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Nanomaterials and hybrid nanocomposites for CO_2 capture and utilization: environmental and energy sustainability

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Anthropogenic carbon dioxide (CO_2) emissions have dramatically increased since the industrial revolution, building up in the atmosphere and causing global warming. Sustainable CO_2 capture, utilization, and storage (CCUS) techniques are required, and materials and technologies for CO_2 capture, conversion, and utilization are of interest. Different CCUS methods such as adsorption, absorption, biochemical, and membrane methods are being developed. Besides, there has been a good advancement in CO_2 conversion into viable products, such as photoreduction of CO_2 using sunlight into hydrocarbon fuels, including methane and methanol, which is a promising method to use CO_2 as fuel feedstock using the advantages of solar energy. There are several methods and various materials used for CO_2 conversion. Also, efficient nanostructured catalysts are used for CO_2 photoreduction. This review discusses the sources of CO_2 emission, the strategies for minimizing CO_2 emissions, and CO_2 sequestration. In addition, the review highlights the technologies for CO_2 capture, separation, and storage. Two categories, non-conversion utilization (direct use) of CO_2 and conversion of CO_2 to chemicals and energy products, are used to classify different forms of CO_2 utilization. Direct utilization of CO_2 includes enhanced oil and gas recovery, welding, foaming, and propellants, and the use of supercritical CO_2 as a solvent. The conversion of CO_2 into chemicals and energy products *via* chemical processes and photosynthesis is a promising way to reduce CO_2 emissions and generate more economically valuable chemicals. Different catalytic systems, such as inorganics, organics, biological, and hybrid systems, are provided. Lastly, a summary and perspectives on this emerging research field are presented.

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1. Introduction

The research related to organic–inorganic hybrid nanocomposites is gaining momentum, and large amounts of data are being generated from different research groups and real fields to tailor the properties of nanomaterials towards their optimal performance. Energy production *via* fossil fuel combustion plays a critical role in carbon dioxide (CO_2) emissions. In an unprecedented way, there is a fast growth of CO_2 levels that disturb the earth's climatic conditions.[1] Therefore, controlling and balancing CO_2 emissions while meeting global energy demand is critical. CO_2 capture, utilization, and storage (CCUS) technologies are the best options for reducing global warming while addressing the energy crisis.[2] Therefore, it is essential to create renewable energy sources to reduce the effects of global warming and satisfy the rising demand for energy.[3–5] The CO_2 released by industries and the burning of fossil fuels is collected and stored using carbon management technologies such as CCUS. The captured CO_2 can also be transformed into various high-value chemicals and fuels, addressing pollution control and energy supply issues. This review introduces the CO_2 cycle with emission sources, storage, and utilization. Different forms of CO_2 utilization are divided into two categories: non-conversion utilization (direct use) and conversion of CO_2 to chemicals and energy products.

2. CO_2 sources and emission

Several sources of CO_2 emission cause an increase in its concentrations in the atmosphere. The CO_2 sources can be classified into natural and human sources. Natural sources include decomposition, plant and animal respiration, ocean release and respiration, and volcanic eruptions. Human sources, which are sources of anthropogenic emissions, include activities such as cement production, deforestation, and the burning of fossil fuels like coal, oil, and natural gas. Some other sources include electricity, heat sector, transportation, and industries. Human activities such as burning oil, coal, and gas, as well as deforestation, are the primary sources of CO_2 emission. The atmospheric concentration of CO_2 has been rising

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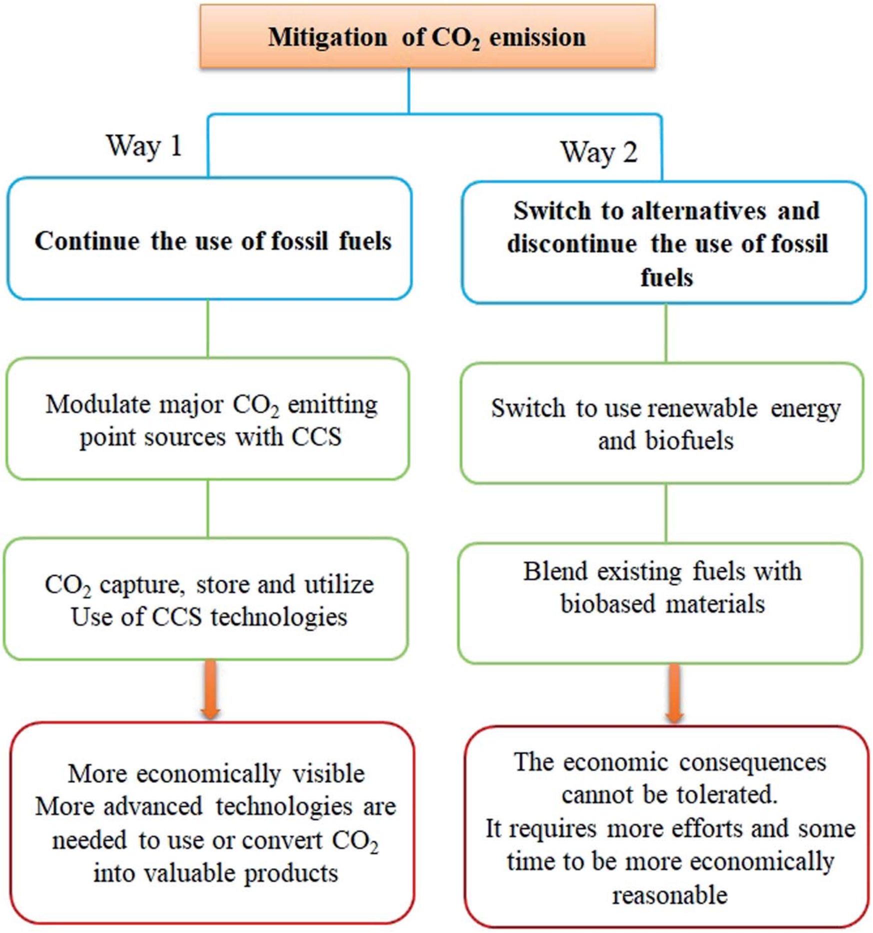

Fig. 1 Possible mitigation of CO_2 emissions.

extensively due to human activities, including the industrial revolution. Human sources of emissions have upset the natural balance by adding extra carbon dioxide to the atmosphere without removing any.

The increase in the global atmospheric concentration of anthropogenic greenhouse gases (GHG), including CO_2, leads to global warming and climate change. The increase in such gases causes ozone layer depletion, which in turn causes the greenhouse effect and global warming, and ultimately climate change. Climate change decreases worldwide agricultural productivity because of low rainfall, changing seasons, and rising temperatures. Global warming, ocean acidification, desertification, and changing weather conditions could all be made worse by the high level of industrial pollution and the indiscriminate production of greenhouse gases into the atmosphere. But among the immediate effects of climate change are issues with food security, migration, health issues, rising sea levels, and severe storms that affect coastal regions.[4] The increase in CO_2 may also indicate a negative impact on the environment, which indicate a decrease in trees and an increase in air pollution, causing several consequences. Environmental degradation is defined as the depletion of environmental resources such as air, water, and soil; the elimination of ecosystems; extinction of wildlife; pollution perceived to be harmful to the ecosystem. Another factor for CO_2 is deforestation, which arises due to the excessive consumption and waste of paper products that come from the trees.

There are two ways to minimize the emission of CO_2. First, fossil fuels can continue to be used with the recommendation to use different CO_2 capture, storage, and utilization methods. Second, people can switch to using alternative clean energies and biomaterials.[6] However, this way seems economically unviable as people cannot bear the high cost of such technologies. So, a combination of both can be a good option until new technologies are developed, Fig. 1.

3. Strategies for minimizing CO_2 emissions

The strategies that can be used to minimize anthropogenic CO_2 emissions include:[7]

(i) Decreasing the production of CO_2 with the use of the sources of renewable energy, such as solar, hydro, and wind, and by increasing energy efficiency.

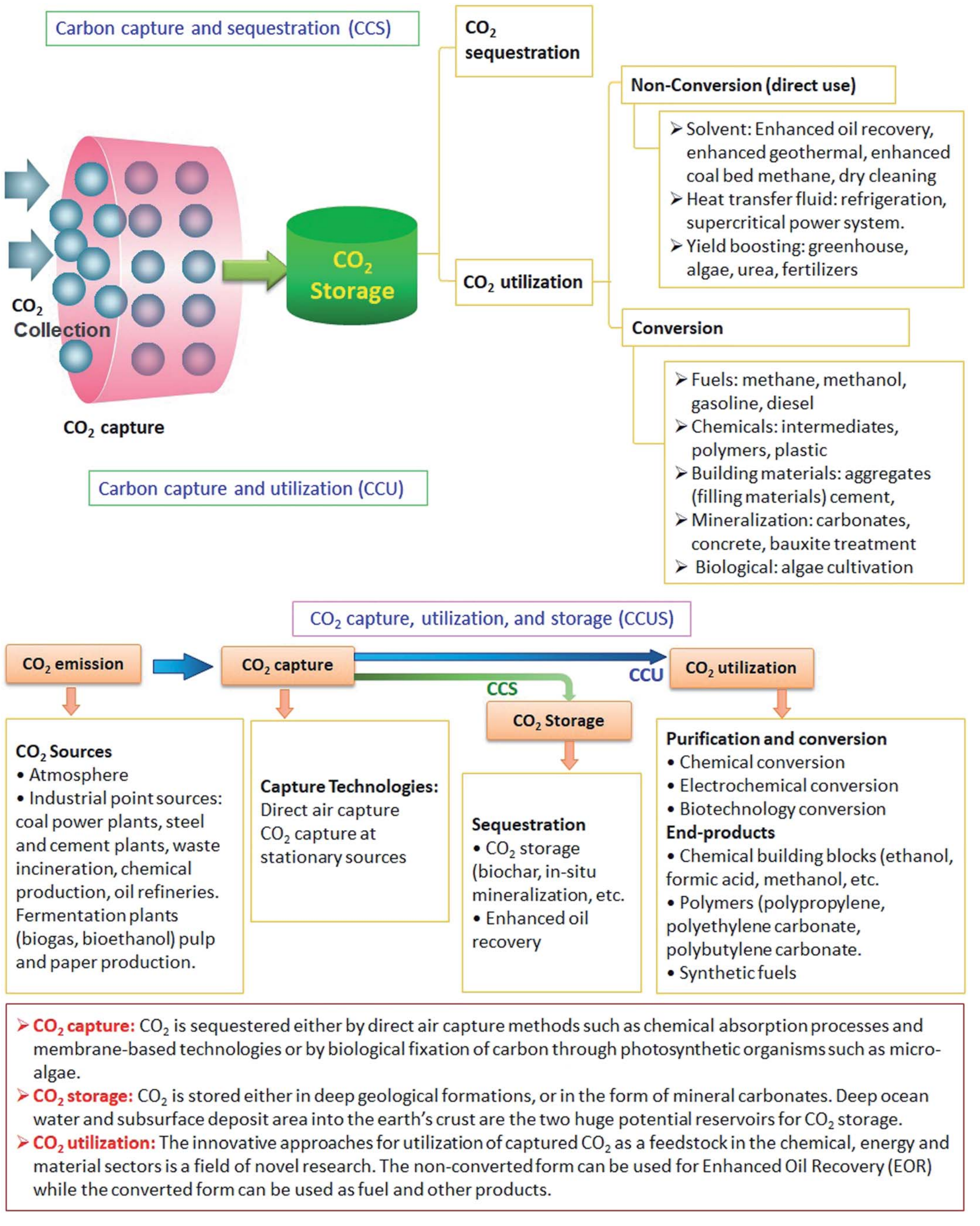

Fig. 2 Illustration of CO_2 steps of emission, capture, storage, and utilization.

(ii) Extracting produced CO_2 from the climate by reforestation and geological storage in deep-sea sediments and underground storage.

(iii) Converting and utilizing CO_2.

In Fig. 2, several of the crucial procedures are displayed. The chemical sector, for example, has a growing demand for carbon, as does the desire to reduce its reliance on fossil fuels. This, combined with the desire to reach net-zero emissions in the future, has sped up feedstock development. As a result, the industry is aggressively developing carbon capture and utilization (CCU) technology to utilize CO_2 as a feedstock alongside new generations of bio-based feedstocks and improved recycled raw materials. In recent years, several encouraging advancements have been made, and commercial items such as cosmetic Plastic Bottles manufactured from waste CO_2 are now accessible.

4. CO_2 sequestration

Carbon sequestration is capturing, securing, and storing CO_2 from the atmosphere. The goal is to prevent CO_2 from warming the atmosphere by stabilizing it in both solid and dissolved forms. The method has great potential for cutting CO_2. There are two basic forms of carbon sequestration; geological and biological.

Generally, sequestration can be done in three different ways: post-combustion capture, pre-combustion capture, and oxy-combustion. In addition, many other separation methods, such as gas phase separation, absorption into a liquid, and adsorption on a solid, as well as hybrid procedures like adsorption/membrane systems, are being researched. As companies move to restorative farming practices, they use the aforementioned procedures to collect the carbon emissions from power plants, factories, fuel-burning enterprises, and new generation animal production facilities.

Storage of CO_2 in vegetation, such as grasslands or forests, as well as in soils and oceans, is known as biological carbon sequestration. While the process of storing CO_2 in underground geologic formations, such as rocks, is known as geological carbon sequestration. Classically, CO_2 is extracted from an energy-related source, such as a power plant or a natural gas processing facility, or an industrial source, such as steel or cement production, and then injected into porous rocks for long-term storage. Carbon capture and storage may allow utilizing fossil fuels until another energy source is introduced on a large scale.

New ways of technological carbon sequestration are explored to remove and store CO_2 from the atmosphere using innovative technologies. Direct air capture of CO_2 can be done directly from the air using advanced technology plants. By developing novel types of chemicals that are capable of identifying and trapping carbon dioxide from the air, scientists are building molecules that can alter the shape. The engineered molecules act as a filter, only attracting CO_2. It is highly of interest to have efficient methods for the CO_2 removal and utilization of a resource for several applications. This includes the use of CO_2 as a raw material to produce graphene.

5. CO_2 capture and separation technologies

Fig. 3 depicts the procedures and materials utilized for CO_2 capture and separation. Briefly, various methods were applied, including absorption, adsorption, separation, membrane, cryogenic distillation, chemical looping, and geothermal and biochemical technologies. CO_2 separation can be achieved by ionic liquid membranes, polymeric membranes, and MOF mixed matrix membranes. CO_2 capture can be achieved using biological separation/fixation techniques such as microalgae, bacteria, and their enzymes.

One of the main CO_2 separation technologies that can be applied to isolate the CO_2 from the fuel gas stream prior to transportation is absorption which can be done using liquid or solid sorbents. Liquor sorbents are absorbed to separate the CO_2 from the flue gas. The sorbent can be regenerated through a stripping or regenerative process by heating or depressurization. CO_2 absorption can be performed by common solvents, ionic liquids, deep eutectic solvents, phase-change ionic liquids, solvents modified with nanoparticles, encapsulated liquid sorbents, novel gas–liquid contactors, and mini- and micro-channels, and rotating packed beds.

Adsorption using a solid sorbent binds the CO_2 on its surfaces. CO_2 adsorption can be performed by carbonaceous materials and nanomaterials, conventional and nanosized zeolites, functionalized sorbents, and swing technologies. Large specific surface area, high selectivity, and higher generation ability are the main criteria for sorbent selection. Another separation method is chemical looping combustion, in which a metal oxide is used as an oxygen carrier instead of using pure oxygen directly for the combustion, as in the case of oxyfuel combustion. During the process, the metal oxide is reduced to metal while the fuel is oxidized to CO_2 and water. In membrane separation, various membranes can allow only CO_2 to pass through, while excluding other flue gas components. Hydrate-based CO_2 separation is a new technology by which the exhaust gas containing CO_2 is exposed to water under high pressure forming hydrates. The CO_2 in the exhaust gas is selectively engaged in the hydrate cages and is separated from other gases. Cryogenic distillation is a gas separation process using distillation at very low temperatures and high pressure. It is similar to other conventional distillation processes except that it is used to separate components of gaseous instead of liquid. Many adsorption procedures are used to achieve CO_2 separation based on regeneration methods. This includes (1) vacuum as well as pressure swing adsorption (VSA and PSA), (2) temperature swing adsorption (TSA), (3) electric swing adsorption (ESA), (4) simulated moving beds (SMB), and (5) purge displacement.[8,9]

Organic cage frameworks (OCFs), pCage-1, and pCage-2 with controlled porosity synthesized from bicyclooxacalixarene cages were reported to have high CO_2 adsorption capacities and adsorption selectivity of CO_2/N_2, that can be the reason for the introduction of N-doped triazine unit.[10] A cross-linked organomagnesium complex (MTF-Mg) has been reported for selective CO_2 adsorption over N_2.[11] The CO_2 preferential adsorption arises from its strong interaction with the exposed magnesium atoms.

In addition, porous organic polymer (HAT-TP) synthesized through a condensation reaction to introduce hexaazatriphenylene (HAT) units to triptycene (TP)-based microporous polymer was reported as an effective recyclable catalyst for chemical conversions of CO_2 to cyclic carbonates with epoxide.[12]

In brief, CO_2 capture technologies include:

➢ Pre-combustion: in this process, the fuel is pretreated before combustion.

➢ Post-combustion: this process removes CO_2 from the flue gas after combustion.

➢ Oxyfuel combustion: in which oxygen, instead of air, is used for combustion.

Most promising capture technologies include capture at large point sources, which is the extraction of carbon dioxide from the flue gases of industrial sources (*e.g.*, power plants, cement, or steel factories). Direct air capture requires more energy than direct capturing CO_2 in flue gases. In addition,

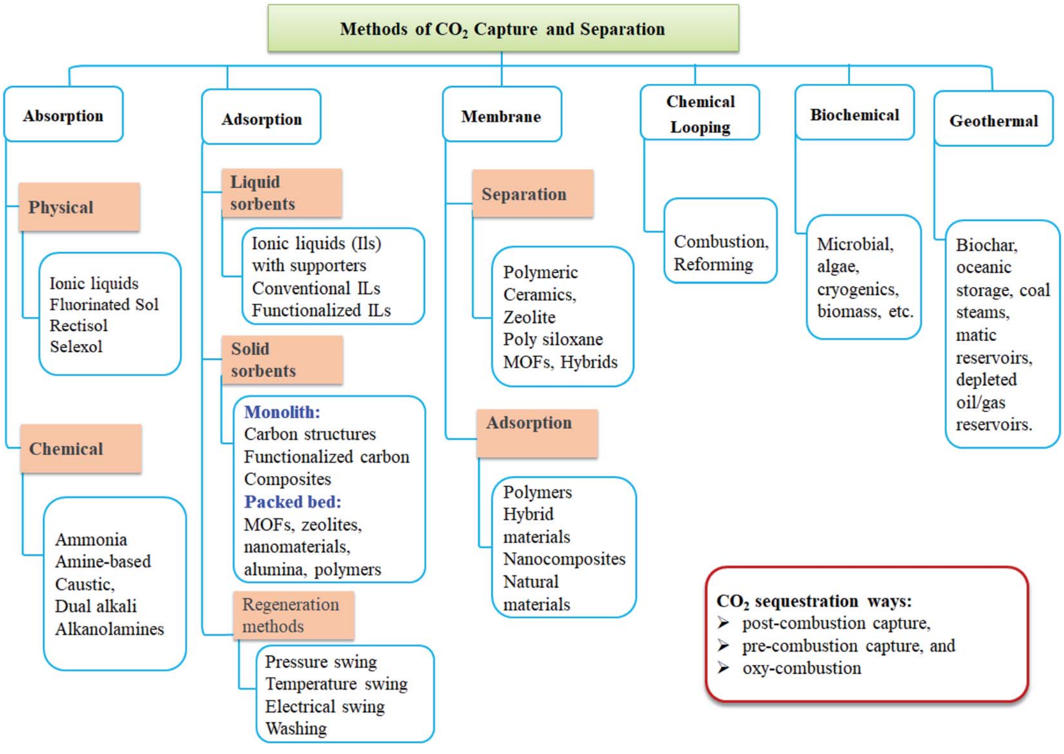

Fig. 3 Classification of CO_2 capture technologies.

capturing the CO_2 emitted by bioenergy production can reduce the atmospheric concentration of CO_2. The general process is called bioenergy with carbon capture and sequestration.

6. CO_2 storage

The CO_2 capture and separation are followed by CO_2 transportation into the storage location. CO_2 storage is the last step in the CCS chain. CO_2 storage can be implemented in different modes classified into natural and man-made modes of storage. Natural modes include terrestrial sequestration, while man-made storage includes storage in geologic formations. The storage strategies include:

Oceanic underground geological storage is considered the most viable sequestration strategy. In comparison to carbonation and oceanic storage, geological storage is preferable due to several factors, including economic considerations, site accessibility (in the case of ocean and mineral sequestration), and associated worries about the security of the stored CO_2 and detrimental environmental effects of mineralization and ocean storage. There are several potential geological storage options, including saline aquifers, depleted oil and gas reservoirs, unmineable coal seams, basalt formations, organic-rich shales, hydrate storage of CO_2 within the subsurface environment, and CO_2-based enhanced geothermal systems.

Deep ocean storage includes the CO_2 injection into deep ocean water. The main proposed approaches for ocean storage are based on the direct dissolution of CO_2 into the seawater.

Mineralization or mineral carbonation: in this strategy, the captured CO_2 is sequestered through the process of mineralization, where CO_2 is reacted with alkaline earth metal oxides or hydroxides, such as calcium-and magnesium-rich minerals, to produce stable carbonates.[13]

Terrestrial sequestration is the capture of CO_2 from the atmosphere and storing of it in soils and vegetation. CO_2 removal from the atmosphere through photosynthesis and prevention of the emission of CO_2 from terrestrial sources are the mechanisms for terrestrial storage.[14]

7. CO_2 utilization

The scientific community opposes CO_2 capture and storage (CCS) because of long-term liability matters, limited cost-effective storage capacity, the probability of leakage, and public acceptance of onshore storage locations.[15] At the same time, deep ocean sequestration would instantly influence lowering pH, enhancing water acidity, and potentially causing ecosystem imbalance.[16]

Carbon capture and utilization (CCU) is a viable alternative to CCS that is gaining traction owing to sustainable progress and is thought to be a long-term solution to the CO_2 problems. CCU explores the use of CO_2 in applications other than storage. CO_2 is a vital raw material for products that continue to require carbon sources. This is because it provides their structure and properties (carbon-containing chemicals). Another reason is using carbon-free energy carriers, such as electricity or hydrogen. CO_2 is one of the few carbon alternative sources to fossil fuels. The chemical feedstocks,[17] refrigerants,[18] cleaning liquids,[19] solvents media,[20,21] inserting agents, and packing gas are examples of CO_2 use attempts that have been demonstrated in recent years.

CO_2 utilization can be classified into non-conversion utilization (direct use) and conversion utilization, Fig. 4. The entire CCU process can be broken down into two steps:

• The initial step in CCU is the capture of CO_2 and separation at the production source.

• The next step is CO_2 utilization performed by (i) non-conversion process to use CO_2 as a solvent, a working fluid, and a heat transfer agent or by (ii) conversion process to use it as a feedstock for the production of fuels, chemicals, and polymers, Fig. 3. The advantages and disadvantages of some of the potential technological ways of CO_2 use are listed in Table 1.

7.1. CO_2 non-conversion utilization (direct use)

CO_2 can be used directly in several applications such as dry ice, carbonated drinks, fire extinguisher, solvent, refrigerants, process fluids, welding mediums, or in algae farms for photosynthesis. It can also be used in large-scale industries to enhance oil recovery, gas recovery, and geothermal systems indirectly. Also, the direct use of CO_2 includes its use as heat transfer fluid in refrigeration, power systems, and other industries. Another example of CO_2 non-conversion utilization is in desalination, where CO_2 is combined with brine at high temperature and pressure, forming hydrates, which may then be extracted to reveal clean water.

In such uses, CO_2 molecules remain pure or dissolved in a mixture and do not react or crack further. However, such direct applications for CO_2 are limited in scale and have a small effect on the overall CO_2 abatement.[22]

7.2. CO_2 conversion utilization

A potential solution to environmental issues like global warming and the energy crisis is the conversion of CO_2 to sustainable and green solar fuel. Technologies like CO_2 capture, storage, and usage provide appealing methods to lower CO_2 emissions. Although CO_2 can be effectively separated *via* CO_2 collection and storage, converting CO_2 into chemicals and fuels is more practical. It converts CO_2 into crucial molecules like carbonate, methanol, salicylic acid, and other substances.

In the conversion process, a carbon–carbon bond or a carbon–hydrogen bond has to be established. Such bond formation requires energy input to activate CO_2 or the other substrates such as reductive coupling. Inappropriately, the carbon–oxygen double bond is very stable (energy of CO_2 750 kJ mol^{-1}) compared with C–H and C–C chemical bonds (430 and 336 kJ mol^{-1}). Commonly, chemical fixation of CO_2 requires: (i) high input of energy to perform reaction activity of substrate (unsaturated compounds, small-ring compounds, and organometallic compounds) and (ii) high reaction temperature and pressure. There are several pathways for CO_2 conversion. These can be classified as shown in Fig. 5.

In brief, the CO_2 conversion reactions can be categorized into two classes:

(i) The first class includes the reactions that do not need a substantial amount of external energy. Hence, the reaction occurs by attaching the CO_2 molecule to the other reactant. These reactions are usually called carboxylation reactions. Consequently, this class involves the production of carboxylates and lactones (RCOOR), carbamates ($R_1R_2NCOOR_3$), ureas (RRNCONRR), isocyanates (RNCO), and carbonates (ROC(O)OR).

(ii) The second class includes the reactions that produce reduced forms of CO_2. Such reduction reactions require a significant amount of external energy. They involve products including; $HCOO^-$ (formates), $[C(O)O]_2^{2-}$ (oxalates), H_2CO (formaldehyde), CO, CH_3OH, CH_4, and C_2H_4. The external energy needed in these reactions is supplied as heat, electrons, or irradiation/photons to break the bonds in CO_2. Such processes are named thermal, electrochemical, and photochemical, respectively. Consequently, catalysis, and high temperature and pressure, are required for lowering the energy barrier toward the formation of C1-building block chemicals, for instance.[23,24]

Such catalytic process of CO_2 includes the formation of chemicals such as urea, methane, methanol, formic acid, formaldehyde, ethylene carbonate, dimethyl carbonate, cyclic carbonates, salicylic acid, cyclic carbonates, polymer building blocks, and polycarbonates.

7.2.1. CO_2 thermal conversion. Thermochemical conversion of CO_2 utilizes catalysts and a combination of heat and pressure to convert CO_2 into valuable products. However, the reversibility of reactions and thermodynamic restrictions on reactions are obstacles to this method. In contrast to procedures like catalytic hydrogenation for the synthesis of methanol, which is created to be decentralized to take advantage of point sources of CO_2, methods like Fischer–Tropsch are developed in large-scale factories to maximize economies of scale. An example is the reverse water gas shift to convert CO_2 and H_2 to CO and H_2O. It may be followed by other processes such as Fischer–Tropsch to produce liquid synthetic fuels such as e-diesel, e-gasoline, and e-kerosene.

7.2.2. CO_2 electrochemical conversion. In electrochemical CO_2, electricity is applied to induce a nonspontaneous reaction of CO_2 reduction. This is similar to water electrolysis for green hydrogen production when the electricity is from a renewable source. Electrolysis is performed at low or high temperatures. The low temperature is more flexible but less energy efficient. High-temperature electrolysis is performed in solid oxide electrolyzer cells and is used to reduce CO_2 into C1 products such as CO or its mixture with hydrogen (syngas). CO_2 is split into CO and O_2, and the process is performed in the gaseous phase at 600–800 °C. With a low-temperature reduction of CO_2, C2+ products such as ethanol, ethylene, and propylene can be produced using an aqueous electrolyte design or membrane electrode assembly.

In bioelectrochemical processes, CO_2 is converted with the support of microorganisms directly in one step. However, it can also be converted with separate production of H_2 in a two-step process. In the first step, hydrogen is produced, then in the second step, hydrogen and CO_2 are fed to a bioreactor

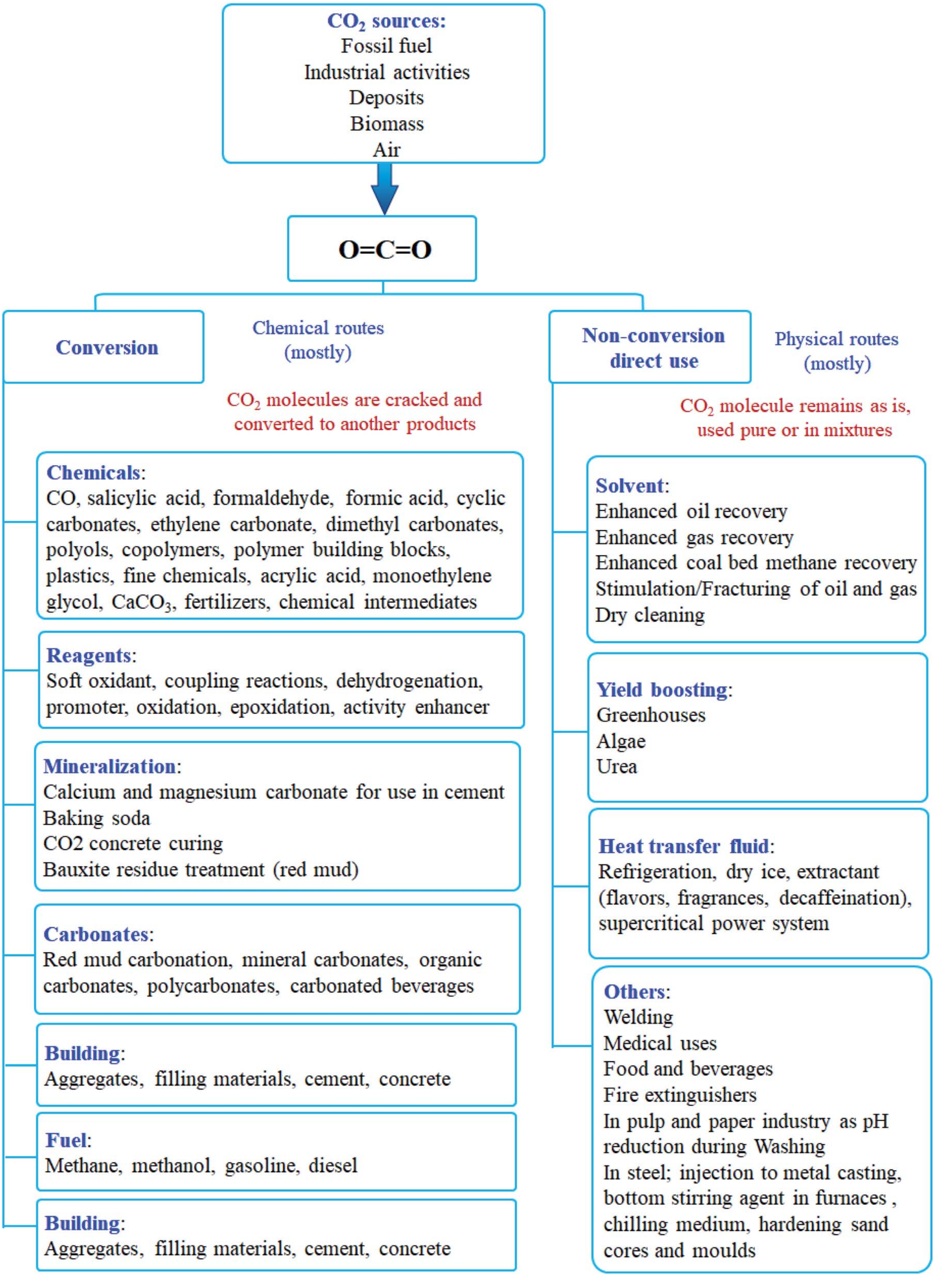

Fig. 4 Classification of CO_2 utilization in various fields and industries.

containing anaerobic methanogenic species for methane production.

7.2.3. CO_2 bio-chemical/enzymatic conversion. CO_2 contains carbon, which is the major component of biofuels. Therefore, CO_2 can be turned into biofuels and bioenergy, making it a potential candidate for renewable energy production. In bioconversion to energy, CO_2 is first captured into a biological system, and then converted into biofuels or

Table 1 Potential technological ways of CO_2 uses

Technology	Description	Advantages	Disadvantages
(i) Non-conversion			
Desalination	CO_2 is combined with brine at high temperature and pressure forming hydrates, which may then be extracted to reveal clean water	➢ Produces potable water or treats water that has been contaminated by a procedure ➢ Enables a revenue stream or cost offset in a system that has already committed to CCS	➢ Costs of power and equipment, however, similar to existing water treatment substitutes
Enhanced oil recovery	CO_2 is pumped into existing oil wells to boost pressure and reduce oil viscosity, allowing for more oil to be retrieved	➢ It is a mature technology with permanent storage and a great potential for CO_2 utilization, as well as an income source to pay the costs of carbon capture	➢ Facilitates further fossil fuel use, producing more CO_2
Enhanced geothermal systems	Supercritical CO_2 is used to transmit geothermal heat or to create electricity directly using a supercritical CO_2 turbine	➢ Improves the efficiency of a renewable energy source and ➢ Provides long-term storage	➢ It takes a long time for a product to be commercialized ➢ Transporting supercritical CO_2 is expensive ➢ A geothermal site requires a grid connection
Enhanced coal bed methane	CO_2 is pumped into partially depleted coal seams, where it is absorbed by coal, causing methane to be displaced to the surface, where it can be recovered and used as a fuel	➢ Methane may replace more carbon-intensive fuel sources ➢ It is with permanent storage	➢ CO_2 adsorbed in coal might cause it to swell and impede routes, causing methane recovery to be hampered ➢ A low cost of methane ➢ CO_2 transportation costs
(ii) Conversion			
Mineralization			
CO_2 mineralization	CO_2 reacts with minerals or industrial waste products. This results in new compounds utilized in constructions, as consumer products, or as a substitute to CCS	➢ Abundant materials (minerals or industrial wastes) ➢ Substitute to CCS	➢ To speed up the process, high energy is used ➢ High material requirements ➢ Minerals and processing costs
Concrete curing	Precast concrete is cured using waste CO_2 flue gas. CO_2 is kept in the concrete as a non-reactive limestone	➢ Low cost *versus* traditional curing ➢ Flue gases can be used directly in the cement industry ➢ Carbon offset opportunity for the cement industry, which produces a lot of pollution ➢ A low-carbon consumer item that has the potential to grow beyond its current market	➢ The product must meet quality requirements ➢ The expense of modifying the curing process
Bauxite residue carbonation	The alkalinity of aluminum mining slurry is reduced by CO_2	➢ Aluminum mine closure and reclamation expenses can be reduced	➢ Cost of concentrating CO_2 ➢ Need access to CO_2
Biological			
Algae cultivation	CO_2 is absorbed by microalgae, which can then be transformed into proteins, fertilizers, and biomass for biofuels	➢ Competitive source of biofuel ➢ Can use flue gas directly ➢ Can result in permanent storage ➢ A tonne of microalgae can fix about two tonnes of CO_2	➢ Algae are sensitive to impurities, pH ➢ Cost of controlling growth and drying conditions ➢ Large area and sunny climate needed for ponds ➢ High energy needs for photobioreactors
Chemicals			
Liquid fuels – methanol	Methanol is produced by catalytically converting CO_2 and hydrogen into methanol, which can be combined with gasoline	➢ The energy carrier eventually replaces fossil fuels, lessening our reliance on them for transportation and other purposes	➢ Inefficient process; requires renewable or low emissions energy to have net CO_2 abatement benefit ➢ Needs low-cost renewable hydrogen ➢ Cost of purifying CO_2
Liquid fuels – formic acid	Formic acid is made by electro-reducing CO_2 in water	➢ Formic acid is a preservative and antibacterial agent that can be utilized as an energy carrier (with hydrogen as the major fuel)	➢ Inefficient process; requires renewable or low emissions energy to have net CO_2 abatement benefit ➢ Chemistry needs to be perfected ➢ Cost of purifying CO_2

Table 1 (*Contd.*)

Technology	Description	Advantages	Disadvantages
Polymers/ chemical feedstock	CO_2 is converted into polycarbonates with the use of a zinc-based catalyst	➢ Flue gas can be used directly; CO_2 has a significant potential usage; a wide range of products (plastic bags, laminates, automobiles, medical components, and so on) are possible ➢ Existing infrastructure can be employed	➢ Non-permanent storage; some CO_2 can be re-emitted as soon as six months
Urea yield boosting	Urea fertilizer is made from ammonia and CO_2	➢ Process emissions intensity is reduced	➢ CO_2 is re-emitted when urea is broken down as fertilizer ➢ Non-permanent storage

bioenergy. Engineered microbes convert CO_2 into value-added bio-based chemicals.[25]

Due to the limitations of natural CO_2 fixing pathways, synthetic CO_2 fixation routes have been developed at levels of *in silico* prediction, *in vitro* testing, and *in vivo* implantation of a synthetic CO_2 fixation pathway. Multiple criteria are considered while designing a synthetic CO_2 fixing pathway. Oxygen-tolerant and kinetically fast carboxylases are considered to incorporate into the pathways. The undesired side reactions are kept at a minimum. After passing the topological, energetic, and kinetic assessment, the resulting designed pathway is anticipated to have quick overall pathway kinetics, high flux, and improved performance compared to natural CO_2 fixing pathways.

The photosynthetic recycling of CO_2 can be used to produce products such as 2-methyl-1-butanol, isobutyraldehyde, and isobutanol, ethanol, butanol, malate, formate, lipids, sugars (hexose, pentose, and triose), biomass, succinate, limonene, isopropanol, acetic acid, isobutanol, and 3-methyl1-butanol, succinic acid, isobutyraldehyde, 1,3-propanediol.[26]

7.2.4. CO_2 catalytic conversion. The catalytic conversion of CO_2 into chemicals is of high interest. Both homogeneous and heterogeneous catalysis processes can be used. Valuable chemicals such as carbonates, carbamates, urethanes, lactones, pyrones, and formic acid and their derivatives can be synthesized by homogeneous catalysts. Heterogeneous catalysis can offer several technical advantages such as stability, separation, handling, and reusing of the catalyst and reactor design. Although CO_2 activation by heterogeneous catalytic routes is still limited, efforts have been made toward synthesizing dimethyl carbonate, cyclic carbonates, and synthetic gas (CO, H_2) and methanol synthesis from CO_2 hydrogenation.[27]

Examples of CO_2 catalytic conversion include CO_2 reforming of CH_4, CO_2 hydrogenation to methanol, formation of dimethyl carbonate from CO_2 and methanol, formation of cyclic carbonate from CO_2 and epoxide, and formation of cyclic carbonate from CO_2 in the presence of ammonium salt, and the reaction of CO_2 and propylene glycol.[28]

Catalytic conversion of CO_2 can be used to form hydrocarbon and non-hydrocarbon fuels. Because of the high stability of CO_2 molecule ($\Delta G_f^\circ = -396$ kJ mol^{-1}), CO_2 conversion into valuable products requires high energy depending on the downward steps for 4+ oxidation state of carbon. CO_2 conversion to HC fuels involves a high energy process, where the C-oxidation state is +2 or lower for possible production of compounds such as HCOOH, H_2CO, CH_3OH, CH_4, and other HCs.[29]

There are two ways to convert CO_2 into hydrocarbon-based fuels; (1) transformation using classical Fischer–Tropsch synthesis [Ramirez] through reverse water-gas shift (RWGS) reaction followed by HC cracking, isomerization and aromatization, (2) CO_2 transformation into methanol (MeOH) followed by the MeOH conversion to HC. The CO_2 is first converted *via* the Fischer–Tropsch synthesis and then followed by coupling with the Fischer–Tropsch catalyst system containing zeolite. This is to allow production distribution and selectivity to olefins and or aromatic. Similarly, combining the CO_2 with MeOH catalyst system, *i.e.*, zeolite, can also allow the generation of useful chemicals *via* the CO hydrogenation.[30]

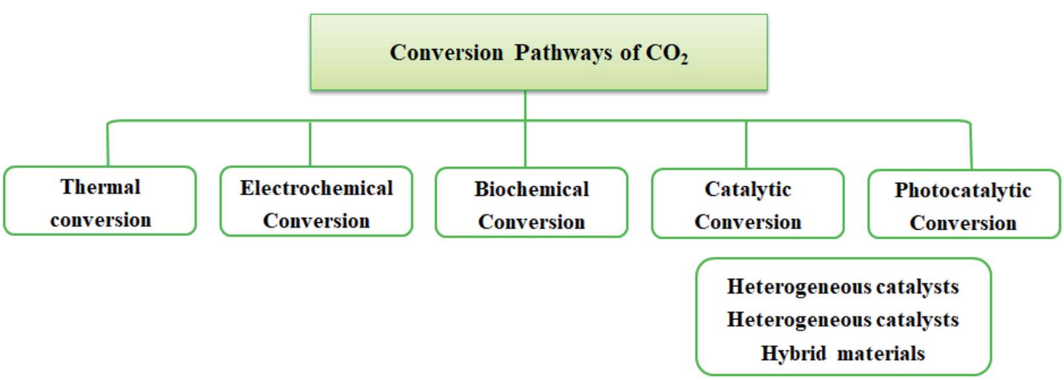

Fig. 5 Conversion strategies of CO_2.

Catalysts such as metals and their oxides, carbon nanostructures, metal–organic frameworks (MOFs), and polymer functionalized materials have been reported for CO_2 conversions.[31] For CO_2 reduction, the one-electron reduction is endothermic and produced ($CO_2^{\bullet}$) is highly reactive. Electrochemical potentials of possible CO_2 reduction reactions in aqueous solutions for the production of different chemicals and hydrocarbon fuels are in equations:

$$CO_2 + e^- \rightarrow CO_2^{\bullet -} \quad E^{\circ}_{redox} = -1.9 \text{ V (NHE)} \tag{1}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH, E^{\circ} = -0.61 \text{ V} \tag{2}$$

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

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

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O, E^{\circ} = -0.38 \text{ V} \tag{5}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O, E^{\circ} = -0.24 \text{ V} \tag{6}$$

$$2H^+ + 2e^- \rightarrow H_2, E^{\circ} = -0.41 \text{ V} \tag{7}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-, E^{\circ} = +0.81 \text{ V} \tag{8}$$

Fig. 6 lists several reactions for the transformation of CO_2 into products that are commercially valuable.[32]

7.2.4.1. Nanomaterials used for CO_2 catalytic conversion. The general classification of the materials and nanomaterials used for CO_2 conversion can be listed in Fig. 7. These materials can be prepared, modified, and used individually or prepared in a hybrid or combination of two or more chemicals. Hybridization of two or more types of these materials may further improve efficiency. For example, carbon materials like graphene, graphene oxide (GO), reduced GO, carbon nanotubes, and graphitic carbon nitride (g-C_3N_4) are commonly used for CO_2 applications. By varying the precursor, performing post-synthetic functionalization, and modification with metal nanoparticles or polymeric branches, the electronic band structures of the carbon nanomaterials and their light absorption features can be tuned, therefore, enhancing the CO_2 conversion and making them attractive for CO_2 applications.[33–35]

Solid substrates are functionalized or modified with amines and ionic liquids[36,37] to have more affinity toward CO_2. Nevertheless, polymers such as amidine and guanidine-based polymers, poly(ethylene-imine), poly(ether imide), and poly(ionic liquid)s (PILs) interact more with CO_2.[38] Other polymers, including polystyrene, polysulfone, or poly(ether-*b*-amide-6), can be utilized due to their controllable porosity, good CO_2 permeability, and selectivity.

Porous organic polymers prepared from specific multidentate organic building blocks are good candidates for CO_2 applications.[39,40] However, polymerization conditions play a key role in their porosity. In addition, cross-linking of polymers is optimized and controlled to get macroporous (>50 nm), mesoporous (2–50 nm), and microporous (<2 nm) materials. This can also impact the pore volume and surface area, which are important parameters affecting the affinity toward CO_2.[41]

Another class of materials is the inorganic materials which can be synthesized with good morphology and high surface area. Examples include spherical nanoparticles, nanowires, nanocubes, and nanosheets. These materials can be easily prepared with controlled properties. For instance, nanoparticles of numerous shapes display various efficiencies for identical catalytic processes owing to the exposure of several crystal facets.[42–44] Metal such as palladium, gold, silver, and copper are the most efficient. With the ability to stabilize the reaction intermediates, metals such as copper are outstandingly active for CO_2 reduction to hydrocarbons. However, in some cases, palladium, gold, and silver form CO.[45,46] MOFs are another class of materials that showed excellent performance in CO_2 applications owing to their crystallinity and high surface area.[47,48] Such materials with crystals show high internal cavities interconnected mainly by small channels to play a key role in several CO_2 applications.[49,50] Heterogeneous catalytic conversion of CO_2 to chemicals and fuels is gaining particular interest because of its better stability, durability, simplicity in separation, handling, and simpler reactor design.

7.2.4.2. Homogeneous and heterogeneous metal complex-based catalysts. Homogeneous and heterogeneous metal complex-based catalysts are used for the electroreduction of CO_2, Fig. 8. In homogeneous catalysis, the metal complex acts as a redox shuttle between the electrode and CO_2. Mostly, the catalyst is in a more highly reduced state due to its acceptance of electrons from the electrode. As a result of the reduction, the catalyst transfers electrons to CO_2 in the solution and returns to its initial state, resulting in an indirect electrolysis reaction.[31] Catalysts are often single atom transition-metal complexes stabilized by ligands in environments that tune the redox potentials of the catalyst. In the stable coordination environments found for typical Ir and Ru metal complexes, there is often a high catalytic selectivity after optimization in the design of the catalyst. However, the difficulties of catalyst recovery after catalytic cycles with considerable energy demands from distillation, filtration, or crystallization to recover the catalyst is a significant impediment in large-scale synthesis.

Catalyst immobilization in surface or electrochemical reactions combines the benefits of homogenous catalysis and selectivity with the capacity to reuse the catalysts. With the reduction of CO_2 as our primary goal, we devised many techniques, including polymerization, noncovalent surface binding, and surface-chemical binding, to make chemically modified electrodes.[51] Surface binding facilitates electron transfer from the electrode to metal complex catalysts on the surface. The electrochemical reduction of CO_2 using heterogeneous catalysts with high surface area is an appealing method. Nanostructured catalysts can produce much improved reactive surfaces with a significant portion of the reactive sites available for catalysis compared to traditional electrodes.

7.2.5. CO_2 photocatalytic conversion. Photocatalytic systems can potentially conduct difficult transformations, which thermal reactions cannot realize. Several materials and nanomaterials used as photocatalysts have been tested to

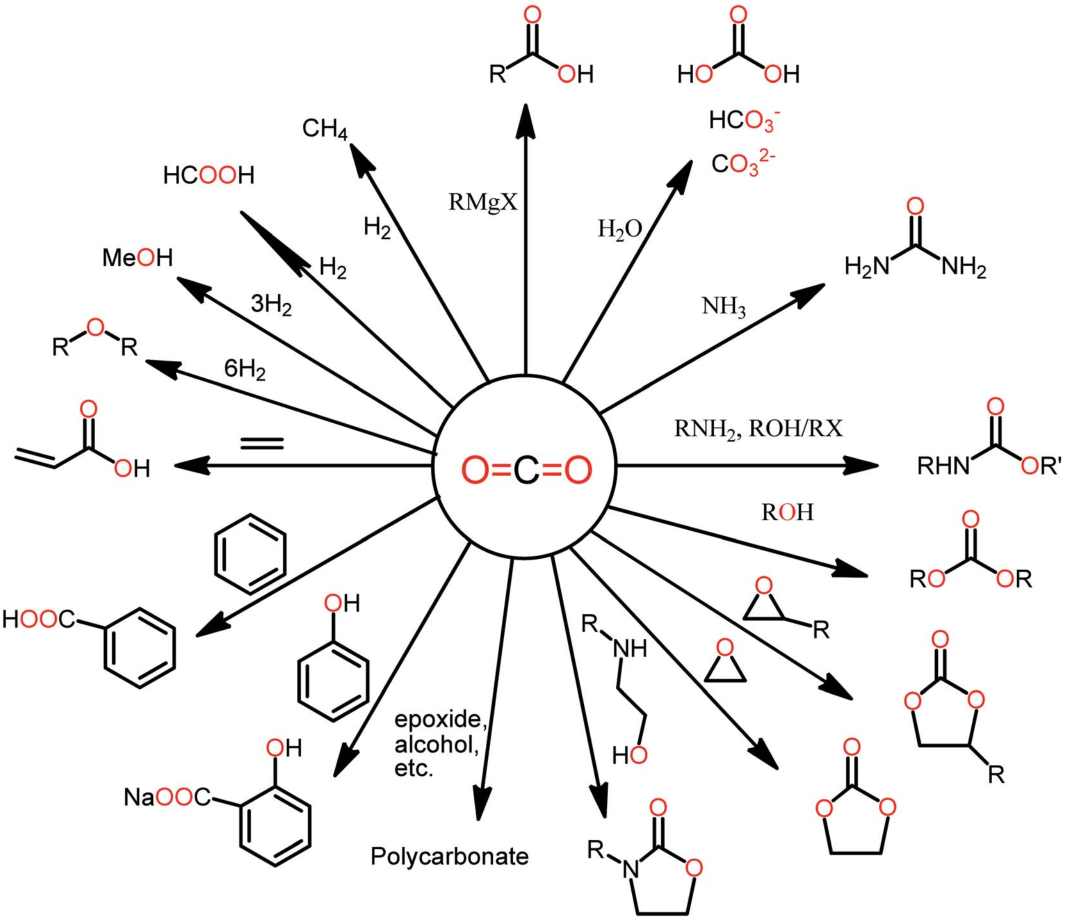

Fig. 6 Directions of the CO_2 chemical transformation to various chemicals.[3]

convert CO_2 into valuable products. These can be classified into different classes, including nanoparticles, nanocomposites, and hybrid materials.[2,23] Understanding the mechanics of CO_2 photoreduction reduces reaction barriers and increases selectivity toward the desired products, resulting in increased CO_2 lowering efficiency. The CO_2 photocatalytic conversion using semiconductor-based catalysts involves, Fig. 9: (1) CO_2 adsorption on the surface of the catalyst, (2) generation of electron and hole pairs after the absorption of light, (3) separation and transfer of charges to the surface active sites, and the generated charges may recombine back in the (4) bulk or (5) on the surface, (6) reduction of the adsorbed CO_2 by accepting an electron, and (7) oxidation of water to give oxygen.

The influencing factors for CO_2 photocatalytic reactions,[54,55] rate-limiting steps,[56] thermodynamic and kinetic requirements,[57] and reaction processes[58,59] have all been reviewed in several reports. For example, the adsorption of reactants on the surface of the catalysts is critical in heterogeneous catalytic reactions, and it is often regarded as the first step in initiating the reaction. CO_2 adsorption on photocatalysts is the first stage in CO_2 photoreduction, and the amounts and states of CO_2 adsorption on photocatalysts can have a big impact on CO_2 reduction processes, efficiency, and product selectivity.[60,61] This component has previously been disregarded. The number of papers looking at the impact of CO_2 adsorption on CO_2 photoreduction has increased in recent years. There are, however, few assessments that summarize these attempts.

Generally, the mechanisms for CO_2 photoreduction can be explained in different ways.[62–65] These mechanisms can be summaries in the steps including:

Step 1: CO_2 and H_2O diffuse into the photocatalyst surface

Step 2: CO_2 and H_2O do move along the photocatalyst surface by surface diffusion to occupy the active sites

Step 3: Light absorption and formation of electrons holes on the surface of the photocatalyst

Step 4: Interaction between adsorbed reactants and charged particles and then recombination of charged particles

Step 5: Desorption of the formed products

7.2.5.1. Photocatalysts requirements. Catalysts should be with: (i) photosensitizer component (to initiate photochemical one-electron transfer), such as organic compounds semiconductors and metal complexes, and (ii) catalyst (to convert one-electron transfer into a multi-electron reduction of CO_2), such as complexes, metal particles, and enzymes. Excellently designed photocatalysts (rhenium(I) complexes) can fill both roles. The photocatalytic efficiency can be evaluated by: (i) product selectivity, (ii) quantum yield = (product/mol)/(absorbed photons/einstein), (iii) the stability of the

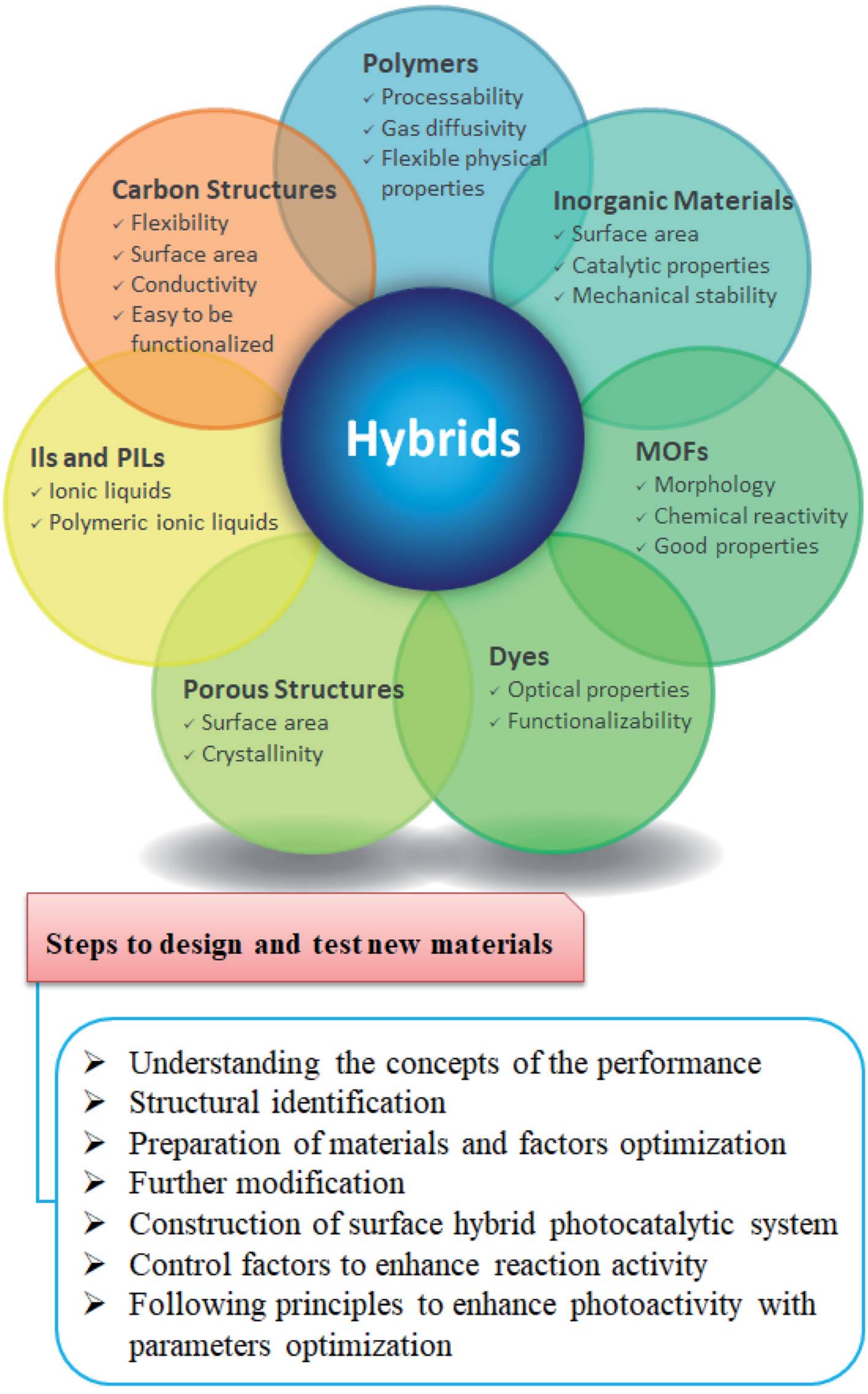

Fig. 7 Examples of building blocks that form hybrid materials for CO_2 application.

photocatalyst given by turnover number (TON) = (product/mol)/(photocatalyst/mol or unit mass), (iv) the photocatalytic cycle speed given by turnover frequencies (TOF) = TON/(reaction time/min).

7.2.5.2. Homogeneous catalysts. Homogenous redox photocatalysts consist of a light-harvesting unit (photosensitizer) and two catalytic sites. One site is for the oxidation process, where a donor provides the electrons, and the other is the reduction site, where the electrons are transferred to an acceptor. Sometimes, the photosensitizer works as photosensitizer and reduction site.[66]

Visible light absorption by the photosensitizer unit leads to the excited state. Commonly used photosensitizers for CO_2 reduction are ruthenium (polypyridyl)-and (bipyridyl)-

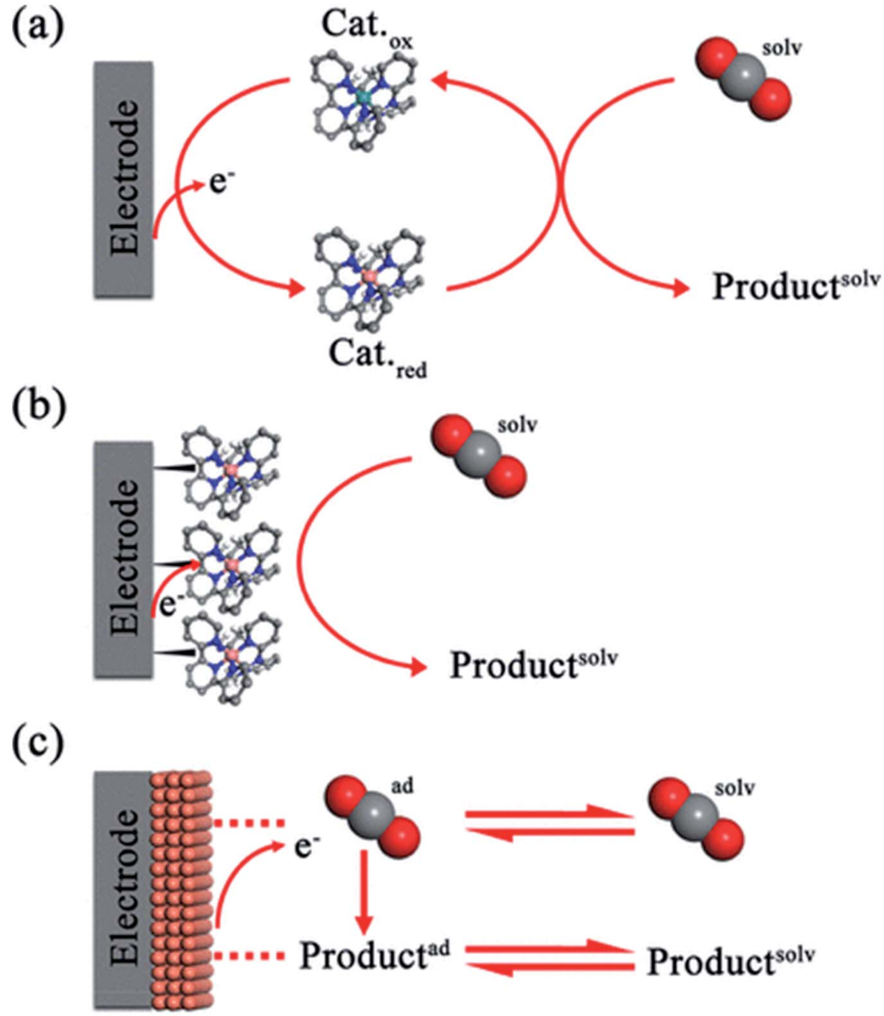

Fig. 8 Reduction of CO_2 by various catalytic mechanisms: (a) homogeneous, (b) immobilized, and (c) heterogeneous way in an electrocatalytic film.[52]

rhenium(I) complexes (2.1 Chromophores). So, the light absorption gives rise to a single metal to ligand charge transfer (^{1}MLCT), which produces a triplet excited state (^{3}MLCT) by inter-system crossing. This ^{3}MLCT state has different redox properties than the ground state. Owing to this state's reducing properties, direct interaction with an acceptor can lead to the one-electron oxidized ground state of the photosensitizer *via* oxidative quenching. In terms of CO_2 reduction, reductive quenching is the more important process. With an electron from the oxidation site, a ground state of electron reduced species is formed, capable of transferring electron to the reduction site to recover the d^6 neutral ground state of the photosensitizer.[67]

When exposed to light radiations of suitable frequencies, the ruthenium-or iridium-based complexes convert CO_2 into CO or formate.[4] A series of anthracene-substituted mononuclear and dinuclear rhenium complexes have been reported for photocatalytic CO_2 reduction showing a good TON value and long life.[5] The anthracene moiety also functions as a sterically bulky group that may inhibit deleterious intermolecular catalyst deactivation pathways.

Examples of the multi-component system include ruthenium(I) diimine photosensitizers, rhenium(II) diimine, photosensitizer, and organic photosensitizers.[41] Moreover, some supramolecular photocatalysts are also used, such as Ru(II)–Ni(I), Ru(II)–Co(III), and Ru(II)–Re(I). An example of the selective catalytic reduction site for the photoreduction of CO_2 over rhenium(I) systems is given in Fig. 10.[28]

7.2.5.3. Heterogeneous catalysts. Several heterogeneous catalysts have been developed, including metal-supported catalysts, perovskites, and solid solution catalysts.[69] The heterogeneous catalyst consists of metal, supports, and promotors. Precious metals (Pt, Rh, or Ru) are known to have high activity and durability and are resistant to coke deposition, although at a high price. The precious metal-based catalysts show high activity in spite of the very small amount of metal catalyst used.

Non-precious metals (Ni or Co) have been widely investigated as well. Non-precious metals such as Ni or Co have been used

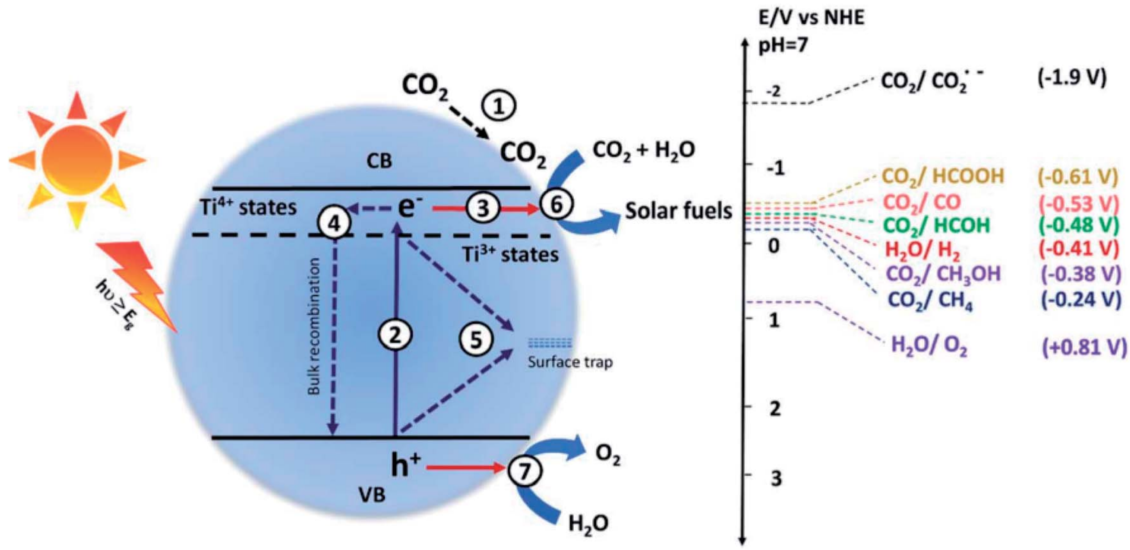

Fig. 9 Steps of photocatalytic CO_2 conversion. The absorption of light energy equal to or greater than the bandgap (E_g) results in the excitation of the electrons from the valence band (VB) to the conduction band (CB), leaving behind holes in the VB. The electrons and holes promote the reduction and oxidation of the reactant molecules.[53]

more for DRM due to their low price and abundance.[70] Ni catalysts have shown a level of activity comparable to precious metals. Alloyed metal catalysts are widely used because they have a different electronic structure than monometallic materials. Monometallic Ni or Fe catalysts have shown poor durability because the monometallic Ni catalyst is easily deactivated by coke deposition, and Fe is not much active for CO_2 conversion.

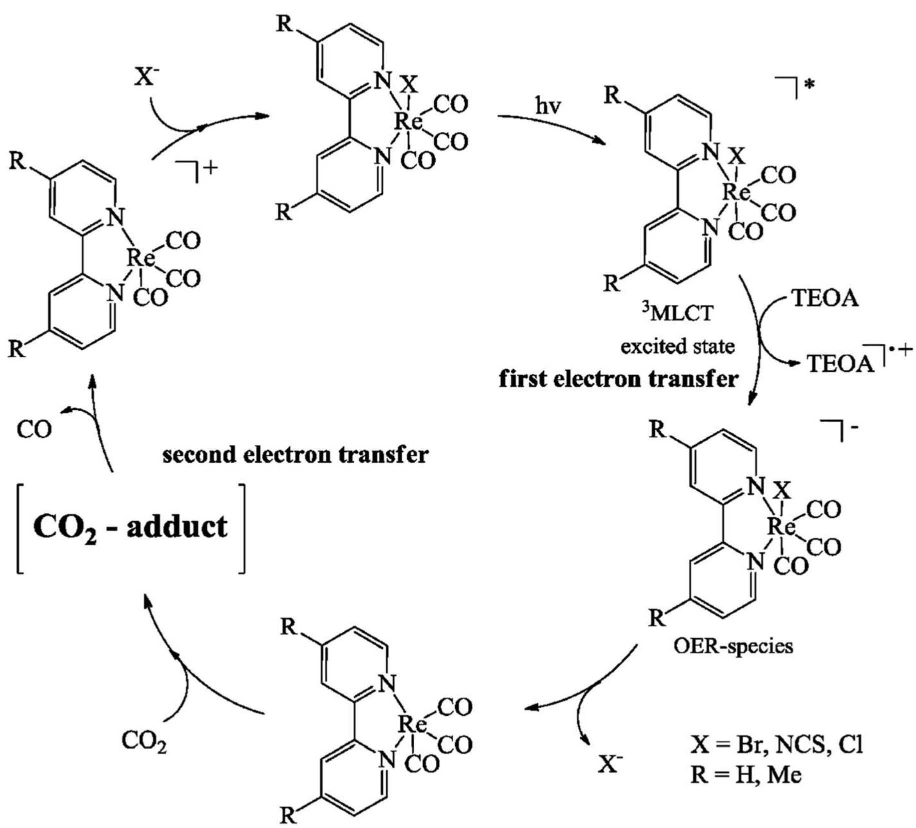

Fig. 10 Catalytic cycle for the photoreduction of CO_2 with (bipyridyl)Re(CO)$_3$X complexes by Hawecker *et al.*[68]

TiO_2, $BaLa_4TiO_{15}$, $SrTiO_3$, WO_3, $NaNbO_4$, and Zn_2GeO_4 are a few of the materials that show promise for use in these applications. Most of these inorganic semiconductors have good structural controllability and stability (the morphology, size, and surface). Titania-based materials, including 1-D (TiO_2 nanowires, nanorods, nanobelts, and nanotubes), 2-D (TiO_2 nanolayers and nanosheets), 3-D, and hierarchical nanostructures, are the most commonly employed catalysts.[16] Enhanced efficiency is attributed to factors such as high surface area, good photogenerated-charges separation, directional charge transport, enhanced light-harvesting owing to light trapping/scattering, and low photon influence, considering the configuration and geometry of the photocatalysts. Semiconductors such as ZnO, CdS, GaP, SiC, WO_3, Ga_2O_3, GaP, $InTaO_4$, MgO, ZrO_2, $BiVO_4$, and $ATaO_3$ are also used. Semiconductors with more negative CB potentials convert CO_2 to CH_3OH. Water worked as a reductant since no reducing reagents were introduced into the reaction solutions.[71,72]

For example, it was reported that AgI/GCN nanocomposite's charge separation process follows the double-transfer mechanism (conventional charge separation mechanism) and Z-scheme process.[73] Upon irradiation, the AgI and GCN material's VB electrons are excited to CB. Therefore, the CO_2 photoconversion occurs at the surface of AgI if the double charge transfer mechanism is employed (Fig. 11a). However, when the Z-scheme mechanism is adopted, the photoconversion of CO_2 occurs on the surface of GCN because the CB value of GCN (-1.12 eV *vs.* NHE) is more negative than the standard reduction potential for the formation of O_2^-, methane, ethanol and acetone, Fig. 11b.

7.2.5.4. Hybrid nanocatalysts. Hybrid materials are composites made by a synergistic combination of organic and inorganic components at the nanometer or molecular level. New properties are created by new electron orbitals formed between them. Hybrid materials such as a photocatalyst consisting of photosensitizer (CdSe quantum dots) and catalyst (Pt/TiO_2) were reported.[74] CdSe quantum dots show a negative shift of CB energy where electron injection into titania can proceed under visible light in an aqueous media forming CH_4 and CH_3OH. Nanoparticles supported on carbon nanotubes, g-C_3N_4, graphene nanosheets, and carbon dots are used for CO_2 photoreduction under vis-light into CO.[75–77] The influence of dye-based organic linkers on CO_2 photoreduction efficiency has been reported using UiO-67. Re_3-MOFs displayed high photocatalytic activity. When Ren-MOFs and Re3-MOFs were coated with silver nanoparticles, the efficiency was seven times enhanced, Fig. 12.[78]

Covalently bonded microporous organic polymers (MOPs) showed high physical and chemical stability. Cooper's group reported on several monomers synthesizing pyrene-based conjugated microporous polymers with 1.94–2.95 eV band gaps, exhibiting high photocatalytic activity.[79] Covalent triazine frameworks (CTFs) are a distinguished subclass of contemporary high-performance nanoporous materials. CTFs with aromatic triazine linkages are constructed by covalently linked light elements (C, N, and H) and boast high porosity, high nitrogen content, and good thermal/chemical stability. Furthermore, a triazine ring connected with electron-rich units can easily form p–n heterojunction *via* the conjugated structure, imparting superior nature to conjugated CTFs, particularly in terms of bandgap tunability and rapid electron separation rates.[80,81]

8. Pilot-scale projects and commercialization

Several well-known industries have expanded their funding for CCUS work. Also, various demonstration initiatives at the pilot scale are underway.[82] Examples are:

• CarbFix in Iceland for CO_2 capture from geothermal fluid and air.

• Drax in the UK for CO_2 capture from biomass power generation.

• STEPWISE in Sweden for sorption-enhanced water gas shift separation testing in the iron as well as the steel industry.

• CIUDEN in Spain for CO_2 storage.

• Geothermal plants for CCUS in Croatia for electricity generation from geothermal hot brine.

CCS is projected to play a key role in achieving global warming goals and turning CO_2 into useful goods.[83,84] As

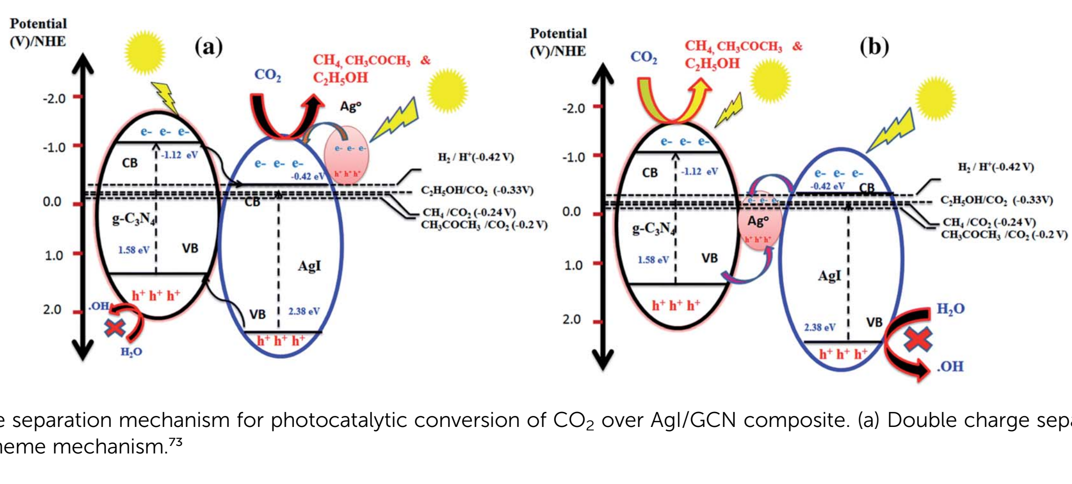

Fig. 11 Charge separation mechanism for photocatalytic conversion of CO_2 over AgI/GCN composite. (a) Double charge separation mechanism; (b) Z-scheme mechanism.[73]

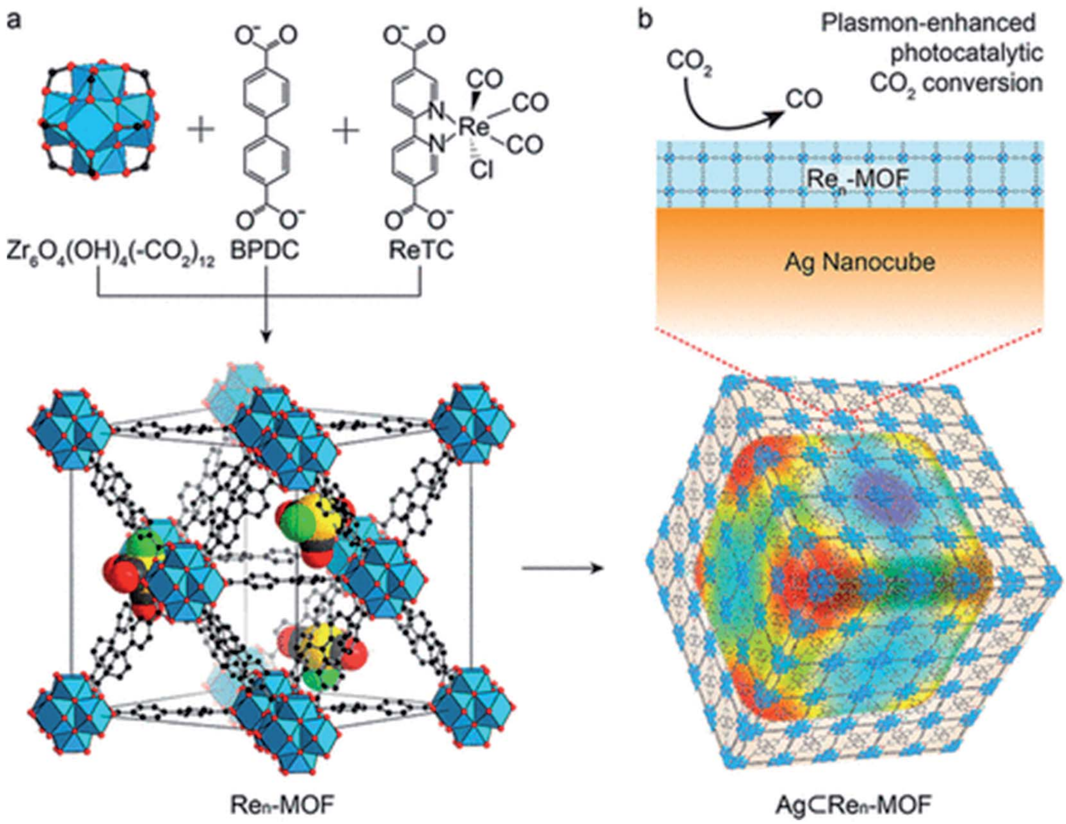

Fig. 12 Structures of Re_n-MOF and Ag-Re_n-MOF for plasmon-enhanced photocatalytic CO_2 conversion (a) and mechanism of conversion (b).[78]

a result, several technologies are being developed to capture, transport, store, and utilize CO_2. Typically, technological development proceeds in stages: (i) bench or laboratory size, (ii) pilot scale, (iii) demonstration scale, and (iv) commercial scale.

These steps can be easily classified into numerous technology readiness levels (TRL), Fig. 13. At the TRL 3, TRL 6, and TRL 7 development stages, there is a glut of technology. Beyond TRL 3, improving a technology necessitates further research money, but methods beyond TRL 5 and TRL 7 necessitate major financial commitment and commercial interests, for example, in the case of some polymeric membranes. The following sections of this article go into greater detail about the technical development of the various CCS technologies.

9. CO_2 use market

Although it is difficult to assess the future market of CO_2 uses, there are some areas and applications of CO_2. These can be listed as:

9.1. CO_2-derived fuels

The carbon in CO_2 can be used to produce fuels that are in use today. The process involves using CO_2 in combination with hydrogen, which is highly energy-intensive to produce carbon-containing fuels that are easier to handle and use than pure hydrogen. Examples are methane, methanol, gasoline, and aviation fuels.

9.2. CO_2-derived chemicals

The carbon and oxygen in CO_2 are promising to be used as an alternative to fossil fuels in producing chemicals, and materials including plastics, fibers, and synthetic rubber. Converting CO_2 to methanol and methane is the most technologically mature pathway.

9.3. CO_2 to building materials

CO_2 can be used to produce building materials to replace the water in concrete. It is called CO_2 curing or as a raw material in its constituents, cement, and construction aggregates. This process involves the reaction of CO_2 with calcium or magnesium to form low-energy carbonate molecules, the form of carbon that makes up concrete. While incorporating CO_2 in the manufacture of cement is still in its early stages of development, CO_2-cured concrete is one of the most established and promising applications of CO_2 utilization.

Construction aggregates, tiny particles used in building materials, can be made by combining CO_2 with industrial or waste products from power plant activities. These include coal fly ash and iron slag, which would otherwise be heaped or kept in landfills, Fig. 14.

9.4. Crop yield boosting

CO_2 can be utilized to increase the yields of biological processes, such as algae growth and greenhouse crop

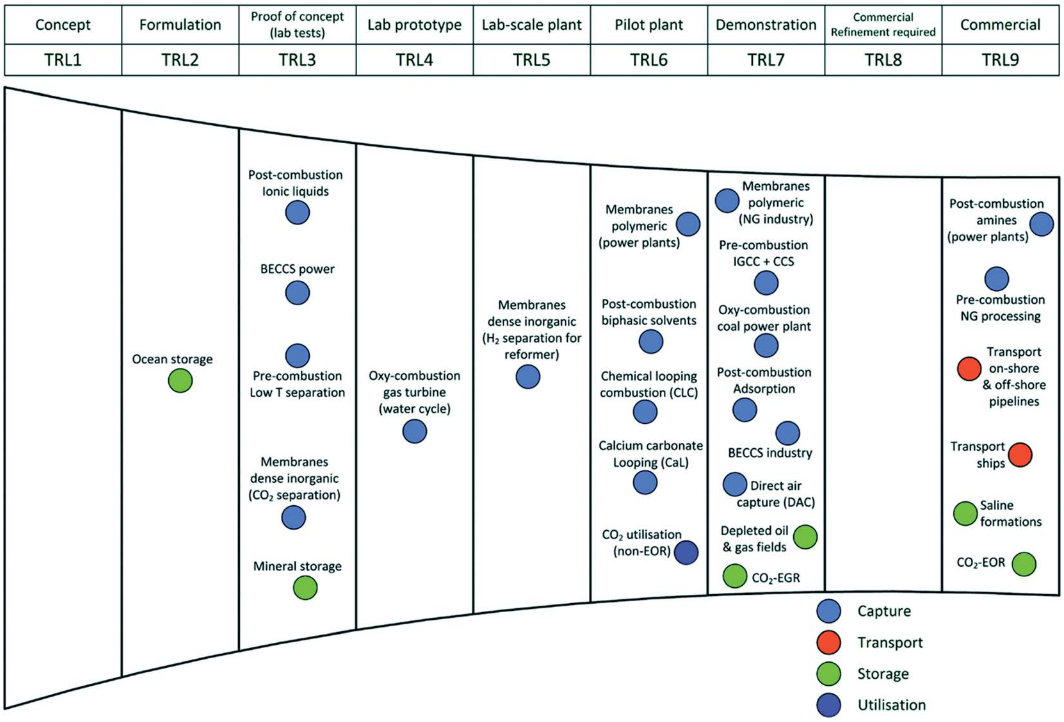

Fig. 13 Carbon collection, storage, and utilization technologies progressing in terms of technology readiness (TRL).[85]

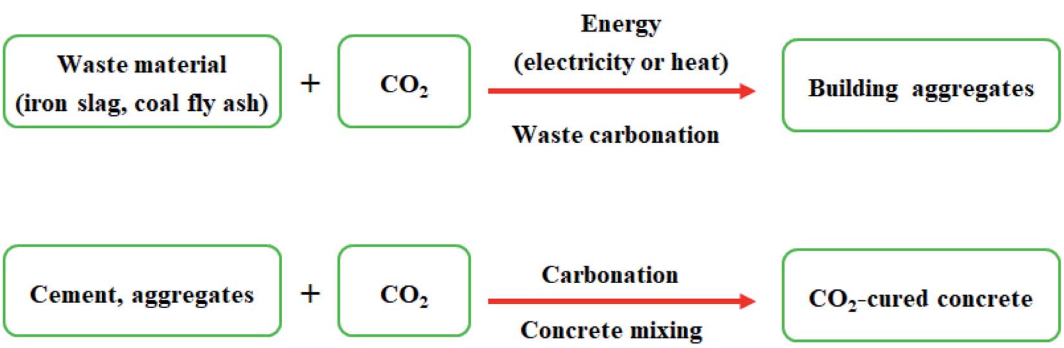

Fig. 14 CO_2 conversion pathways into CO_2-derived building materials (building aggregates or CO_2-cured concrete).

cultivation. The most developed use for increasing yields is using CO_2 with low-temperature heat in industrial greenhouses.

10. Conclusion and future perspective

In summary, one of the key issues facing our world is the rapid increase in atmospheric carbon dioxide (CO_2) concentrations. As a result, considerable interest has been in regulating CO_2 emissions and lowering atmospheric CO_2 concentrations to avoid a worldwide disaster. To reduce CO_2 emissions, various approaches have emerged including:

➢ Developing and converting to environmentally friendly energy sources;

➢ Improving energy efficiency and utilizing current processes;

➢ CO_2 collection and sequestration;

➢ Converting CO_2 to valuable products.

There has recently been a surge in interest in capturing CO_2 emissions and either permanently immobilizing them or chemically converting them into useful goods. This has prompted the creation of many strategies, approaches, and techniques aimed at reducing CO_2 levels through green energy alternatives as well as capturing and converting CO_2 into value-added products.

The use of CO_2 in commercial technology is based mostly on a trade-off between performance and environmental benefits.

Overall, this review is based on containing and utilizing CO_2 using organic–inorganic hybrid materials. The range of potential CO_2 uses involves direct use, by which CO_2 is not chemically altered (non-conversion), and the use of CO_2 by transformation, *via* multiple chemical and biological conversion processes to fuels, chemicals, and building materials. The strategy/technologies come under CO_2-Capture Utilization and Storage (CCUS). CCUS is far better than CCS because the former utilizes/transforms CO_2 into valuable products like ethylene, ethanol, methanol, formic acid, and formaldehyde. The transformations can be achieved using various materials, such as organic–inorganic hybrid-nanocomposites. Contemporary research should primarily focus on sustainable science to immediately address global warming.

The market for CO_2 use is expected to increase, with opportunities related to building materials, and as a carbon source for fuels and chemicals. However, some key factors affect the future market for CO_2-derived products, including scalability, competitiveness and climate benefits, and the visibility of the technologies.

Conflicts of interest

There are no conflicts to declare.

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