produced in high yields (Figure 15A).⁵⁵ This protocol paves an alternative avenue for CO₂ utilization by harnessing solar energy.

Recently, Lu's group realized the visible-light-driven one-pot carbonylation reaction under 1 bar of CO₂ at room temperature using an MOF material containing a Co single site, an ultrafine CuPd nanocluster, and porphyrin photosensitizers.⁵⁶ This composite material can be easily prepared by the in situ reduction of Cu(NO₃)₂·3H₂O and K₂PdCl₄ in the presence of

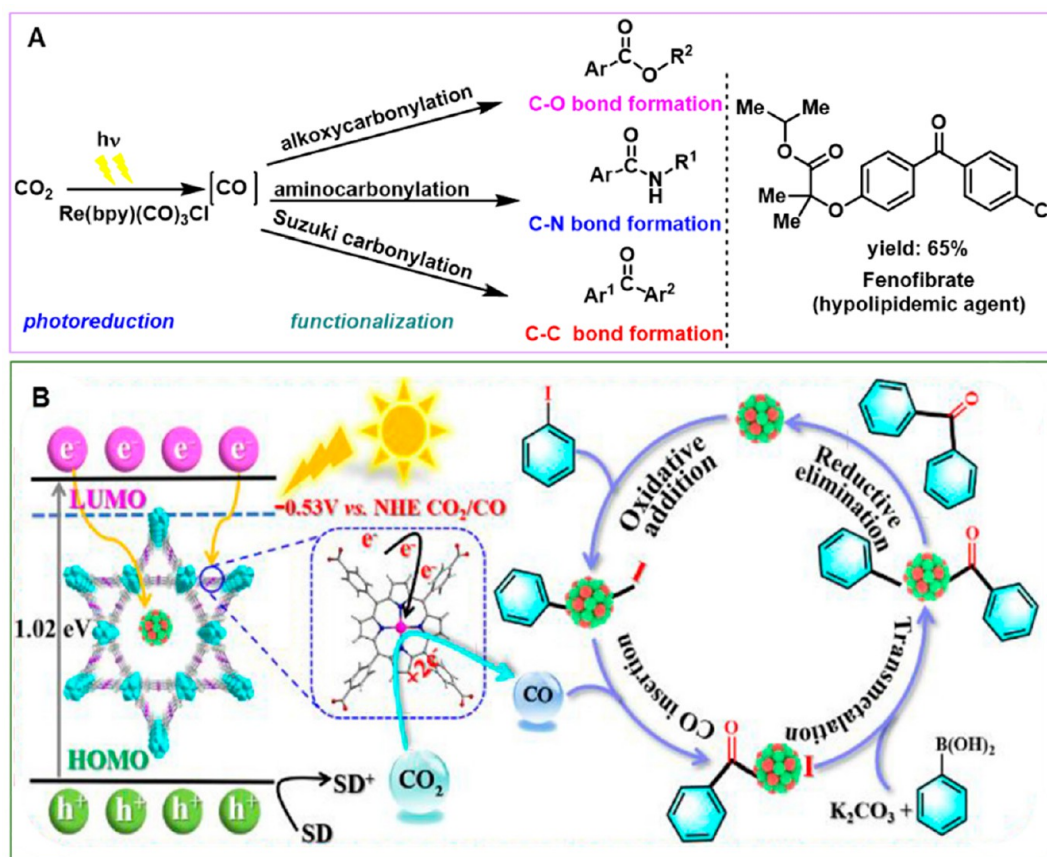


Figure 15. (A) Photoreductive functionalization of CO_2 was performed in two reactors. (B) Solar-driven carbonylation with CO_2 promoted by a MOF-based composite catalyst. Reproduced with permission from ref 56, copyright (2021) American Chemical Society.

MOF, and the MOF is made from ZrCl_4 and 5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin cobalt (CoTCPP). In the reaction, the MOF structure can harvest light energy, and the excited electrons are then transferred to Co sites for CO_2 reduction. After that, the ultrafine CuPd nanocluster encapsulated in the MOF promoted the Suzuki/Sonogashira reactions with in situ-generated CO, giving the target products in over 90% yield and 97% selectivity (Figure 15B).

3.3. Electrocatalytic CO_2 Valorization Integrated with Organic Synthesis

Conventionally, the oxygen evolution reaction (OER) occurs on the anode in ECO_2RR . Recently, replacing OER with organic compound oxidation in ECO_2RR has become an attractive field because this strategy has great potential to lower electricity consumption and get valuable oxidation products.^{57,58}

Guided by this, we paired ECO_2RR and 5-hydroxymethylfurfural (HMF) oxidation using the noncovalently immobilized 4-(*tert*-butyl)-phenoxy cobalt phthalocyanine (TBP-CoPc) and pyrene-tethered 2,2,6,6-tetramethylpiperidin-1-oxyl (Py-TEMPO) on carbon nanotubes (CNTs) as electrocatalysts, respectively (Figure 16A).^{59,60} These two supported catalysts can be used in the electrolytic cell with trielectrode or dielectrode configuration (Figure 16B and 16C). Even with the cell voltage input from the solar panel, 95.4% selectivity and a turnover number of 52 172 for CO and a 69.9% yield of 2,5-furandicarboxylic acid (FDCA) can still be achieved. In order to regulate the reduction product of ECO_2RR , we fabricated a bismuth-based MOF cathode through the solvothermal method

using 2,5-furandicarboxylic acid and Bi^{3+} and then loaded it on carbon paper (Bi-FDCA MOF) as the cathode (Figure 16D–16F). When paired with 5-hydroxymethylfurfural (HMF) oxidation at the $\text{Ni}(\text{OH})_2/\text{carbon paper}$ -based anode in a trielectrode electrolytic cell, 95.6% FE_{HCOOH} (Faraday efficiency) is achieved concomitant with 75.0% FE for FDCA (Figure 16G). It is revealed that the bismuth-based MOF can be in situ transformed to bismuth carbon oxide during electrolysis (Figure 16H,16I), which acts as an active catalyst for HCOOH generation.

4. CONCLUSIONS AND PERSPECTIVE

By far, thermocatalysis, photocatalysis, and electrocatalysis are considered to be the three main strategies for performing CO_2 valorization. As listed in Table 1, several thermocatalytic CO_2 conversions have been industrialized, while the photo- and electrocatalysis are still in the R&D stage. To improve the technical economy, developing low-cost, highly efficient, and robust catalysts is crucial.

In this Account, we summarize our work on CO_2 conversion strategies and corresponding catalyst development in the past decade. In the early stage of our research, we focused on exploring novel CO_2 conversion strategies and gaining insight into the activation and transformation mechanism of CO_2 . As a consequence, CO_2 capture and in situ transformation, visible light-driven photoreductive functionalization, and renewable energy-facilitated CO_2 conversion were proposed, and highly efficient molecular catalysts were developed accordingly.

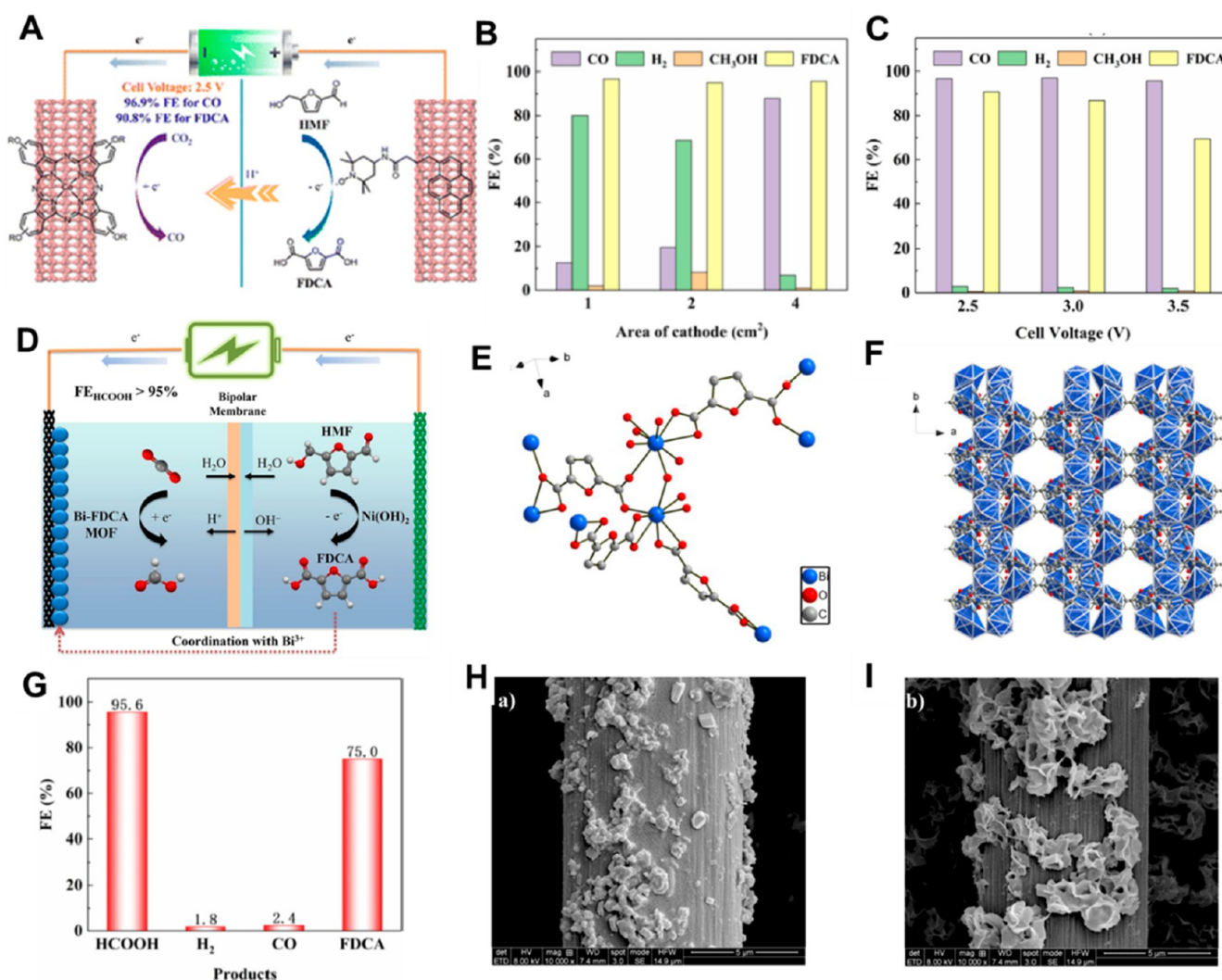


Figure 16. (A) Paired electrolysis of CO₂ and HMF with the immobilized TBP-CoPc cathode and Py-TEMPO anode. (B) Product distribution in the trielectrode electrolytic cell when varying cathode areas. (C) Product distribution at different cell voltages in the dielectrode electrolytic cell. (D) Paired electrolysis of CO₂ and HMF with the Bi-FDCA MOF cathode and Ni(OH)₂ anode. (E) Coordination situation and (F) packing pattern of the Bi-FDCA MOF crystal (CCDC number: 2201237). (G) Product distribution after the electrolysis. (H) SEM images of Bi-FDCA before electrolysis and (I) after electrolysis. Reproduced with permission from ref 60, copyright (2023) Wiley-VCH.

Table 1. Comparison of Different Catalytic Methods for CO₂ Conversion

	Thermocatalysis	Photocatalysis	Electrocatalysis
Energy source	Thermal and chemical energy	Light energy	Electric energy
Development stage	Some transformations have been commercialized	Research and development level	Research and development level
Reaction scope	Nonreductive and reductive transformations	Mainly focused on reductive transformations	Mainly focused on reductive transformations
Available product	Bulk chemicals, fine chemicals, and energy-related small molecules	Energy-related small molecules	Energy-related small molecules
Scalability	Easy	Difficult	Easy
Cost efficiency	Depends on the specific reactions and catalytic systems	Relies on the low-cost and robust catalysts	Relies on the low-cost and robust catalysts and paired electrolysis strategy to improve the energy efficiency
Environmental impact	Lower than for traditional petrochemical methods	Low	Low

With the understanding of the CO₂ transformation principle and aiming at constructing multifunctional catalysts to realize directional CO₂ conversion, we set out to fabricate heterogeneous catalysts by incorporating catalytic units into nanomaterials. Initially, carbonaceous materials with intrinsic or immobilized catalytic sites and MOFs were fabricated and

applied to thermocatalytic CO₂ conversion, affording valuable chemicals such as cyclic carbonates, carboxylic acids, and oxazolidinones under mild reaction conditions with facile catalyst recovery.

Recently, nanomaterials used for the PCO₂RR and ECO₂RR have been investigated in our laboratory. And the Re-bipyridine,

Fe-porphyrin, and Co/Ni-bipyridine complexes were incorporated into the POP matrix, amphiphilic polymer, and MOL, respectively, to inhibit the aggregation of the archetypal metal complex and provide a controllable local chemical environment, and the resulting materials are proven to be efficient photocatalysts. As for ECO₂RR, the polypyrrole-supported, sulfonylphenoxy-decorated CoPc was prepared to realize the diluted CO₂ reduction. Concurrently, immobilized 4-(*tert*-butyl)-phenoxy cobalt phthalocyanine and a Bi-based MOF cathode have been synthesized to promote solar energy-driven ECO₂RR paired with HMF oxidation.

The diversity of the nanomaterials and their ability to immobilize and arrange multiple catalytic units and functional groups endow them with great potential in various CO₂ conversion strategies, particularly for multistep reactions such as CO₂ capture and in situ conversion and photoreductive functionalization with CO₂. However, the related investigations are still sporadic and more function-oriented nanomaterials are expected in the future. On the other hand, the complexity of nanomaterials poses challenges in reaction mechanism exploration and industrial application. Therefore, it is essential to employ a range of characterization techniques, including diffuse reflectance infrared Fourier transform spectroscopy and neutron diffraction, alongside computational approaches to understand the synergism of different catalytic sites in reactions and to gain a deeper understanding of the nanomaterials' structural evolution. Furthermore, the scale-up and cost-effective preparation methods for the nanomaterials are also needed for its industrial application.

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Author Contributions

CRedit: **Li-Qi Qiu** conceptualization (equal), methodology (equal), resources (equal), writing-original draft (equal), writing-review & editing (equal); **Hong-Ru Li** conceptualization (equal), methodology (equal), resources (equal), supervision (equal), writing-original draft (lead), writing-review & editing (equal); **Liang-Nian He** conceptualization (equal), funding acquisition (lead), methodology (lead), project

administration (lead), resources (equal), supervision (lead), writing-original draft (equal), writing-review & editing (lead).

Notes

The authors declare no competing financial interest.

Biographies

Li-Qi Qiu received her Ph.D. in 2022 from Nankai University, and her research focused on the solar energy utilization and photocatalytic conversion of CO₂ to value-added chemicals. Then she worked as a postdoctoral researcher at the University of Tennessee, Knoxville. Her research was mainly focused on developing novel porous ionic liquids/nanomaterials for CO₂ capture and conversion and membrane separation.

Hong-Ru Li received her Ph.D. in chemical technology and engineering from Tianjin University in 2008, working under the direction of Prof. Shu-Fen Li and focusing on the thermodynamics of CO₂. She then joined Nankai University as a lecturer in the College of Pharmacy. In 2014, she went to the University of Minnesota (Twin Cities, MN, USA) as a visiting scholar in the Department of Biomedical Engineering with Chun Wang as the host professor. When she returned to China, she joined Liang-Nian He's group at Nankai University, and her current research interests are CO₂ transformation and biomass valorization.

Liang-Nian He obtained a doctorate in chemistry from Nankai University in 1996. Currently, he is a professor of chemistry at Nankai University and a fellow of the Royal Society of Chemistry. His research interests cover green chemistry, renewable carbon energy chemistry, and CO₂ chemistry including CO₂ activation and catalytic conversion to fuels/value-added chemicals, catalysis in green solvents, biomass conversion, and green technology related to desulfurization. He's group proposed novel concepts and strategies for CO₂ chemistry, e.g., the in situ transformation of CO₂, namely, integrating CO₂ capture and subsequent conversion in a carbon-neutral cycle, and developed the reductive functionalization of CO₂ and green technology related to desulfurization as well as renewable energy-driven CO₂ valorization in a sustainable way. On the other hand, He is also dedicated to the rational design of effective materials for CO₂ capture and conversion based on mechanistic investigations. Furthermore, several CO₂ conversion technologies developed in his group are being applied to industrial applications.

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