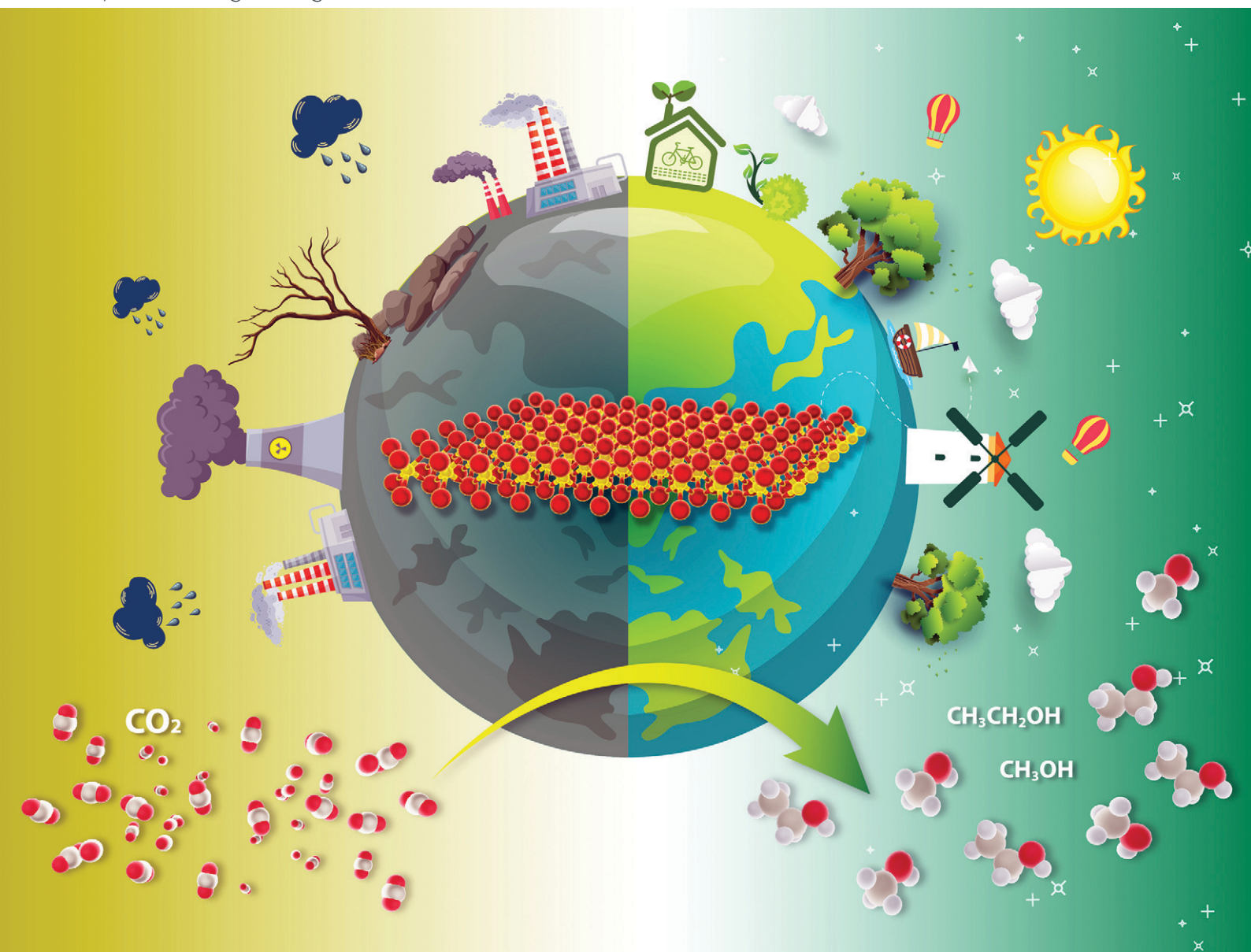


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Impact of structure, doping and defect-engineering in 2D materials on CO₂ capture and conversion

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The investigations on anthropogenic carbon dioxide (CO₂) capture and conversion play a vital role in eradicating global warming and the energy crisis. In this context, defect-engineered two-dimensional (2D) nanomaterials have received much attention in recent years. Herein, the significance of 2D nanomaterials such as graphene, transition metal dichalcogenides, hexagonal boron nitride, MXenes, graphitic carbon nitride, metal/covalent organic frameworks, nanoclays, borophenes, graphynes and green phosphorenes for CO₂ capture and conversion has been emphasized. Further, the intrinsic mechanism of CO₂ adsorption and conversion is discussed in detail. Theoretical and experimental studies among 2D materials highlight that N-doped porous adsorbents based on graphene and MXenes are more suitable for CO₂ adsorption applications. Also, more emphasis is given to outlining and discussing the role of various 2D nanomaterials and their hybrids as photocatalysts, electrocatalysts, photoelectrocatalysts, and thermocatalysts to transform CO₂ into valuable products. Although immense efforts are deployed in developing 2D catalysts for the conversion of CO₂, challenges such as agglomeration, poor yield, difficulties in analysing the 2D structures for catalytic factors, poor knowledge and in-depth understanding of the reaction mechanisms, high cost, etc. limit their large scale production and commercialization. More detailed theoretical and experimental investigations are required to develop 2D nanostructures with optimum properties for large-scale capture and conversion of CO₂.

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1. Introduction

Carbon dioxide (CO₂) is a significant integrant, which accounts for around 65% of total greenhouse gas emissions. The major impacts of global warming due to CO₂ emissions include rising sea levels, ozone layer depletion, dip in water supplies, acidification of the ocean, infectious diseases, unpredictable weather conditions, etc. In this context, carbon capture and storage (CCS) and carbon capture and utilisation (CCU) effectively abate CO₂ emissions.^{1–4} In general, CCS includes various physical and chemical methods and sequestration procedures and so it is implemented *via* different stages such as CO₂ capture, transportation and storage. The standard

techniques to capture CO₂ include pre-combustion, oxy-fuel combustion and post-combustion. The captured CO₂ is compressed, transported and stored into geological reservoirs. In capture processes, the capture and separation of CO₂ is carried out through the adsorption using solvents, solid sorbents, pressure/vacuum swing, membrane and cryogenic separation, and chemical looping combustion technologies. In general, CCU includes: 1) direct utilisation of CO₂ in the food and packaging industries as a carbonating, packaging and preservative material, 2) direct utilisation of CO₂ in enhanced oil and coal-bed methane recovery, 3) conversion of CO₂ into chemicals and fuels where CO₂ could be used as a building block for the production of value-added products, 4) mineral carbonation, and 5) utilization of CO₂ for the cultivation of microalgae for biofuel production⁵ (Fig. 1).

In general, capture technologies are based on aqueous amine sorbents requiring a high regeneration cost and therefore the capture of CO₂ *via* adsorption using solid adsorbents is preferred.³ The adequate adsorption energy, easy CO₂ capture/release process, high selectivity, good thermal and mechanical stability and reusability are the essential criteria for a promising adsorbent. Based on this, several types of

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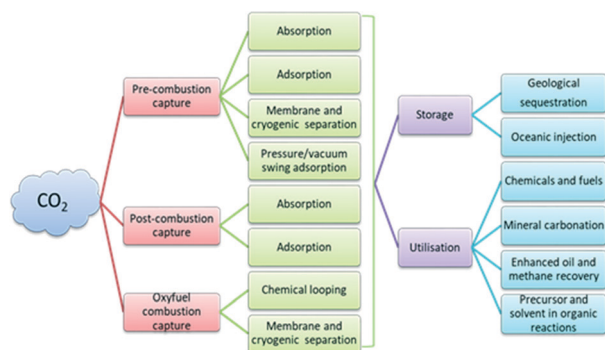


Fig. 1 Schematic of the technologies available for CCS and CCU.

carbonaceous and non-carbonaceous materials such as carbon nanotubes, graphene, activated charcoals, polymeric materials, aerogels, zeolites, metal organic frameworks (MOFs), *etc.* have been proposed to capture CO₂.

The catalytic conversion of CO₂ to valuable products such as methane, carbon monoxide, acetic acid, formic acid, methanol, ethanol, *etc.* is an efficient tool for the effective utilization of the stored CO₂. However, the major hindrance in the conversion of CO₂ to valuable chemicals lies in its thermodynamic inertness and associated high C=O bond dissociation energy (750 kJ mol⁻¹) which is higher than that of C–O, C–C and C–H bonds. The demand for an excessive negative redox potential ($E_{\text{redox}}^{\circ} = -1.90$ eV vs. NHE) for the electron transfer in CO₂ to deliver active species makes



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photocatalytic, electrocatalytic and photoelectrocatalytic conversion tough. On the other hand, thermocatalytic CO₂ conversions are carried out at a high temperature and

pressure with the catalytic support from alkali and alkaline earth metal-based oxides and hydroxides in order to overcome the thermodynamic stability and inertness of CO₂.⁶



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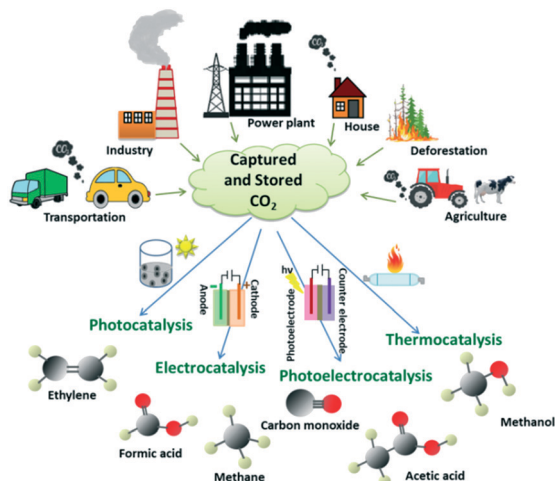


Fig. 2 Different sources of CO₂ emission and the utilisation of captured/stored CO₂ by catalytic conversion to value-added products.

Different sources of CO₂ emission and its effective utilization by various techniques are depicted in Fig. 2.

After the discovery of graphene, the research on 2D nanomaterials has proliferated, and a wide range of materials such as transition metal dichalcogenides (TMDCs), hexagonal boron nitride (h-BN), MXenes, graphitic carbon nitrides (g-C₃N₄), metal/covalent organic frameworks (COFs and MOFs), borophenes, graphynes, green phosphorenes, *etc.*

have been studied. Further, due to the quantum confinement effect in few-layered systems, one can observe exponentially high electronic, optical and mechanical properties when compared to their bulk counterparts. Also, the presence of enduring excitons and trions developed due to the augmented coulombic interactions between charge carriers in semiconducting 2D nanomaterials makes them a prodigious candidate in various disciplines. Further, the enhanced surface area with tuneable physical and chemical properties of 2D materials makes them promising in catalysis, energy storage and optoelectronic applications.^{7–10}

Few-layered 2D nanosheets with unveiled surface atoms have a tendency to escape from the lattice to form defects which in turn can enhance the catalytic performance due to the reduction in the coordination number of the surface atoms. Therefore, the defect engineering of these materials plays a significant role in improving the catalytic performances.¹¹ Due to the aforementioned reasons, the research on catalytic conversion and adsorption of CO₂ by 2D materials is considerable.

Several reviews on CO₂ capture & storage^{1–5,12–16} and its catalytic conversion into valuable products^{17–21} have been published with a prime focus on the technologies. For instance, the recent developments in the use of physisorbents such as carbon nanotubes, graphene, zeolites, silica materials, and MOFs for the removal of CO₂ have been addressed.³ Recently the significance of nanomaterials such

Table 1 Comparison of CO₂ adsorption capacities of 2D materials and traditional solid adsorbents

Type of adsorbent	Materials used	Operating conditions		Adsorption capacity (mmol g ⁻¹)	Ref.
		Pressure (bar)	Temperature (°C)		
2D adsorbents (pristine/doped/defected)	Graphene	11	25	21.6	26
	rGO/N-doped porous carbon composite	5	25	5.77	27
	Fe ₃ O ₄ /graphene	11	25	60	28
	PANI/GO	20	27	3.2	29
	PPy/rGO	1	0	6.8	30
	Porous BN	1–20	25	1.68.3	31
	C doped BN	1	0	~5.5	32
	MXene, M ₂ N	1	727	7.96	33
	Ti ₃ C ₂ T _x	4	25	5.79	34
	g-C ₃ N ₄ nanosheets functionalized with ionic liquid	15	25	42.93	35
Zeolites	Octadecylamine modified MMT	50	25	7.16	36
	Core-shell zeolite-5A@MOF-74	20	25	13.8	37
	Zeolite NaX	1	25	7.04	38
	Li-LSX zeolite	1	60	4.43	39
Activated charcoal	Zeolite SSZ-13	1	25	3.98	40
	Activated carbon derived from nanocellulose	1	0	5.52	41
	N-Doped activated carbon	1	0	5.12	42
	Catalytically activated carbon	1	0	4.36	43
	Physically activated carbon	1	25	3.52	44
MOFs	Activated carbon derived from biomass	1	50	1.1	45
	Amine-functionalized vanadium-based MOF	1	25	1.9	46
	Cu ₃ (NH ₂ BTC) ₂ MOF	0.1	50	1.41	47
	Aluminum trimesate-based MOF	10	25	10.22	48
	In(III)/Pd(II)-Based MOF	1	0	4.1	49
Silica	MOF/GO composite	1	0	6.8	50
	APTES functionalized SBA-15 silica	1	30	1.2	51
	Silica xerogel	7.5	25	1.8	52
	Amine-grafted mesocellular silica foams	1	60	1.54	53

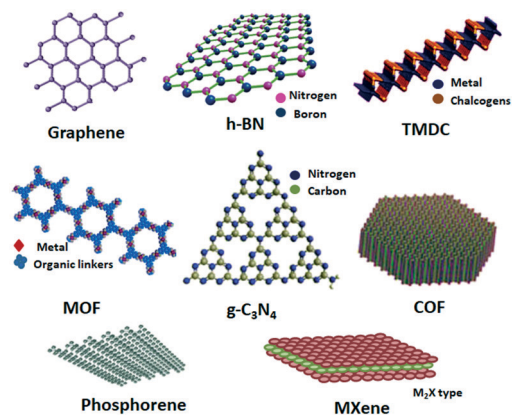


Fig. 3 Structures of common 2D materials used for CO₂ adsorption and conversion.

as MOFs, COFs, zeolites, silicon-based materials, porous organic polymers, layered double hydroxide (LDH)-based materials, metal oxides and nanocarbon materials for the adsorption of CO₂ has been reported.¹ Further, an analysis on the engineering aspects of MOFs for enhanced CO₂ capture and conversion has been reported recently.²² A comparison of CO₂ adsorption capacities of 2D materials with traditional solid adsorbents is given in Table 1. Apart from the CO₂ adsorption analyses, a recent study highlighted the defect engineering, surface modification and hybrid construction strategies to modify 2D nanomaterials for enhanced photocatalytic reduction of CO₂.¹⁷ The structural, electronic, thermodynamic and reactive properties of 2D photoelectrocatalysts were examined by Torrisi *et al.* The major outputs of the study include the investigations on the monolayer phases of selected bulk catalysts and the unconventional chemical behaviour of these materials in CO₂ reduction.²³ It is reported that there are lot of challenges involved in the electrochemical reduction of CO₂ using 2D nanomaterials and the exploration of quantum dots or metal modified porous carbon sheets, heterostructured 2D materials, and inexpensive non-noble 2D metals as electrocatalysts is essential for the future continuation of research in this field.¹¹ In another study, catalytic conversion of CO₂ using heteroatom-doped carbon materials has been addressed.²⁴ A comprehensive study on photoelectrochemical

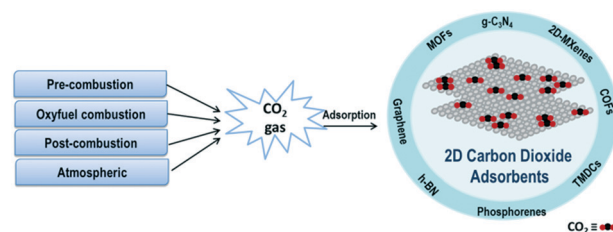


Fig. 5 Schematic of the applications of 2D materials for CO₂ adsorption.

conversion of CO₂ to value-added products was recently reported with special emphasis on the materials for the electrode, mechanisms, and reactor design.²⁵ Nevertheless, there are no comprehensive reports on the utility of 2D nanomaterials for both CO₂ adsorption and conversion by various techniques. Herein, the recent progress and the prominence of 2D materials for CO₂ capture, photocatalysis, electrocatalysis, photoelectrocatalysis, and thermocatalysis have been summarized. This article starts with an overview of different techniques for CO₂ capture and it is followed by a detailed study of recently suggested 2D nanomaterials and their hybrids such as graphene, TMDCs, h-BN, MXenes, MOFs, COFs, g-C₃N₄, nanoclays, borophenes, graphynes, green phosphorene, *etc.* in CO₂ adsorption/conversion applications. The structures of common 2D materials used for adsorption and conversion of CO₂ are given in Fig. 3.

2. Fundamentals of carbon dioxide capture

The technologies behind CCS in power plants include pre-combustion capture, oxy-fuel combustion capture and post-combustion capture.^{2,3,5,15} In pre-combustion capture, as the name indicates, CO₂ is captured and stored before the combustion process of the fossil fuel. It can also be defined as a decarbonisation procedure of traditional fuels such as natural gas or coal before producing energy out of them. The two major events involved in this technology are the formation of synthesis gas (syngas) and steam reforming reactions. In this process, the reaction of the fuel with air or O₂ leads to the formation of syngas comprising CO and H₂.⁵⁴ The purified syngas undergoes a water-gas shift reaction (WGS) where CO is treated with steam to produce CO₂ and H₂. Also, the steam reforming stage delivers H₂ (43%), H₂O (21%), CO (11%) and CO₂ (6%) as major products.⁵⁵ By physical or chemical absorption, adsorption or separation methods, CO₂ is captured and stored for its effective utilisation. In general, the high-pressure CO₂ produced in the pre-combustion technique is compressed and liquefied for storage, transportation, and future use. The H₂ from the steam reforming process can be purified for use in fuel cells or it can be used to produce valuable chemicals. In the oxy-fuel combustion process, the fuel is combusted with pure oxygen to produce flue gas rich in CO₂. The main drawback with this process is the requirement of pure oxygen in massive amounts, which abates its commercialization efforts. Except for this

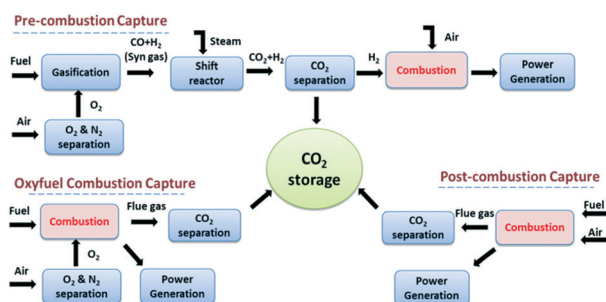


Fig. 4 Schematic of various CO₂ capture processes.

problem, the oxy-fuel combustion process is an attractive one with easy CO_2 separation, reducing the volume of flue gas and NO_x gases with minimal efficacy penalty.^{14,56} Researchers speculated that it would be the best available CO_2 -free power generation method once it got commercialized.⁵⁶ In post-combustion capture, CO_2 is separated or removed from the flue gas after fuel combustion. The exhaust flue gas is purified before the capture of CO_2 to remove the traces of nitrogen, sulphur, and dust. Out of the different technologies described above, post-combustion carbon dioxide capture is the most significant, especially in power plants since the capture unit can be added to the plant even after constructing the power plant.⁵⁷ Fig. 4 represents the different CO_2 capture processes.

Amine-based chemical solvents are used as absorbents to separate H_2 and CO_2 formed in the pre-combustion and post-combustion processes because of their high CO_2 absorption capacity. However, chemical or physical solvents are not encouraged because of their high viscosity, toxicity, flammability, corrosiveness, extensive energy demand especially in the regeneration stage and low H_2 - CO_2 selectivity.^{2,5,57,58} On the other hand, CO_2 uptake using solid adsorbents such as zeolites,⁵⁹ activated carbons,^{60,61} and MOFs⁶² is attractive due to their high CO_2 adsorption efficiency, selectivity, low energy requirements, easy recovery and stability.^{3,63} The curtailed adsorption efficiency of MOFs and activated carbons at elevated temperature is a major issue with the pre-combustion process.² Therefore CO_2 adsorbents based on lithium silicate nanosheets⁶³ and Nd-doped lithium silicate⁶⁴ were introduced as adsorbents.

The techniques for CO_2 adsorption using solid materials include pressure swing adsorption (PSA), vacuum swing adsorption (VSA), temperature swing adsorption (TSA), moisture swing adsorption (MSA), electric swing adsorption (ESA) and temperature vacuum pressure swing adsorption (TVPSA) and out of these, the most commonly used techniques are PSA, VSA and TSA.³ In the PSA technique, pressure higher than 1 bar is used, while in VSA, pressure lower than 1 bar is used and the regeneration of the adsorbent is done by reducing the pressure.¹² In TSA, the



Fig. 6 Schematic of the synthesis of the N-doped porous rGO composite for CO_2 adsorption and supercapacitor applications. "Reproduced from ref. 27 with permission from Elsevier, copyright 2021".

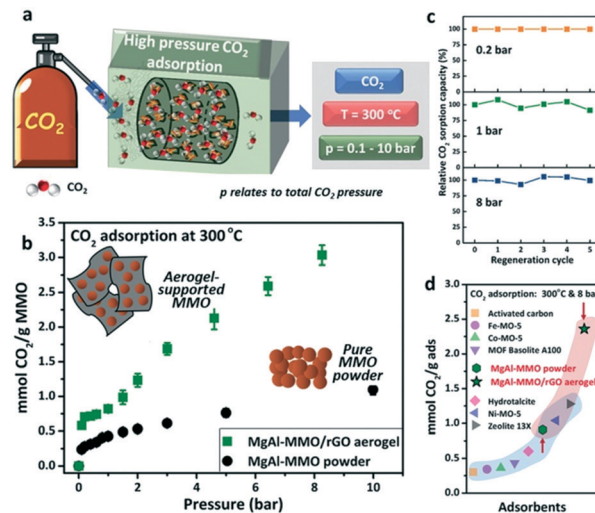


Fig. 7 CO_2 adsorption by MgAl-MMO/rGO aerogels at high pressure and temperature (a); CO_2 adsorption isotherms in a pressure range of 0.2 to 10 bar (b); relative CO_2 adsorption capacities at 0.2, 1, and 8 bar CO_2 pressure (c); comparison of sorption capacities with other reports (d). "Reproduced from ref. 108 with permission from Wiley-VCH, copyright 2020".

adsorbent bed is heated to elevate the adsorption temperature and then cooled for desorption. In general, for the separation of CO_2 from the flue gas, VSA is considered more efficient than PSA because applying pressure to the large area feed is economically not viable.¹² Usually, in CO_2 capture by the adsorption process, a spherical column is packed with the adsorbent and CO_2 containing gas is passed through the column.¹ During the adsorption process, when gas molecules are in the close vicinity of the adsorbent, they got attracted to the electronic environment of the adsorbent surface. The gas molecule–solid surface interaction can result in the reduction of the free energy of the surface, and therefore, more and more gas molecules can be accumulated on the solid surface before adsorption.³ The adsorption process can be physical or chemical depending on the type of interaction between the adsorbent and adsorbate. Due to the absence of chemical bond formation in physical adsorption, the energy penalty for the regeneration of CO_2 is more diminutive. In physical adsorption, along with the van der Waals attraction of CO_2 and the adsorbent, electric quadrupole moment (EQM)-electric field gradient interactions are also taking place. The value of EQM is the main factor deciding the selectivity of gases and therefore, carbon dioxide molecules with a high EQM value can be adsorbed on the solid surface compared to nitrogen molecules.³ The necessary criteria to be satisfied by the material for an economical and operational implementation of CO_2 capture include a significant CO_2 adsorption capacity ($\sim 3\text{--}4 \text{ mmol g}^{-1}$), high CO_2 selectivity, fast adsorption/desorption kinetics, adequate mechanical strength, low heat of adsorption, and low cost. Nanomaterials are promising candidates for the adsorption and catalysis of CO_2 because of their large surface-to-volume ratio and the presence of a

considerable number of reactive sites. Besides, the affinity of nanomaterials towards the target molecules can be enhanced by surface modification,^{65,66} making them interesting for CO₂ capture and conversion applications.

3. Two-dimensional nanomaterials for CO₂ adsorption

Recently, 2D materials such as graphene (or reduced graphene oxide (rGO)),^{67–72} molybdenum disulphide (MoS₂),^{73–76} h-BN,^{77–81} MXenes,^{33,82} 2D MOFs & COFs,^{8,21,83,84} g-C₃N₄,⁸⁵ phosphorenes, nanoclays, *etc.* (Fig. 5) have been used as adsorbents for CO₂ capture.⁸⁶

3.1 Graphene

Graphene is an excellent 2D material with unique features such as zero bandgap energy, transparency (97.7%),⁸⁷ high concentration of charges (10^{13} cm^{-2}),⁸⁸ charge mobility,⁸⁹ current density ($1.18 \times 10^8 \text{ A cm}^{-2}$),⁹⁰ mechanical strength (0.2 TPa)⁹¹ and thermal conductivity ($\sim 5000 \text{ W mK}^{-1}$).⁹² The common problem in TSA/VSA/PSA processes for CO₂ capture is the temperature instability of the adsorbent, especially in TSA mode. Mechanical disintegration of the adsorbent due to the tight packing of the adsorbent column and the subsequent reduction in the surface area of the adsorbent is an associated concern. Because of the excellent mechanical strength, thermal conductivity and stability of graphene, the compact packing of the adsorbent column is stable even after repeated or cyclic processes.⁹³ This makes graphene-based materials a wonderful candidate to substitute for traditional adsorbents. The main factors deciding the gas adsorption efficiency of graphene are its ultra-microporous structure, availability of active sites, high specific surface area, and the presence of functional groups for better interaction between the adsorbate and adsorbent. The gas adsorption capacities of pristine graphene oxide (GO) or reduced graphene oxide (rGO) can be further improved by various physical⁹⁴ or chemical activation processes^{95–97} in which the porosity of the material can be tuned for CO₂ capture. Therefore, top-down and bottom-up techniques such as the use of electron beams, nanosphere lithography, barrier-guided chemical vapour deposition, catalytic hydrogenation, photocatalytic oxidation, chemical etching, *etc.* can be employed to produce and control the lattice⁹⁸ of graphene to improve CO₂ adsorption capacities. Similarly, the removal or introduction of defects in the lattice of graphene can cause an enhancement in CO₂ adsorption capacity⁹³ by creating pores with suitable radii to accommodate CO₂ gas molecules. In another study, CO₂ adsorption states on monolayer epitaxial graphene grown on a SiC (0001) substrate at 30 K were analysed by temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT).⁷¹ In this, CO₂ gas was introduced onto the sample surface through a pulse gas dosing system. The coverage of CO₂ on graphene was determined by XPS

and TPD. The analysis showed a physisorption behaviour for CO₂ on graphene, confirming the previous results reported.^{26,99} From the binding energies of CO₂ in C 1s and O 1s of XPS spectra, they have inferred that the adsorption and desorption of CO₂ on graphene is in the physisorption regime and the nature of interaction between CO₂ and graphene was studied by DFT calculations.⁷¹ Recently, adsorption-induced clustering of CO₂ on graphene nanosheets was studied through computational analysis.⁶⁸ The results showed that above a particular amount of surface coverage, the CO₂ gas molecules that are selectively adsorbed tend to form clusters of different sizes with the possible formation of dimers or trimers. The reason for this cluster formation is the quadrupole–quadrupole interaction between CO₂ molecules and this was facilitated by the favourable alignment of atoms on different molecules with opposite partial charges.⁶⁸ To model graphene they have selected coronene (C₂₄H₁₂) and circumcircumcoronene (C₉₆H₂₄), and computational analyses were carried out by DFT (B3LYP-D/6-31+G*) and molecular dynamics (MD).

The gas adsorption properties of carbon-based adsorbents can be further improved by doping with heteroatoms such as nitrogen (N), sulphur (S) or boron (B) to enhance the molecular interactions with CO₂.^{100–102} Later, the role of boron moieties in the CO₂ adsorption ability of borane modified rGO was examined *via* experimental and theoretical calculations.¹⁰³ Through FTIR analysis, the physisorption of CO₂ on boron doped rGO was evidenced and according to them, by introducing substitutional boron defects, the charge distribution can be altered to yield good selectivity to the nearest carbon, which is adjacent to the defected site. An adsorption capacity of 1.81 mmol g^{-1} was observed at 1 atm and 25 °C. Later, the dual doping of graphene with N and S and theoretical calculations using DFT and *ab initio* thermodynamics were carried out.¹⁰⁴ Superior CO₂ adsorption performance and better selectivity for CO₂ over N₂ were also predicted in their study. CO₂ adsorption in N-doped rGO blended with activated charcoal was examined in another work. The maximum adsorption capacity of 3.81 g g^{-1} at 7 bar and 75 °C was obtained for the combination of activated charcoal and N-doped rGO (50NRGO) in the ratio of 50:50, and the CO₂ adsorption capacity was directly correlated with the enhanced surface area ($9916.88 \text{ m}^2 \text{ g}^{-1}$) of the sample.¹⁰⁵ Recently, N-doped few-layer graphene/Pebax mixed matrix membranes (MMMs) were developed for CO₂ capture.¹⁰⁶ The role of N-doping on few-layer graphene in enhanced CO₂ capture, selectivity, diffusivity, solubility, and permeability was analysed through simulation studies and was well correlated with the experimental findings. In a study, a novel rGO/N-doped porous carbon (NPC) composite (surface area of $865 \text{ m}^2 \text{ g}^{-1}$) was synthesized by a one-pot hydrothermal and KOH activation method with a CO₂ adsorption of 5.77 mmol g^{-1} at 298 K and 500 KPa. The CO₂ adsorption analysis without N-doping resulted in a reduced CO₂ adsorption of 2.07 mmol g^{-1} , and this shows the relevance of N atom doping in the graphene-based system.

CO₂ adsorption analysis reveals that the adsorption properties of the samples were increased with an increase in activation temperature up to 600 °C and a GO addition of 1%. The kinetic studies revealed that the isotherms were well fitted with the Redlich–Peterson isotherm model, indicating the chemical and physical adsorption of CO₂ in rGO/NPC samples.²⁷ Fig. 6 shows the schematic for the preparation of the rGO/N-porous composite for CO₂ adsorption and supercapacitor applications. In another work, the collective effects of the availability of pores with suitable size and the presence of functional groups (N, P, S, and O) on graphitic structures on the CO₂ adsorption behaviour were analysed using Grand Canonical Monte Carlo simulation (GCMC) and DFT.¹⁰⁷

Aerogels are a new class of soft sponge-like materials with a large surface area, high porosity, and low density with excellent environmental applications. In general, graphene-based aerogels were prepared by the wet chemical method from graphene oxide (GO), which enables the formation of a 3D network in aqueous solutions through lyophilization, followed by reduction to form reduced graphene oxide aerogels with partially restored graphitic properties.¹⁰⁸ Metal nanoparticle incorporating hybrid graphene aerogels showed maximum performance in various applications. Recently, a novel mixed metal oxide (MMO)/rGO aerogel was studied for CO₂ at high pressure (8 bar) and high temperature (300 °C). A sorption capacity of 2.36 mmol g⁻¹ was observed for MgAl MMO/rGO aerogels, whereas MgAl MMO powder showed a sorption capacity of 0.91 mmol g⁻¹.¹⁰⁸ Fig. 7 shows the CO₂ adsorption at high pressure and temperature of MgAl MMO/rGO aerogels. A novel graphene-based semi-coke-like porous and nitrogen-rich layered sandwich material was examined for CO₂ adsorption. The material with a surface area of 701.53 m² g⁻¹ and 74% microporosity showed an adsorption capacity of 7.11 mmol g⁻¹ at 30 bar and 298 K with probable physisorption of CO₂. A better CO₂/N₂ selectivity was observed because of the presence of N functionalities added into the system and N functionalities were introduced by the nucleophilic substitution of the semi-coke-like material with ethylenediamine (EDA).¹⁰⁹ A polyethylenimine modified GO (GEPM) sheet with high porosity, surface area and 3D structure was reported. The material showed a CO₂ adsorption capacity of around 11.2 wt% at 1.0 bar and 273 K, which was higher when compared to GO and hydrothermally reduced graphene (HTG). The high CO₂ adsorption capacity of GEPM was mainly due to the presence of basic sites since the effect of the surface area on the CO₂ adsorption was not correlated through their study. For instance, the BET surface area of GEPM, HTG, and GO was 476 m² g⁻¹, 876 m² g⁻¹ and 31 m² g⁻¹, respectively, and the corresponding CO₂ uptake of these materials was 11 wt%, 8.1 wt% and 7.5 wt%. Even though HTG possesses a high surface area, the CO₂ adsorption capacity of HTG was comparable with GO. However, the CO₂ intake of GO was justified by the presence of oxygen-containing functional groups and surface heterogeneity associated with GO.¹¹⁰ In another work,

heterostructures containing BN(OH)_x nanosheets with B and N co-doped graphene aerogels (BN-GA) were proposed for CO₂ adsorption.¹¹¹ BN(OH)_x nanosheets were added as a swelling agent and to prevent the restacking of GO during the solvothermal synthesis, whereas the doping with B and N imparts more adsorptive sites by destroying the electrical neutrality of C. BN-GAs with mesoporous structures and a surface area of 169.9 m² g⁻¹ showed a CO₂ adsorption of 2.1–2.9 mmol g⁻¹ at 273 K and 1.0 bar.

As discussed earlier, N doping of graphene can enhance the CO₂ adsorption due to the chemical interaction of CO₂ gas molecules with N doped adsorbents. Highly efficient traditional sorbents are only amine systems, and so the introduction of the conducting polymer polyaniline (PANI) to graphene is of interest because of the presence of primary and secondary amine moieties.^{29,112}

The preliminary investigation on CO₂ adsorption using PANI/HEG (hydrogen exfoliated graphene) was reported by Mishra *et al.*, and they have achieved adsorption capacities of 75, 47 and 31 mmol g⁻¹ at 11 bar pressure and at 25, 50 and 100 °C, respectively. The physical and chemical adsorptions of CO₂ were evidenced by FTIR spectroscopy. The PANI/HEG sorbent showed good cyclability; the capacity of the reused sorbents was only 2–3% lower than that of the fresh sorbent.⁸² Later, physicochemical adsorption of CO₂ on the Fe₃O₄/HEG hybrid was reported by the same group.²⁸ Similar to their previous results, CO₂ adsorption capacities of 60, 35, and 24 mmol g⁻¹ were observed at 11 bar pressure and at 25, 50, and 100 °C, respectively, and the physicochemical adsorption of CO₂ on the solid adsorbent was identified using FTIR spectra. Though the surface area of Fe₃O₄/HEG (98.2 m² g⁻¹) is lower when compared to that of HEG (443 m² g⁻¹), the enhanced CO₂ adsorption in Fe₃O₄/HEG was attributed to the chemical interaction between Fe₃O₄ and CO₂, as evidenced from FTIR analysis. Later, research on the CO₂ adsorption ability of graphene oxide (GO) hybridized

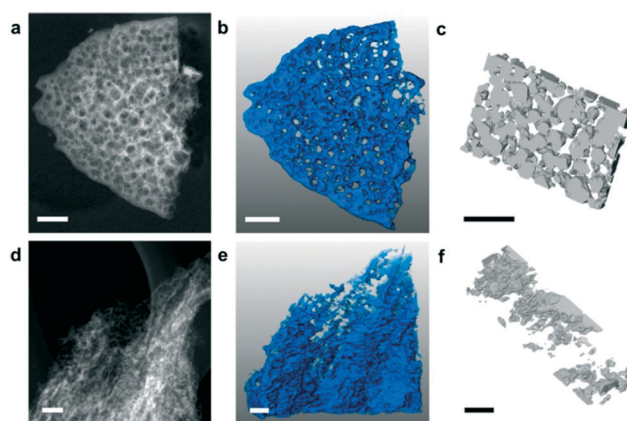


Fig. 8 STEM images of BN synthesized using urea (BN-U5) (a) and BN synthesized using urea and melamine (BN-MU1:5) (d); 3D tomography of BN-U5 (b) and BN-MU1:5 (e); 3D reconstruction of pores of BN-U5 (c) and BN-MU1:5 (f). "Reproduced from ref. 31 with permission from American Chemical Society, copyright 2017".

with Fe_3O_4 and PANI was carried out and it showed an increment in adsorption capacity of GO from 0.25 mmol g^{-1} to 2.3 mmol g^{-1} by the incorporation of Fe_3O_4 and then to 3.2 mmol g^{-1} after the introduction of PANI to the binary system of Fe_3O_4 and GO. The improved CO_2 adsorption capacity of the ternary system is mainly attributed to the increased porosity and micropore volume of graphene oxide due to the functionalization with Fe_3O_4 and PANI. The low adsorption energy of the hybrid hints at the physisorption of CO_2 (ref. 29), while chemisorption of CO_2 on the adsorbent was not evidenced through their study. Similar to PANI, polypyrrole (PPy) was also introduced to graphene for CO_2 adsorption. N-Doped porous carbon obtained *via* chemical activation of PPy/graphene composites using potassium hydroxide solution is reported in a study. The chemical activation led to the N-doping of porous carbon in PPy, while the graphene units remain intact. PPy/graphene adsorbents with different weight percentages of GO were synthesised by *in situ* chemical polymerisation of pyrrole in the presence of GO using ammonium persulphate as an oxidant and the subsequent reduction of GO hybrids with hydrazine yielded PPy/graphene hybrids. The chemical activation using KOH solution was carried out at different temperatures (400, 500, 600, and 700°C). The maximum CO_2 adsorption capacity of 4.3 mmol g^{-1} was observed for the adsorbents activated around 600°C , and this is due to the formation of microporous structures with a pore size of 1.72 nm , which in turn can lead to a better adsorption and adsorbate-adsorbent interaction.¹¹³ In a similar study, a chemically activated porous PPy/rGO was reported. Potassium citrate was used as an activation agent at 700°C and the porous PPy/rGO material with a BET surface area of $1650 \text{ m}^2 \text{ g}^{-1}$ and 92% microporosity showed an adsorption capacity of 6.8 mmol g^{-1} at 0°C and 760 mm Hg .³⁰

3.2 Transition metal dichalcogenides

Transition metal dichalcogenides (TMDCs) are semiconductors of the type MX_2 , where M is the transition metal atom such as Mo or W and X is a chalcogenide atom like S, Se or Te. TMDCs are a promising alternative to graphene because of their direct bandgap, robustness, and atomic level thickness with 2D characteristics.¹¹⁴ Recently, various strategies are adopted for the synthesis of TMDs such as plasma-assisted synthesis,¹¹⁵ mechanical exfoliation,¹¹⁶ ion intercalation assisted liquid exfoliation,¹¹⁷ wet chemical synthesis, chemical vapor deposition (CVD),¹¹⁸ *etc.* Among TMDCs, MoS_2 has been widely used in various environmental applications such as gas adsorption and subsequent reduction to valuable chemicals. The initial attempt on CO_2 capture based on a 2D MoS_2 membrane was carried out by Shen *et al.* and they have reported MoS_2 incorporating Pebax polymer mixed matrix membranes with good CO_2 permeability and selectivity. MoS_2 with stronger adsorption energy for CO_2 (205 meV) than N_2 (137 meV) easily got adsorbed. The diffusion or permeation through the

membrane occurs because of the dissolution of the adsorbed gas in the membrane.¹¹⁹ In a similar way, studies on a defect-free Pebax- MoS_2 membrane obtained by solution casting with different amounts of MoS_2 loading from 0 wt% to 5.66 wt% were explored. The highest CO_2 permeability of 67.05 Barrer and CO_2/N_2 selectivity of 90.61 were observed for the 4.67 wt% MoS_2 incorporating Pebax membrane. Further, the molecular simulation studies proved that the CO_2 solubility and selectivity of the mixed matrix membrane were significantly improved after the addition of MoS_2 due to its high affinity towards CO_2 .¹²⁰ Later, the influence of the electric field on the adsorption behaviour of CO_2 on the MoS_2 monolayer was analysed¹²¹ by carrying out a systematic investigation using DFT calculations on various parameters such as interactions of CO_2 with MoS_2 in the absence/presence of an electric field, reaction mechanisms of adsorption, optimization of electric fields for CO_2 capture and finally a comparison with N_2 adsorption by the adsorbent. The DFT calculation showed that an electric field can alter the interaction levels between the adsorbate and adsorbent. For instance, by applying of an electric field of 0.004 a.u. , CO_2 showed strong interaction with MoS_2 . However, this interaction was least in the absence of an electric field and this was evidenced by the easy release of CO_2 once the electric field was turned off. In contrast, the presence or absence of an electric field did not affect the capture of N_2 , and this indicates that MoS_2 can act as a selective adsorbent for CO_2 , especially in the presence of an electric field during the post-combustion process where CO_2 and N_2 are the major components of the combustion gas.¹²¹ In another study, Cu nanoparticle incorporating MoS_2 for CO_2 adsorption and catalytic reduction reactions was analysed. The hybrid made at a particular concentration of Cu and MoS_2 ($\text{Cu}/\text{MoS}_2\text{-1}$) showed better adsorption performance ($0.44 \text{ cm}^3 \text{ g}^{-1}$) than other hybrids [$\text{Cu}/\text{MoS}_2\text{-2}$ ($0.41 \text{ cm}^3 \text{ g}^{-1}$), $\text{Cu}/\text{MoS}_2\text{-3}$ ($0.27 \text{ cm}^3 \text{ g}^{-1}$)] and bare MoS_2 ($0.22 \text{ cm}^3 \text{ g}^{-1}$). The enhanced CO_2 adsorption in the hybrids was explained by the additional adsorption of CO_2 molecules on the surface of Cu nanoparticles.¹²² Further, a theoretical approach for the CO_2 adsorption on the MoS_2 monolayer was made and the DFT calculations reveal the different occupancies of CO_2 molecules on the 2D monolayer surface with low energy cost ($\Delta E = -57.9 \pm 2.5 \text{ kJ mol}^{-1}$) and this points to the adsorbate's physisorption on the adsorbent. The interaction energies calculated for MoS_2 were larger when compared to graphene, which hints at the suitability of MoS_2 nanosheets over graphene for greenhouse gas adsorption applications. Also, from simulation studies, they have inferred that the adsorption process is controlled by van der Waals interactions where CO_2 molecules were arranged parallel to the monolayers of the MoS_2 surface.⁷⁶ Cho *et al.* have compared the NO_2 gas adsorption on MoS_2 which is aligned in three different ways such as horizontally aligned MoS_2 with an exposed basal plane, vertically aligned MoS_2 with exposed edges and a mixture of horizontally & vertically aligned MoS_2 layers (exposed basal plane and edges)

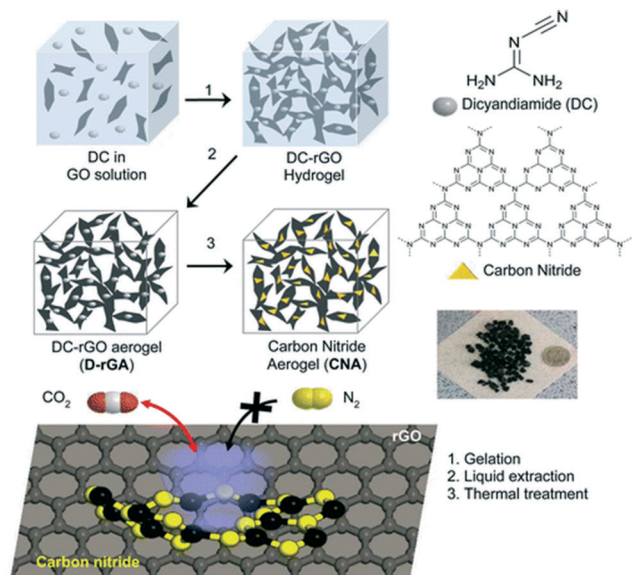


Fig. 9 The preparation of carbon nitride aerogels for the selective adsorption of CO₂ over N₂. "Reproduced from ref. 135 with permission from American Chemical Society, copyright 2015".

synthesized using a CVD process. They reported that gas adsorption is highly dependent on the alignment of MoS₂ layers, and a significantly higher gas adsorption was observed in edge sites of vertically aligned MoS₂ compared to MoS₂ with an exposed basal plane. The experimental results were well correlated with DFT calculations, where strong NO₂ binding energies near the edge sites of MoS₂ were observed.¹²³ Based on these results, researchers had concluded that the presence of S-vacancies or defects on the MoS₂ surface is desirable for the adsorption of non-polar gases. Also, they stated the importance of tuning the surface of the adsorbent to obtain reactive edge sites on MoS₂ flakes to target a specific gas of interest.⁷³ For this, they have investigated the effect of nitrogen doping on defective and non-defective MoS₂ surfaces for CO₂ adsorption properties. MoS₂ with 1S vacancy and MoS₂ with ternary N doped 1Mo vacancy samples showed strong CO₂ binding energies (0.908 eV and 1.818 eV) and this reveals that the defective and N doped MoS₂ can have enhanced CO₂ adsorption due to the covalent and electrostatic interactions with the gas molecule. Conversely, the defect-free MoS₂ showed weak van der Waals interactions with CO₂ leading to poor adsorption characteristics. Moreover, the selective adsorption of CO₂ over N₂ was identified for the defective and N-doped MoS₂, and so the importance of heteroatom-doping and defects in the structure of MoS₂ for the enhanced molecular adsorption of CO₂ was pointed out.⁷³ A theoretical investigation of the gas adsorption behaviour on MoSe₂ was examined using DFT calculations. The results indicated the poor adsorption of CO₂ and CO gases by MoSe₂ monolayers, whereas the material was found to be more sensitive towards the adsorption of NO₂ and NO. The high selectivity of MoSe₂ towards NO₂ and NO was attributed to the distinct charge

transfer between the adsorbate and adsorbent¹²⁴ and this indicates the inability of MoSe₂ for CO₂ adsorption applications.

3.3 Hexagonal boron nitride

Hexagonal boron nitride (h-BN) nanosheets are 2D structures and have excellent electrical, thermal, and optical properties with broad applications. A few layered h-BN synthesised from boric acid and urea through a chemical route with a high surface area (927 m² g⁻¹) was found beneficial for CO₂ capture applications.¹²⁵ Porous and few layered h-BN nanosheet adsorbents from MgB₂ and NH₄Cl with a good micropore volume showed a CO₂ adsorption of ~10 cc g⁻¹ with a CO₂/N₂ selectivity of 26.3.¹²⁶ The BN adsorbent with a surface area of 235 m² g⁻¹ showed the maximum CO₂ adsorption at 760 Torr at 298 K. Marchesini *et al.* have investigated the CO₂ adsorption capacity of BN synthesized by using single and multiple N precursors. For instance, BN synthesized using urea showed a microsponge-like structure with the existence of nanometre ranging mesopores, whereas BN synthesized using urea and melamine showed the presence of a crumbled nanosheet with inhomogeneous small mesopores. The scanning transmission electron microscopy (STEM) tomography images of the BN samples are shown in Fig. 8. The high surface area (1900 m² g⁻¹) BN sample prepared by using multiple N precursors showed a CO₂ adsorption of 1.6 mmol g⁻¹ at 1 bar, 25 °C and 8.3 mmol g⁻¹ at 20 bar, 25 °C. They have also evaluated the CO₂ sorption capacity of pelletized and non-pelletized BN samples and it was about 1.1 mmol g⁻¹ and 1.6 mmol g⁻¹, respectively, at 1 bar and 25 °C.³¹ Further, the effect of C doping on BN sheets was demonstrated by the preparation of a novel C-doped BN with significant CO₂ adsorption properties. A CO₂ uptake of ~2.9 mmol g⁻¹ was observed for BN while C-doped BN showed an adsorption of ~5.5 mmol g⁻¹ at 273 K and 1 bar.³² The effect of charge on the BN nanomaterial on CO₂ adsorption was investigated by DFT calculations. BN with a negative charge showed strong interaction with CO₂ while spontaneous desorption of CO₂ from the BN surface was evidenced once the electrons were removed from the system. The charged BN showed high selectivity for CO₂ capture from a gas mixture containing CO₂/CH₄/H₂.⁸¹ Similarly, the effect of an electric field on CO₂ adsorption and selectivity was analysed using DFT calculations. The application of a vertical electric field increases the binding energy of CO₂ on h-BN sheets and it was inferred that the h-BN is a suitable candidate for CO₂ adsorption from the gas mixture containing H₂, CH₄, N₂, CO, and H₂O, especially in the presence of an electric field.⁸⁰ In a study, the incorporation of the BN nanomaterial in PVA, and subsequent foam formation by freeze drying for CO₂ adsorption was demonstrated. The high gas adsorption of 340% was ascribed to N functional groups and high surface area associated with the BN-PVA foam.⁷⁸ In another study, the interactions between the gas and the adsorbent surface

and the mechanism of CO₂ adsorption on h-BN nanosheets were analysed using DFT and MD calculations.⁷⁷ The report claims the physisorption of CO₂ gas molecules on h-BN nanosheets. The significance of tuning and functionalising the pores of the adsorbent to improve the CO₂ adsorption is highlighted in their study.

3.4 MXenes

MXenes are another class of 2D materials that have received significant attention beyond graphene, TMDCs, and h-BN. They are early transition metal carbides and carbon nitrides such as Ti₂AlC, Ti₃AlC₂, Ti₃C₂, Ti₂C, Nb₂C, V₂C, Ti₃CN, *etc.* with metallic conductivity and strong ionic, covalent and metallic bonds.¹²⁷ The general formula for MXene is M_{n+1}X_nT_x (*n* = 1, 2, 3), where M is the early transition metal, X is carbon or nitrogen, and T represents terminal functional groups. MXenes are produced by selective etching of group III A or IV A elements using hydrofluoric acid. Due to the toxic nature of HF, other environmentally friendly methods adopted are alkali treatment,¹²⁸ electrochemical etching,¹²⁹ Lewis acid etching,¹³⁰ *etc.* The CO₂ uptake by 2D MXene carbides (M₂N) was analysed by DFT calculations, and a gas loading capacity of ~2.3 to 7.96 mol kg⁻¹ at low CO₂ partial pressure and high temperature was achieved and this hints at its practical utility for CO₂ adsorption directly from the atmosphere.³³ The relation between the microstructure of carbide MXenes (Ti₃C₂T_x, V₂CT_x) and the CO₂ adsorption properties was analysed.³⁴ DMSO intercalated Ti₃C₂T_x with a surface area of 66 m² g⁻¹ and high volume capacity of 502 Vv⁻¹ showed a CO₂ adsorption capacity of 5.79 mmol g⁻¹ at 298 K and 0–4 MPa. Similarly, the effect of the thickness of carbide MXenes was analysed by DFT calculations, and the results confirmed the efficiency of these materials for CO₂ capture with a minor influence from the thickness of the

material. Also, the surface of different carbide MXenes (M_{n+1}C_n; *n* = 1 to 3, M = Ti, Zr, Hf, V, Nb, Ta, Mo, and W) was analysed and the largest adsorption energy was observed for the system with a d² electronic configuration and then for d³ and d⁴ systems.⁸² A similar type of DFT calculation on CO₂ adsorption and conversion based on M₂C type MXene was carried out and the results indicate that the presence of a surface lone pair of electrons is the driving force for the adsorbate–adsorbent interactions.¹³¹ In another study, the adsorption/desorption rate of CO₂ on 2D M₂N materials (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W) was analysed using DFT calculations. The study evidenced the existence of adsorbed anionic CO₂^{δ-} species with significant MXene to CO₂ charge transfer. The considerable adsorption energy (–3.13 eV) makes M₂N more suitable than M₂C for efficient CO₂ capture and storage. Due to the high electronegativity N layer, M₂N can withdraw a higher charge density from the metal than the C layer in M₂C, and this implies a reduction in the charge transfer from the metallic layer of MXene to CO₂ in M₂C type MXene.¹³² In a study, effective adsorption of CO₂ gas (≈12 mol kg⁻¹) on individual sheets of 2D Ti₃C₂T_x carbides was reported.¹³³ Recently, the CO₂ separation capacity of the Ti₃-C₂T_x incorporating Pebax mixed matrix membrane was compared with a GO filled membrane. Around 20 wt% of Ti₃-C₂T_x was able to disperse in the matrix due to the good level of interfacial interactions arising from the presence of polar groups present in MXene. In contrast, only 5 wt% of GO was able to be incorporated in the Pebax matrix. The high level loading of MXenes was found to be beneficial especially under humid reaction conditions, but it was not promising under dry conditions.¹³⁴

3.5 Carbon nitride

Graphitic carbon nitride (g-C₃N₄) has received tremendous attention because of its excellent properties and similarities with 2D graphene and it consists of hexagonally organized heptazine (tri-*s*-triazine) units linked through tertiary amines. The conventional exfoliation of carbon nitride is of less interest because of the tightly packed heptazine units.¹³⁵ However, the synthesis of g-C₃N₄ through the direct pyrolysis of N-rich precursors like urea makes it more approachable.⁸⁵ Since the nitrogen species in g-C₃N₄ is of low alkalinity, the interaction between g-C₃N₄ and CO₂ is weak, and the use of pristine g-C₃N₄ for CO₂ adsorption application is limited. However, amine functionalization *via* chemical grafting or physical impregnation can lead to more adsorbent–adsorbate interactions. For instance, the physical impregnation of polyethyleneimine (PEI) with g-C₃N₄ was analysed for CO₂ adsorption applications. A CO₂ adsorption capacity of 3.77 mmol g⁻¹ was observed for PEI-C₃N₄ composites at 100 °C and ambient pressure, which was superior to pristine g-C₃N₄. The study inferred that the presence of amine groups on the composite surface, not the surface area, plays a major role in deciding the CO₂ adsorption capacity.⁸⁵ Reduced graphene oxide aerogel was reported as a template platform for the

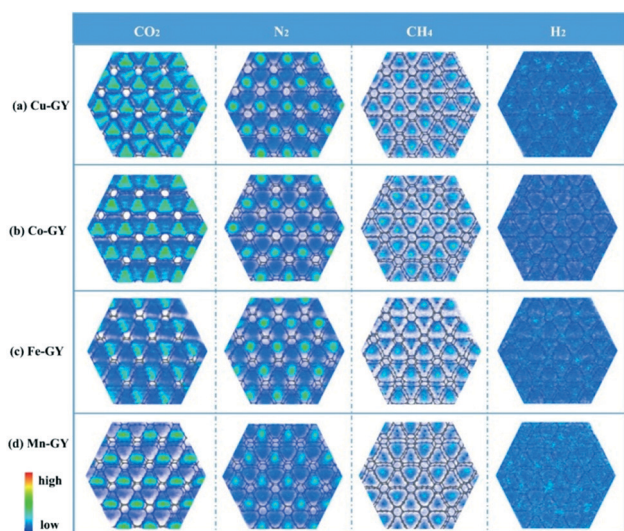


Fig. 10 CO₂, N₂, CH₄ and H₂ gas distributions on TM-GY. “Reproduced from ref. 147 with permission from Elsevier, copyright 2021”.

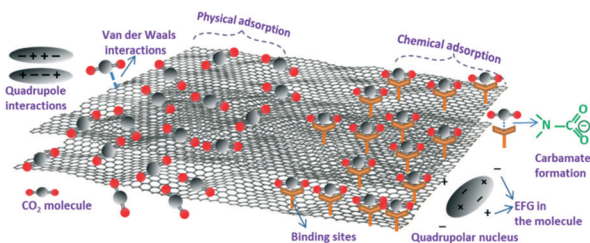


Fig. 11 Interaction between CO₂ and the adsorbent during physical and chemical adsorption.

growth of porous carbon nitride with a good surface area for CO₂ adsorption applications. The gelation of the carbon nitride precursor (dicyandiamide) incorporating graphene oxide solution, and the subsequent solvent exchange, liquid extraction and thermal treatment resulted in the formation of carbon nitride-graphene oxide aerogels. The schematic of the synthesis of carbon nitride aerogels for selective CO₂ capture is shown in Fig. 9. A CO₂ adsorption capacity of 0.43 mmol g⁻¹ at 0.1 bar and 300 K was observed for these aerogels with excellent regeneration capability ($R = 97.6\%$) and high CO₂ selectivity.¹³⁵ In another study, a high-pressure investigation of ionic functionalized graphitic carbon nitride for CO₂ adsorption was analysed. CO₂ adsorption of g-C₃N₄ nanosheets functionalized with an ionic liquid (1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide ([BMIM][TFSI])) was analysed at 15 bar pressure and 25 °C showing a sorption capacity of 42.93 mmol g⁻¹ which was higher as compared to g-C₃N₄ nanosheets (19.78 mmol g⁻¹) and bulk g-C₃N₄ (8.54 mmol g⁻¹). Due to the combined effects of physisorption and chemisorption, an enhanced interaction between CO₂ and ([BMIM][TFSI]) functionalized g-C₃N₄ nanosheets was achieved and this led to a high CO₂

uptake.³⁵ The non-noble metal single-atom catalysts of Fe, Co, Ni and Cu supported on g-C₃N₄ were recently explored for CO₂ adsorption. DFT calculations revealed that the CO₂ adsorption energies of Fe-g-C₃N₄, Co-g-C₃N₄, Ni-g-C₃N₄, and Cu-g-C₃N₄ were -0.40, -0.16, -0.21, and -0.17 eV, respectively.¹³⁶

3.6 Other 2D materials

MOFs and COFs have been reported for gas adsorption applications. An ultrathin mixed matrix membrane containing a 2D MOF was prepared, and the addition of lamellar 2D copper 1,4-benzenedicarboxylate (MOF) nanosheets led to the formation of dense membranes with good CO₂ selectivity (15.6), and high CO₂ permeance (407 GPU) was reported.¹³⁷ MOFs are linked by unstable coordination bonds, particularly under heat and humid conditions, and this structural instability is a significant problem, especially for CO₂ capture in pre or post-combustion processes. However, COFs are linked by covalent bonds and are structurally stable to use under drastic conditions of CO₂ capture. Further, the introduction of N functionalities and the pore size tuning of COFs make them interesting for gas adsorption applications.¹³⁸ 2D COFs are mainly used in the preparation of membranes for the capture and separation of CO₂ gas.^{137–140} Water-soluble COFs with 2D characteristics and porosity were prepared and blended with commercial polymers to form mixed matrix membranes (MMMs). The defect-free and mechanically stable COF incorporating MMMs showed better selectivity and gas permeability when compared to the pristine polymer membrane.¹⁴⁰ In another work, DFT and MD calculations under thermodynamic conditions of a post combustion

Table 2 Adsorption capacities of various 2D nanomaterials and their hybrids

Adsorbent	BET surface area (m ² g ⁻¹)	Operating conditions		Type of adsorption	Adsorption capacity (mmol g ⁻¹)	Ref.
		Pressure (bar)	Temperature (°C)			
Graphene	42.87	11	25	Physisorption	21.6	26
Borane modified rGO	514	1	25	Physisorption	1.81	103
rGO/N-doped porous carbon composite	865.1	5	25	Chemisorption and physisorption	5.77	27
MgAl MMO/rGO	96.8	8	300	—	2.36	108
N-Rich graphene based semi-coke-like material	701.53	30	25	Physisorption	7.11	109
B and N co-doped graphene aerogels (BN-GA)	169.9	1	0	—	2.1–2.9	111
PANI decorated graphene	—	11	25	Chemisorption and physisorption	75	82
Fe ₃ O ₄ /graphene	98.2	11	25	Chemisorption and physisorption	60	28
PANI/GO	5	20	27	Physisorption	3.2	29
PPy/rGO	1650	1	0	—	6.8	30
N-Doped MoS ₂	—	—	—	Chemisorption and physisorption	—	73
Porous BN	1900	1–20	25	Chemisorption and physisorption	1.68.3	31
C doped BN	—	1	0	Physisorption	~5.5	32
MXene, M2N	—	1	727	Physisorption	7.96	33
Ti ₃ C ₂ T _x	66	4	25	Physisorption	5.79	34
Polyethyleneimine/g-C ₃ N ₄	1.2	1	100	Physisorption	3.77	85
C ₃ N ₄ functionalized porous rGO aerogel	450	0.1	27	Physisorption	0.43	135
g-C ₃ N ₄ nanosheets functionalized with ionic liquid	182.9	15	25	Chemisorption and physisorption	42.93	35
Cu doped graphyne	—	1	25	Chemisorption	8.46	147
Polyphosphoric acid modified MMT/rGO hybrid	50.77	1	25	Physisorption	0.5	150
Octadecylamine modified MMT	11.82	50	25	Chemisorption	7.16	36

process were applied on a diamine linked 2D COF membrane for CO₂ gas adsorption. The results hint at the physisorption and better selectivity for CO₂ gas molecules over N₂ by the 2D COF.¹³⁸ An ultrathin membrane was fabricated in a recent study by layering two intrinsically charged ionic covalent organic nanosheets. The layered ultrathin hybrid membrane showed better gas separation properties compared to their counterparts. The overall H₂/CO₂ separation performance was excellent compared to literature results.¹⁴¹ Recently, a 2D COF and 3D MOF dual layered membrane was reported for H₂/CO₂ separation. A 3D MOF film with vertical binding sites to accommodate a 2D COF producing a 2D COF composite membrane with superior H₂/CO₂ selectivity (32.9) and high permeability was reported.¹³⁹

Borophene is a new type of 2D material and it is a single-layered boron-based material with all four different phases being metallic.¹⁴² DFT calculations demonstrated the utility of conductive borophene nanosheets for gas adsorption applications. The binding strength of CO₂ molecules on the adsorbent can be enhanced by introducing an extra electron to it, which leads to a CO₂ capture capacity of up to $6.73 \times 10^{14} \text{ cm}^{-2}$.¹⁴³ Later, the gas (CO, NO, CO₂, NO₂, H₂S, and NH₃) adsorption properties of borophene were analysed relative to the adsorption energies. The negative values of adsorption energy indicated the strong adsorption characteristics of the gases on the adsorbent. Further, the introduction of a transition metal into borophene reduced the adsorption energy, and this indicates the advantages of transition metal doping on borophene for enhanced CO₂ adsorption.¹⁴⁴ The adsorption of gas molecules (CO, CO₂, NH₃, NO, NO₂ and CH₄) on borophene was analysed by DFT calculations, and the studies revealed the chemisorption of all gases except CH₄ on borophene.¹⁴⁵

Another new type of 2D nanomaterial is green phosphorus and its monolayer variant green phosphorene. The CO₂ adsorption properties of the phosphorene slit pores were studied using DFT and GCMC calculations, and the adsorption of natural gas was analysed at 300 K and pressure up to 3 MPa. The simulation results indicate the better selectivity for CO₂ over CH₄ in a binary mixture of CO₂/CH₄ with an enhanced adsorbate-adsorbent interaction, especially at a high mole ratio of CO₂ in the gas phase.⁸⁴ Recently, the strong adsorption of NO, NO₂, CO, and CO₂ gases on green phosphorene was analysed using theoretical calculations.¹⁴⁶ Another 2D material included in the C family is graphyne, which is one atom thick and consists of sp and sp² carbon atoms. Very recently, first row transition metal doped graphynes for enhanced CO₂ adsorption with good selectivity using grand canonical Monte Carlo (GCMC) and DFT techniques were investigated by researchers. The transition metals (TM) like Cu, Co, Fe and Mn were selected for doping with graphyne and the most stable Cu doped graphyne (Cu-GY) exhibited a high CO₂ uptake of 8.46 mmol g^{-1} at 298 K and 1 bar. The enhanced stability of Cu-GY is due to the high cohesion and formation energies, and the Cu-GY adsorbent showed good selectivity for CO₂ over methane

(~ 330.61), nitrogen (~ 912.68), and hydrogen (~ 2640.94) gases. The high CO₂ adsorption capacity and selectivity of Cu-GY are due to its high isosteric heat (40 kJ mol^{-1}), which was higher than other TM-GY adsorbents. The 2D density of different gases on the TM-GY adsorbent was analysed using Monte Carlo configurations at 298 K and 1 bar (Fig. 10). The green areas in the plot represent the high density of gases while the blue area shows the low density of gases. Fig. 10 shows the CO₂ adsorption abilities of TM-GY with low H₂ adsorbing properties. The strong interaction of gas molecules with metal doped graphyne and the multilayer adsorption on the adsorbent make graphyne a promising material for CO₂ separation and capture applications.¹⁴⁷

Nanoclays are another class of 2D materials of layered mineral silicate with a few nanometer thickness and exceptionally high mechanical properties. Since they are based on a mineral, nanoclays are one of the most economical and abundant solid adsorbents used for pollutant removal. Montmorillonite (MMT) clay is widely used, and it is under the smectite group. Layers of MMT contain an octahedral sheet with an Al cation sandwiched by two tetrahedral sheets with the main silicon cation.¹⁴⁸ The major drawback of clay-based materials for CO₂ adsorption is their low efficiency CO₂ uptake under moist conditions and this was due to the diffused water molecules that prevent the capture of gas molecules. In the absence of water molecules (dry conditions), one can expect high CO₂ uptake due to nano-channels in the clay for the intercalation of CO₂ molecules. An analysis of variance (ANOVA) study was carried out to predict the major process variable on CO₂ adsorption. The results indicated the importance of temperature and pressure on the adsorption process. Under optimum conditions of temperature and pressure of 25 °C and 9 bar, a CO₂ adsorption of 100.67 mg g^{-1} was achieved and a good agreement between theoretical and predicted (104 mg g^{-1}) values of gas adsorption was observed.¹⁴⁸ Like the above-mentioned study, an ANOVA treatment was tried on NaOH modified MMT by the same research group. Under optimum conditions of temperature (65 °C), pressure (1 bar), acid concentration (5.99 M) and wt% NaOH (39.76%), a CO₂

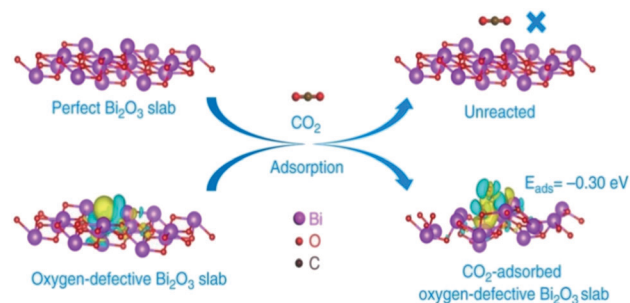


Fig. 12 Schematic of the DFT studies showing selective adsorption and conversion of CO₂ on oxygen defective Bi₂O₃ nanosheets. "Reproduced from ref. 172 with permission from Nature, copyright 2019".

adsorption of 105.55 mg g^{-1} was observed with a desirability index of 0.996, which reveals the good correlation between experimental and predicted gas adsorption values.¹⁴⁹ In another study, the effect of surface modification of MMT with polyphosphoric acid and hybridization with rGO for CO_2 adsorption at 25°C and 1 bar was analysed and the modified MMT/rGO hybrid showed a CO_2 adsorption of $\sim 0.5 \text{ mmol g}^{-1}$ at low pressure.¹⁵⁰ Another method to improve the gas adsorption properties of pristine MMT is the functionalization or grafting nitrogen functionalities to MMT. Therefore, octadecylamine modified MMT was prepared, and showed a CO_2 uptake of 7.16 mmol g^{-1} at room temperature and high pressure of 50 bar while the pristine MMT showed only 3.47 mmol g^{-1} under similar conditions.³⁶

To summarize, a greater amount of CO_2 adsorption was evidenced by nitrogen doping or by introducing nitrogen functionalities in the system and this is due to the chemisorption of the CO_2 adsorbate on the solid adsorbents. The chemisorption of CO_2 on N doped adsorbents was explained through the Lewis acid–base interactions, in which CO_2 is a weak Lewis acid due to the presence of electron deficient C and negatively charged nitrogen sites act as Lewis bases. Further, in N-doped systems, the interactions between EQM of the CO_2 molecule and local polarization in nitrogen-doped adsorbents enhance the CO_2 adsorption energy, leading to selective and higher CO_2 adsorption from the flue gases.⁶ However, in amine functionalized adsorbents,

surfaces exhibit a different type of interaction with CO_2 molecules. The primary, secondary or tertiary amine functionalized adsorbents interact with CO_2 via the formation of the zwitterion intermediate to form carbamates. In the absence of water, which is an additional free base required for the formation carbamate from the intermediate, another mole of amine is utilized. Thus, in the absence of water molecules, two moles of amine are required to capture one mole of CO_2 .¹⁵¹ Nonetheless, due to reduced thermal stability of amine functionalised adsorbents, N doped adsorbents are preferred for CO_2 capture. On the other hand, during physical adsorption, along with the van der Waals attraction of CO_2 and the adsorbent, EQM–electric field gradient interactions are also taking place. The value of EQM is the main factor deciding the selectivity for gases and therefore, carbon dioxide molecules with a high EQM value will be attracted and adsorbed on the solid surface when compared to low EQM N_2 gas. Fig. 11 represents the possible types of interactions taking place during the adsorption of CO_2 on the adsorbent. Another strategy to improve the adsorption capacity is developing porous adsorbents with an adequate surface area and varied morphology. Therefore, we can conclude that high surface area adsorbents with N doping could deliver enhanced CO_2 adsorption characteristics. The CO_2 adsorption capacities of various 2D nanomaterials and their hybrids are summarized in Table 2. It showed that high adsorption capacities have been achieved for 2D nanomaterials by implementing high CO_2 pressure (10 to 30 bars) which hints at their utility for CO_2 capture during post and pre-combustion capture processes. However, the developments of 2D nanomaterial-based adsorbents which can adsorb an adequate amount of CO_2 from the atmosphere make them more attractive due to the possibility of direct removal of CO_2 from the atmosphere. From the data described in Table 2, we can infer that N-doped porous or aerogel materials based on graphene or MXenes are expected to have future advances in low-pressure CO_2 adsorption applications.

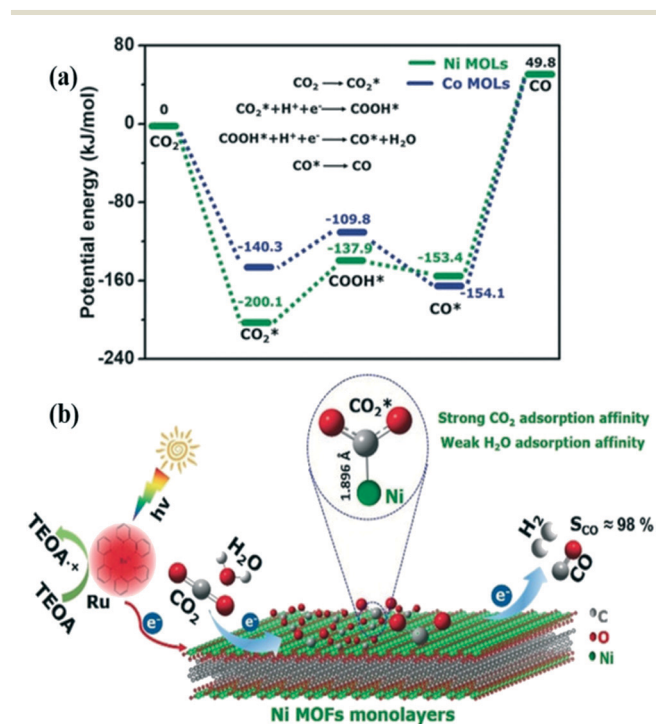


Fig. 13 (a) The potential energy diagram calculated by the DFT studies explaining the energy barriers associated with the conversion of CO_2 to CO . (b) Schematic illustration of CO_2 reduction over Ni-MOFs. $[\text{Ru}(\text{bpy})_3]^{2+}$ acts as a photosensitizer, and triethanolamine (TEOA) is used as a sacrificial electron donor. “Reproduced from ref. 174 with permission from Wiley-VCH, copyright 2018”.

3.7 Impact of defect engineering on CO_2 adsorption

Structural disorders or defects are vital features that can affect the physical and chemical properties of solid materials. These defective sites can serve as active points during various chemical and physical reactions. In 2D materials, common defects such as vacancies, dopants, substitution, edges and grain boundaries have been observed, leading to enhanced material properties. Apart from these, defect engineering in 2D nanomaterials can be triggered by plasma, electron beam, ozone, and chemical treatments. Defect engineering can be exploited for increased CO_2 gas adsorption capacities of 2D solid adsorbents. For instance, the defect engineering of sp^2 carbon of graphitic structures of graphene was analyzed using a van der Waals-corrected DFT calculation for improved CO_2 capture and separation. The topological defects on graphene such as vacancies (mono, di), Stone–Wales defects,

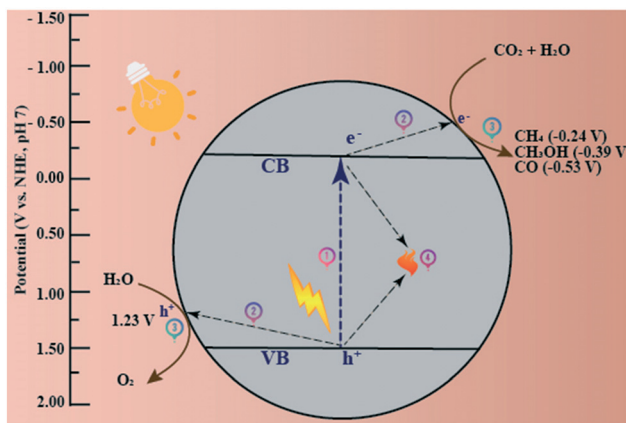


Fig. 14 Schematic of the four different steps involved in the photocatalytic CO₂ reduction by a heterogeneous catalyst. (1) Light absorption, (2) migration of charge carriers to the photocatalytic surface, (3) water oxidation and CO₂ reduction, and (4) recombination of electrons and holes. Thermodynamic potential values associated with water oxidation and CO₂ reduction into CO, CH₄ and CH₃OH are also reported.

strained graphene (by compression and tensile forces), and graphene folds were considered for the evaluation of the binding energy of gases (CO₂ and CH₄). Their study reveals that the concave sites in rippled graphene geometries and SW defect sites can enhance the sorption/binding properties.¹⁵² In another study, DFT calculations of CO₂ adsorption on a defected graphene sheet hint at the physisorption of the gas molecule on the top of the vacancy. Later, the surrounding vacancy can lead to lactone formation and subsequent chemisorption of CO₂. The model suggested a reaction pathway that ends up in the desorption of O₂ with a minimum energy penalty.¹⁵³ The defect engineering of MoS₂ for better CO₂ gas adsorption was analyzed using DFT calculations. The results highlighted the importance of Mo, S vacancies, and N doping for improved CO₂ gas adsorption compared to defect-free MoS₂. According to their study, MoS₂ with one sulfur-vacancy and tertiary nitrogen-doped one Mo-vacancy led to enhanced gas adsorption.⁷³ Similarly, the gas adsorption properties of MOFs can be improved by defect engineering by influencing the factors such as the density of co-ordinatively unsaturated sites, pore size, and specific surface area. As an example, mesopores can be created with vacancy defects, or one can make a porous coordination network compound from a dense coordination network system through defect engineering.¹⁵⁴ The CO₂ adsorption and sensing properties of a pristine and defected black phosphorene were analyzed using DFT calculations. A significant change in the bandgap was observed after vacancy doping, and the initial CO₂ sensitivity was markedly improved by a factor of 50 upon the defect engineering of black phosphorene.¹⁵⁵ In a study, defect engineering of a 2D ferromagnet, Fe₃GeTe₂, was carried out using DFT calculations to suggest an adsorbent with enhanced gas adsorption properties. The Te-deficient Fe₃GeTe₂ monolayer can adsorb CO₂ and H₂O covalently on the surface of the

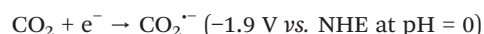
adsorbent. However, physisorption of gases was observed with the defect-free ferromagnet. Also, the estimated adsorption ability of defected Fe₃GeTe₂ was higher than MoS₂ and MXenes.¹⁵⁶ Even though there are a few reports on the theoretical aspects of defect engineering in 2D materials for enhanced CO₂ adsorption, research focusing on experimentation in this area should be well explored for future developments.

4. Catalytic conversion of CO₂

The conversion of CO₂ to valuable chemical feedstocks is of paramount importance to the chemical industries.²⁵ Many of the existing technologies for converting CO₂ to value-added products are not cost-effective. So, the research community is keen to identify catalytic materials able to perform CO₂ reduction with lower energy input. Among the various materials currently researched, 2D materials are of particular interest because of their high selectivity and mild reaction conditions.^{7,11,157,158}

4.1 Thermodynamics and kinetics of CO₂ reduction

The CO₂ molecule has a low electron affinity, and its transformation is a thermodynamically uphill process.¹⁵⁹ The CO₂ transformation occurs by a nucleophilic attack at the carbon atom, and C=O bond dissociation requires a relatively high energy of 750 kJ mol⁻¹.¹¹ A single electron transfer to the CO₂ molecule to generate the CO₂^{•-} radical is considered the first step in the CO₂ reduction mechanism.



CO₂^{•-} radical generation is associated with a highly negative reduction potential value of -1.9 V (vs. NHE), and therefore CO₂ reduction processes need higher overpotential values.¹⁶⁰ The single-electron transfer step (first step) turns out to be the rate-limiting step of CO₂ reduction owing to the higher reorganisation energy between the linear CO₂ molecule and bent CO₂^{•-} radical.¹⁶¹ Hence the thermodynamic barrier linked to the CO₂ activation step eventually decreases the efficiency of CO₂ reduction processes.

Another mechanism for CO₂ reduction involves the multiple proton-coupled electron transfer (PCET) processes.^{162,163} PCET is necessary to avoid the activation barriers and excludes the formation of unstable intermediates.¹⁶⁴ As the name suggests, the PCET mechanism kinetically relies on the concentration of protons available in the system. CO₂ reduction to methanol and methane requires the transfer of six and eight protons, respectively.^{165,166} As the number of protons and electrons involved in the PCET reaction increases, it escalates the complexity of the reaction.¹⁶¹ Therefore, various reports of CO₂ conversion to valuable products like methanol and methane reveal drawbacks such as poor selectivity and low conversion efficiency.^{167,168} The hydrogen evolution reaction (HER) from water is kinetically more favourable than CO₂

reduction. Consequently, proton reduction competes with CO_2 reduction and decreases the efficiency of CO_2 transformation.¹⁶⁹ The readers are redirected to previous reviews for a detailed understanding of the thermodynamic and kinetic aspects of CO_2 reduction reactions.^{161,170}

4.2 Structure function relationship in CO_2 reduction catalysts

Correlating the structural features of the 2D catalyst with the catalytic performance is an exciting area to be explored. An in-depth analysis of the specific structural features and understanding their role in the catalytic mechanism help researchers in modulating the catalyst for obtaining the desired products. Fine-tuning the oxygen vacancies and single atoms present on the catalytic surface can help achieve the selectivity to the product.^{171,172}

In a recent study, Bi_2O_3 nanosheets with oxygen vacancies were demonstrated to fix CO_2 to dimethyl carbonate.¹⁷² The oxygen vacancies present on the atomic layers decreased the adsorption energy of CO_2 on the surface and enhanced the generation of the $\text{CO}_2^{\cdot-}$ radical by a single-electron transfer. The difference in the charge density observed between non-defective Bi_2O_3 nanosheets and oxygen defective Bi_2O_3 nanosheets provided insights into the possibility of electron localisation around the oxygen vacancies. DFT calculations arrived at a negative adsorption energy of -0.30 eV for the CO_2 adsorbed on oxygen defective Bi_2O_3 nanosheets (Fig. 12). On the contrary CO_2 chemisorption was not observed on the non-defective Bi_2O_3 nanosheets owing to their weak interaction with CO_2 . In a similar study, atomic layers of SnS_2 with varying oxidation degrees were synthesized to understand the correlation of oxidized sulfides and their efficiency for CO_2 to CO conversion.¹⁷³ DFT calculations concluded that electron localization occurring at the oxidized domains of SnS_2 was stabilizing the COOH^* intermediate formation resulting in a decreased CO_2 activation energy. The mildly oxidized SnS_2 layers were reported to have a CO_2 to CO conversion rate 2.6 times higher than the pristine SnS_2 atomic layers.

In another study, the CO_2 to CO conversion performances of Ni-MOFs and Co-MOFs were compared.¹⁷⁴ In the presence of 10% diluted CO_2 , Ni-MOFs showed a 96.8% CO selectivity with a quantum yield of 1.96%. But the CO_2 to CO conversion efficiency of Co-MOFs was negligible in the diluted CO_2 .

Experimental and theoretical investigations demonstrated the specific adsorption affinity of CO_2 molecules over the Ni-MOFs and the resulting formation of Ni- CO_2 adducts (Fig. 13, schematic representation). The CO_2 to CO reduction pathway proceeds through a COOH^* intermediate. The DFT calculations revealed the potential energy barrier associated with CO_2^* to COOH^* conversion to be 62.2 kJ mol^{-1} for the Ni-MOFs (Fig. 13). But the CO_2^* to COOH^* energy barrier for the Co-MOFs was 30.5 kJ mol^{-1} , suggesting that the COOH^* formation is kinetically favorable on the Co-MOFs compared to the Ni-MOFs. DFT studies, along with the experimental findings, concluded that the initial adsorption of CO_2 over the Ni-MOFs is the rate-determining step of CO_2 to CO conversion, rather than the electron transfer process.

The role of single atoms (palladium and platinum) anchored on $\text{g-C}_3\text{N}_4$ ($\text{Pd/g-C}_3\text{N}_4$ and $\text{Pt/g-C}_3\text{N}_4$) in the CO_2 reduction reaction was investigated by DFT calculations.¹⁷⁵ Introducing Pd and Pt single atoms on the $\text{g-C}_3\text{N}_4$ surface enhanced the visible light absorption capacity. Here $\text{g-C}_3\text{N}_4$ was the source of hydrogen (H^*) via the HER, and the single atoms (Pd and Pt) were the active sites responsible for CO_2 reduction. DFT studies concluded that the $\text{Pd/g-C}_3\text{N}_4$ catalyst is efficient in transforming CO_2 to HCOOH with a barrier of 0.66 eV, whereas the $\text{Pt/g-C}_3\text{N}_4$ catalyst was suitable for selectively reducing CO_2 to CH_4 with a barrier of 1.16 eV. In another study, surface alkalisation of Ti_3C_2 MXenes was reported to have improved the selectivity for CO_2 reduction to CH_4 .¹⁷⁶ Similarly, a ruthenium nanoparticle incorporating layered double hydroxide (LDH) was efficient in reducing CO_2 to CH_4 .¹⁷⁷

4.3 Photocatalytic reduction of CO_2

The reduction of CO_2 to renewable chemicals/fuels in the presence of sunlight and semiconductors is called photocatalytic CO_2 reduction (PCCR).^{178,179} This multistep process is possible under both UV and visible light irradiation, yielding hydrocarbons and alcohols with respect to the distinct potentials exhibited by photocatalysts.^{180,181} Nevertheless, PCCR is remunerative in the case of economic and environmental terms but inferior in terms of efficiency and selectivity, as the conventional photocatalysts are overwhelmed with the high charge carrier recombination rate and inept reactor design, apart from poor light harvesting ability leading to low yield.¹⁸² To ease these shortcomings, among many suggested ameliorating efforts such as bandgap engineering, co-catalyst loading, non-metal doping, and construction of heterojunctions, choosing a low-dimensional photocatalyst should be the fundamental and baseline norm for designing a flawless photocatalyst.

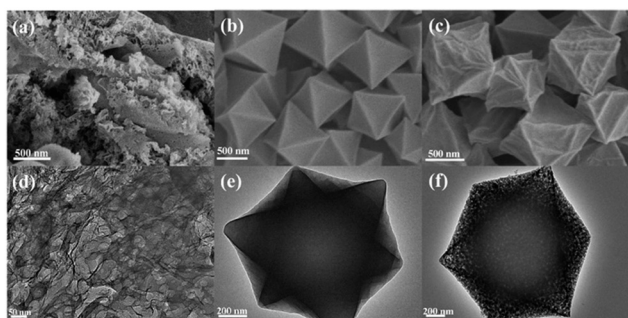


Fig. 15 SEM and TEM images of (a and d) pristine $\text{g-C}_3\text{N}_4$; (b and e) bare $\text{NH}_2\text{-MIL-101(Fe)}$; (c and f) MCN-3 heterostructure. "Reproduced from ref. 203 with the permission from American Chemical Society, copyright 2020".

4.3.1. Mechanism of photocatalytic CO₂ reduction. The adsorption of CO₂ molecules on the surface of the photocatalyst is a critical step in reducing CO₂ to valuable chemicals. A detailed description with schematic diagrams on the possible modes of CO₂ adsorption on the photocatalyst surface can be found in previous reviews.^{25,167,183} The adsorbed CO₂ molecule on the surface loses its linear structure, resulting in the lowering of the LUMO levels of CO₂.^{184,185} Now the CO₂ molecule accepts the photogenerated electrons from the photocatalyst, and various reduced products are formed. Different strategies such as incorporating surface defects, introducing a co-catalyst, and increasing the surface area are reported to improve the surface adsorption ability of the CO₂ molecule on the photocatalyst.^{186–188}

The crucial processes involved in PCCR are summarized in Fig. 14.¹⁸³ At first (1), light radiation with energy higher than the bandgap of the photocatalytic material leads to the generation of electron-hole pairs in the photocatalyst. Then (2), the electrons and holes migrate to the photocatalyst surface. Later the photogenerated electrons reduce the CO₂ molecules into valuable products, and the holes convert H₂O to O₂ (3). The recombination of electron-hole pairs in PCCR reactions takes place (4). The first two steps in photocatalytic CO₂ reduction are the same as those of water splitting. The surface interactions that occur on the photocatalyst determine the fate of the reaction: CO₂ reduction or proton reduction.

4.3.2. 2D material assisted photocatalytic reduction of CO₂. 2D nanosheets are superior in photocatalysis to 1D and 0D due to their large surface area, ample surface active sites, augmented electron mobility, better electron transfer platform, and outstanding photocatalyst support.¹⁸⁹ 2D photocatalysts include graphene,¹⁹⁰ g-C₃N₄,¹⁹¹ TMCDs,¹⁹² metal oxides,¹⁹³ LDHs,¹⁹⁴ MXenes,¹⁹⁵ h-BN,¹⁹⁶ *etc.* The allure lies beneath their innate advantage of having refined light absorption properties besides a reduced electron-hole migration distance to the photocatalyst surface enriched with defects that render bandgap modulation and charge transfer to the adsorbate. The photocatalytic process can be identified by a series of reactions comprising adsorption of CO₂ onto the surface, photo-generation, separation, and subsequent transportation of charge carriers, and the chemical reactions between adsorbed CO₂ and charge carriers.

A practical tactic to improve the photocatalytic performance of the GO nanosheets was devised recently by increasing the defect density on the GO surface. When defects are created, more active sites could trap the photo-excited charge carriers and suppress the recombination process, reliable enough to advance without any hole scavengers like water and providing a result three times better than non-irradiated GO.¹⁹⁷ This conventional notion conflicting study revealed the role of defect density in the photocatalytic activity. The less defective graphene decorated TiO₂ exhibited up to a seven-fold rise in CH₄ formation with

respect to pristine TiO₂. Compared to rGO with higher defect density, graphene facilitates the smooth diffusion of photo-generated electrons to the reactive sites, triggering the electrical mobility following the photo-reduction process.¹⁹⁸ The fabrication of Cu₂O/rGO composites was conducted by a one-step microwave method, where the CO₂ reduction activity of Cu₂O spotted to have risen dramatically, apparently six times higher than Cu₂O and fifty times higher than the Cu₂O/RuO_x junction, pinpoints the significance of rGO in the process. Together with the enhanced stability of Cu₂O, the proficiency in charge separation and mobility can be ascribed to rGO and its protection function providing an economically viable photoreduction of CO₂, which can thus exclude expensive and rare noble metals like Pt, Pd, Au, Ag, *etc.*¹⁹⁹ Generally, CO₂ reduction and water splitting are two rival reaction processes that co-occur during the CO₂ reduction process in water resulting in poor yield due to the sheer competition for reactive sites. A manipulated rGO nanosheet, which created more individual reactive sites, was explored, effectively separating and distributing the excess excitons generated by quantum-sized photocatalysts. Here, they fabricated a rGO composite of bismuth monoxide quantum dots (rGO-BiO QDs) furnished with an exclusive charge transfer pathway by a typical hydrothermal method. The synergistic effect resulted in the formation of H₂ and CH₄ yielding up to 102.5 and 21.75 μmol g⁻¹ h⁻¹, respectively, in the absence of any noble metals or sacrificial agent, beating the direct water splitting production rate, to date.²⁰⁰

Unlike graphene, g-C₃N₄ is a conjugated polymeric visible-light-driven photocatalyst with many hallmark features, including band structure, thermal and chemical stability, *etc.* In g-C₃N₄ the conduction band (CB) edge is necessarily negative for CO₂ reduction, and it can proceed without any co-catalysts. In a study, g-C₃N₄ with two different precursors was fabricated with a large surface area mesoporous flake-like structure from urea with enhanced

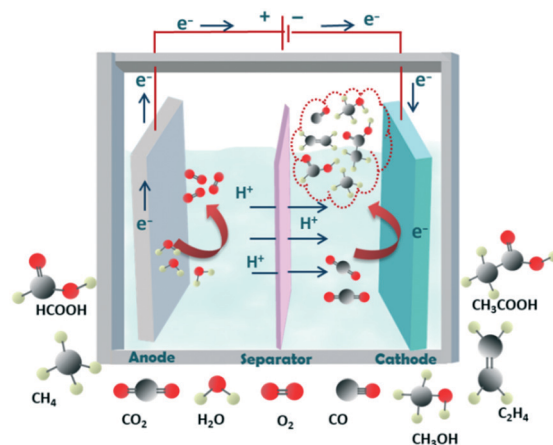


Fig. 16 Schematic diagram representing the formation of various valuable products via the electrochemical CO₂ reduction method.

photocatalytic activity compared with the non-porous flaky photocatalyst derived from the melamine precursor. However, the latter exhibited a selective formation of C_2H_5OH .²⁰¹ Still, a high recombination rate of the photogenerated charge carriers is an everlasting challenge to an efficient photocatalyst. The progress in the photocatalytic applications of g- C_3N_4 -based semiconductors for CO_2 reduction was summarised in which they suggested a few modifications which can bring about a hike in adsorption and charge separation rates such as structural tuning, elemental doping, co-catalyst addition, and so on.²⁰²

Doping a non-polar element like carbon quantum dots on g- C_3N_4 offers many benefits, such as bandgap tapering and electron-withdrawing effects, which facilitate light absorption and separation of charge carriers. The doping activates the photoreduction with advanced reaction kinetics on the non-polar modified surface, presenting six times the yield (CO and CH_4) devoid of any detectable H_2 relative to the bare g- C_3N_4 under similar conditions. This is because of the facile adsorption of the non-polar adsorbate on the modified adsorbent.²⁰⁴

Forming heterojunctions with other photocatalysts is a widely applied strategy to encourage charge separation and thus improve the overall catalytic performance. For instance, the MOF-based/g- C_3N_4 photocatalytic system is a versatile and promising means of promoting photocatalytic efficiency for CO_2 reduction owing to its large surface area and unique porous structure.²⁰⁵ In a recent study, the NH_2 -MIL-101(Fe)/g- C_3N_4 -X (MCN-3) heterosystem bearing coordinated unsaturated metal sites and an amino functional group was developed where a solid-gas interfacial route emerges in between the adsorbate and photocatalyst, which boosts the CO_2 adsorption ability besides selectivity, generating CO 6.9 times higher than pristine g- C_3N_4 under visible light irradiation.²⁰³ Fig. 15 shows the morphology of bare g- C_3N_4 with a sheet-like agglomerated architecture. The TEM image (Fig. 15d) exhibits a wrinkled lamellar structure with cured layers composed of pores, whereas NH_2 -MIL-101(Fe) (Fig. 15b and e) gives an octahedral morphology with a smooth surface. There is not much distinct morphological change that occurs after the formation of heterostructures indicating the uniform dispersion of g- C_3N_4 particles into the octahedral crystals (Fig. 15c and f).

Carving metal oxides such as TiO_2 , ZnO , Fe_2O_3 , SnO_2 , and WO_3 into thin atomic layers unveils a new arena of hidden exotic properties, including rich reactive sites with a better charge carrier transport and efficient light absorption besides natural resistance to oxidation.^{206,207} Among these promising 2D materials, ZnO sheets are benign and highly stable, becoming a non-polar graphene-like structure (g- ZnO) when the thickness gets reduced into a few layers in which the electronic structure is immensely dependent on the number of layers. In a study, the concept of steering the quantum confinement effect in the out-of-plane direction by engineering the interlayer coupling and surface activity of ultrathin films was examined to discover the film thickness

of materials. In their study, the effect of thickness from the bulk to a monolayer on photocatalytic reduction of CO_2 by ZnO was studied through DFT calculations.²⁰⁸ One of the most chemically stable, environmentally sound and highly recognized photocatalysts is TiO_2 , challenged with limited redox ability and a short light response range that can be tackled by forming vastly recommended heterojunctions. Recently He *et al.* came up with a Ti_3C_2 MXene quantum dot decorated 2D/2D TiO_2 / C_3N_4 core-shell photocatalyst with a boosted CO_2 reduction activity generating CO and CH_4 as products with thrice the CO evolution rate compared to its pristine forms. Here, Ti_3C_2 , usually a renowned 2D layered MXene featuring a fascinating work function and reduced activation energy for CO_2 reduction, acts as a potent co-catalyst in 0D form, with most of the properties similar to its 2D counterparts.²⁰⁹ Lately, the potential of 2D MXenes as co-catalysts for an efficient photocatalytic CO_2 reduction was verified, which has been attributed to their smooth conductivity, rich active sites, and enlarged specific surface area.²¹⁰

2D metal chalcogenides such as MoS_2 , WS_2 , $MoSe_2$, WSe_2 , SnS_2 , *etc.* are versatile materials that can be candidates for photocatalysts and non-noble metal co-catalysts considering their catalytic activity, availability, and affordability. They are generally utilized in H_2 production but are now starting to be applied in the field of CO_2 photoreduction.^{179,211,212} The superior photocatalytic activity is claimed by MoS_2 nanosheet-covered TiO_2 fibers with a narrow bandgap and tuneable conduction band. The proposed material has an excellent photosensitizing effect originating from the presence of MoS_2 nanosheets, which generated a better yield of methane and methanol products.²¹³ Correspondingly, a WSe_2 -graphene- TiO_2 ternary system was fabricated *via* a simple ultrasonic technique and the influence of WSe_2 and graphene nanosheets on the bandgap of TiO_2 was found, enhancing its photocatalytic performance under UV/Vis light.²¹⁴ In a similar study, a SnS_2 / TiO_2 based 2D-2D heterojunction photocatalyst was prepared hydrothermally by depositing ultrathin SnS_2 nanosheets onto titania nanosheets. The so-formed photocatalyst produced methane with a yield of $23 \mu mol^{-1} g^{-1} h^{-1}$, which is 20, 10, and 9 times higher than pristine titania, titania nanosheets, SnS_2 nanosheets, respectively, indicating the importance of metal chalcogenides as co-catalysts in photocatalysis.²¹⁵

A developing category of anionic clays, namely, layered double hydroxides (LDHs), are reliable CO_2 reduction photocatalysts with a high sorption capacity for adsorbates between the layered space and flexible catalytic properties with respect to the chosen metal cations.^{216,217} Amidst quite a few LDHs, Zn -Al LDH reduces CO_2 to CO , while Cu -containing LDH promotes an efficient reduction to produce methanol. More incredible performance is evident with the collaboration of another 2D material like g- C_3N_4 . For instance, a heterojunction between $NiAl$ -layered double hydroxide ($NiAl$ -LDH) and g- C_3N_4 nanosheets was engineered *via* a simple *in situ* hydrothermal method.²¹⁸ The system exhibited the highest CO evolution rate of 8.2

$\mu\text{mol h}^{-1} \text{g}^{-1}$, which is five times better than pristine g-C₃N₄ and nine times better than the pure NiAl-LDH without the presence of any sacrificial agents owing to the synergic effect between the two nanosheets. Besides the effective interfacial contact due to the 2D/2D architecture the catalyst showed arrested recombination, prominent charge carrier transport to the surface and CO₂ adsorption rate. Recently a study highlighted the capability of LDH-based photocatalysts in the arena of photocatalytic CO₂ conversion, projecting their excellent physicochemical and electrical properties. Due to the favourable redox chemistry ascribed to its 2D structure, the LDH material enriched with surface hydroxyl groups providing basicity, better visible-light harvesting ability, and reliable stability, becomes a suitable choice for coupling with other 2D materials for an innovative photocatalysis.¹⁹⁴

Besides the photocatalysts mentioned above, a few more developing 2D materials are yet to be explored more for CO₂ reduction. For instance, h-BN nanosheets; covalent triazines having better stability, abundant nitrogen content,²¹⁹ efficient visible light harvesting, and a tuneable bandgap;²²⁰ and black phosphorus with a flexible bandgap, high exciton mobility, *etc.*,²²¹ are examples. Unlike typically used catalysts such as graphene and g-C₃N₄, hexagonal boron nitride (h-BN), a honeycomb-like 2D material, exhibits ionic properties endorsing directional transfer of electrons to the adsorbate, promoting the active carbon species. An oxygen atom-tailored ultrathin BN nanosheet was engineered to improve the optical absorption and adsorption efficiency of the photocatalyst. Contrary to the normal adsorption process, CO₂ is chemisorbed onto the catalyst surface, enabling a continuous electron delivery, CO₂ activation, and interfacial interaction which helps to decrease the activation energy of the transformation process. The reported rates of the products (H₂ and CO) were 3.3 and 12.5 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively, which can be considered a pioneering work in the rational design of metal-free photocatalysts.¹⁹⁶ Likewise, in a recent study, black phosphorus and a covalent triazine framework (CTF) have been devised *via* self-assembly, which enhanced the selectivity for CO₂ reduction to methane over CO. A strong interaction between CO and the catalyst surface prevents the desorption of CO, which helps in the further reduction to methane, and this is a novel strategy for selective and efficient catalysis.²²² To conclude, among many challenges, a key obstacle in developing an ideal and efficient photocatalyst is that only a single electron is excited by a photon aside from deficient solar light harvest. It invokes a dire need for attention and action in the coherent architecture of a perfect photocatalyst which can be viewed as the most reliable and economic approach in reducing the globally threatening CO₂ and producing green fuels.

4.4 Electrochemical CO₂ conversion

The electrochemical process has gained substantial attention in converting CO₂ to useful and value-added fuels and

commodity chemicals (methane, CO, formic acid, methanol, ethylene, and ethanol) utilising electricity from renewable sources to resolve the energy and environmental problems and to maintain a healthy balance between energy supply and global carbon content. A large amount of activation energy is required for one-electron reduction of CO₂ and HER in protic media, which limits the selectivity of the electrochemical CO₂ reduction (ECR) process.^{223,224} In addition, a well-matched equilibrium potential for the formation of CHO, CO, and COOH results in poor selectivity by inhibiting the tuning of the intermediates to the precise product.²²⁵ Moreover, the poor solubility of CO₂ in aqueous solutions led to low current density. These limitations like poor selectivity,²²⁶ high over-potential,²²⁷ low current density,²²⁸ and poor energy efficiency of ECR limit the industrialisation of the process.

4.4.1. Basics of electrochemical reduction of CO₂. The electrochemical CO₂ reduction process is of particular interest because of the possibility of coupling the electrochemical reaction with renewable energy resources such as solar energy and wind power.²²⁹ Electrochemical CO₂ reduction reactions can be performed at normal temperature and pressure. In addition, electrochemical reactions can be easily controlled by varying the parameters such as external voltage and electrolyte.^{230,231} The electrochemical CO₂ reduction processes are achieved *via* multiple PCET mechanisms.²³² A schematic illustration showing the production of various value-added products in an electrochemical cell *via* CO₂ reduction is presented in Fig. 16.

Some of the key parameters that are used to measure the performance of an electrocatalyst include the (a) overpotential (η), (b) current density, (c) faradaic efficiency, (d) energetic efficiency, (e) turnover frequency and (f) Tafel slope.¹¹ Overpotential is defined as the difference between the thermodynamically determined reduction potential of a reaction and the actual reduction potential value in which the reaction is experimentally observed.²³³

Faradaic efficiency is defined as

$$E_{\text{Faradaic}} = \frac{\alpha n F}{Q}$$

where α is the number of electrons transferred, n is the number of moles of the products formed, F is Faraday's constant, and Q is the charge passed.²³⁴ Turnover frequency (TOF) represents the activity of the material per catalytic site. The value of the Tafel slope provides an idea of the rate-determining step (RDS) and suggests the reaction pathway involved.²³⁵ According to practical scenarios, an overpotential of around 100 mV is required to achieve sufficient reaction rates. Consequently, cell voltages usually surpass the formal reduction potential values of the overall reaction.²³³

4.4.2. Recent progress in ECR of CO₂ using 2D materials. In recent years, research work has been keenly pursued to develop stable, energy-efficient, and low-cost electrocatalysts to promote the kinetically sluggish ECR process.^{236–238} In

view of this, a wide variety of catalysts including TMDCs,^{239,240} MXenes,²⁴¹ carbon-based materials,²⁴² MOFs,^{243,244} metal-based complexes,²⁴⁵ single atom catalysts,²⁴⁶ *etc.* have been developed, and in this section, we will focus on the ECR process using 2D nanomaterials. The layered 2D materials with stronger in-plane chemical bonding interactions possess abundant active sites and more exposed active edge sites, which paves the way to achieve highly efficient catalysts. An atomic level investigation of catalytic mechanisms can be analysed based on the well-defined structure of the 2D nanosheets.²¹¹ Homogeneous as well as heterogeneous catalysts have been used for the activation of the reduction process in ECR processes.²⁴⁷ Even though good product selectivity and high efficiency can be achieved by homogeneous catalysis through controlling the active site of the catalyst, these systems suffer from drawbacks of high cost, toxicity, low stability and a difficult post-separation process.²⁴⁸ On the other hand, heterogeneous nanocatalysts have gained a significant level of attention for their high activity and stability with a large active surface area.²⁴⁹ The catalytic activity can be evaluated by parameters including current density, onset potential, overpotential, faradaic efficiency and turnover frequency. The homogeneous electron transfer between the electrode and electrolyte is the main principle behind electrocatalysis. So, current density (amount of current per unit area) is a necessary parameter in the electrocatalysis process. The onset potential is the voltage required to reach a current at which the reaction starts. An efficient catalyst reduces the onset potential and power consumption. The overpotential is the difference between the actual reaction potential and thermodynamic potential that is the additional voltage required to overcome the resistance due to collisions between ions during the transfer of ions from the bulk to the electrode surface. The selectivity and efficiency of an ECR process can be analysed by faradaic efficiency.²⁵⁰

Recently, 2D graphene has gained much attention as a promising candidate for CO₂ ECR due to its excellent physical, electronic, and mechanical properties.^{24,25,251} The studies on graphene-based materials reveal that doping of graphene with heteroatoms like boron, phosphorous, nitrogen, *etc.* shows better ECR efficiency than pristine graphene. As we already discussed, during the process the selectivity of CO₂ ECR over the hydrogen evolution reaction (HER) is a significant concern. In a study the development of porous Zn NPs wrapped with thin rGO layers for selective CO₂ ECR over HER was reported. They found that the current density for the CO production of the pristine ZnO catalyst remains unchanged while the current density for the HER process selectivity is suppressed upon the incorporation of rGO layers. The suppression is tuned by varying the amount of rGO in the catalyst and 94% FE is achieved. The decoupling of the HER from CO₂ ECR is due to the fast proton consumption and low bulk concentration of protons upon increased rGO coverage in the catalyst.²⁵² Later, the achievement of better activity and selectivity towards CO₂

reduction on metal and nitrogen co-doped graphene *via* first-principles calculations was reported. The Co and N co-doped graphene with a nitrogen coordination number of one to three possess poor selectivity towards CO₂ reduction over the HER. When the coordination number reaches five, the selectivity is found to be higher for CO₂ reduction to CO than the HER. This result implies that the coordinative environment of metal atoms significantly influences the activity of the catalyst for both CO₂ reduction and the HER.²⁵³ These first principles calculations provide useful information to engineer active and selective catalysts for CO₂ reduction to CO. The stability of the electrocatalyst is another concern for the ECR processes. A highly stable dual-atom Ag₂/graphene catalyst was developed with a CO faradic efficiency of up to 93.4% with a current density of 11.87 mA cm⁻² at -0.7 V and exhibited excellent stability for more than 36 h. The interaction of Ag atoms with carbon and oxygen atoms of CO₂ stabilises the CO₂ adsorption intermediate and thus reduces the barrier for the formation of the *COOH intermediate.²⁵⁴ Immobilisation of Ni²⁺ ions on N-doped graphene *via* a facile ion adsorption process was carried out. The metal immobilization on N-doped graphene creates cyclam-like moieties, enhancing the electrocatalyst's selectivity and activity for CO₂ reduction. The catalyst achieves 92% CO production faradaic efficiency at 0.68 V with a current density of 10.2 mA cm⁻².²⁵⁵ In another study, the effect of bismuth (Bi) nanoparticle support interaction in rGO nanosheets on ECR of CO₂ to formate has been studied. The Bi/rGO synthesised by the hydrothermal method shows two times higher faradaic efficiency for value-added formate generation when compared to physically mixed Bi/rGO samples. This reveals that the Bi support interactions boost the CO₂ reduction by altering the electronic structure and interfacial electron transfer between Bi and graphene.²⁵⁶ Recently, many publications related to graphene-based electrocatalysts have been reported, revealing that graphene-based materials may shed new light on engineering efficient electrocatalysts for CO₂ reduction.

Ultrathin 2D TMDCs have been widely used for energy related electrocatalysis including H₂ evolution, CO₂ reduction, O₂ reduction/evolution, *etc.* due to their exceptional electronic and chemical properties. TMDCs provide a good platform for the study of the structure-performance relationship at the atomic level.²⁵⁷ The CO₂ reduction performed using WSe₂ starts at an extremely low overpotential of 54 mV with a current density of 18.95 mA cm⁻² and CO reduction faradaic efficiency of 24%. On comparing the results with bulk Ag and Ag nanoparticles, the TMDC possesses higher performance for ECR of CO₂. The DFT calculations show that COOH* intermediate formation using WSe₂ is exergonic due to the strong binding interactions with the metal edge sites of the TMDC which is absent in Ag nanoparticles (endergonic). So the formation of CO is kinetically more favourable in WSe₂ compared to Ag nanoparticles.²⁵⁸ Ultrathin MoTe₂ layers have been fabricated for the ECR of CO₂ to methane with an FE of 83% and a

durable activity for greater than 45 h at a relatively high current density of 25.6 mA cm^{-2} at an applied potential of -1.0 V . This result reflects more exposed active sites in the MoTe_2 layers, which help to achieve improved efficiency for ECR.²⁵⁹ Doping the edge atoms of TMDCs with suitable dopants can alter the electronic properties to enhance the electrocatalytic performance. Abbasi *et al.* synthesised Nb and Ta doped MoS_2 and the prepared $\text{Mo}_{0.95}\text{Nb}_{0.05}\text{S}_2$ structure showed the lowest onset potential and highest CO_2 reduction activity. This can be attributed to a decrease in binding strength of Mo edge atoms to CO with Nb doping.²⁶⁰ The kinetically slow CO desorption process can be promoted by doping with V, Zr, and Hf. The factor that influences the catalytic activity is the closeness of the dopant to the active Mo site rather than the concentration of the dopant used. DFT calculations suggest that the d-band center energy from the Fermi level controls the electronic properties and the CO desorption mechanism. The closer the d-band to the Fermi level, the weaker the CO adsorption. Doping of MoS_2 with V, Zr and Hf leads to shifting of d-band centers to the Fermi level and makes CO desorption easier.²⁶¹ Undoubtedly, these results show the attractive effect of TMDs for electrocatalysis applications.

MXenes, 2D transition metal carbides, and nitrides provide an active platform for selective CO_2 ECR owing to the presence of mixed surface terminations.^{262,263} Analyses on $-\text{OH}$ and $-\text{F}$ terminated MXenes for CO_2 ECR were carried out. It was reported that the H atom of the $-\text{OH}$ functional group present in $\text{Sc}_2\text{C}(\text{OH})_2$ and $\text{Y}_2\text{C}(\text{OH})_2$ assists in forming stable intermediate structures, thus lowering the overpotential.²⁶⁴ They also analysed Ti and Mo-based MXene catalysts by combining theoretical and experimental methods for CO_2 reduction with an $-\text{F}$ terminal functional group. The CO_2 reduction of Ti_2CT_x and Mo_2CT_x MXene results in formic

acid production with an FE of 56% at -1.8 V on Ti_2CT_x .²⁶⁴ The terminal functional group plays a vital role in the selectivity of the reduction process. DFT simulations predict that the $-\text{F}$ termination destabilises COOH^* leading to a more negative limiting potential for CO_2 reduction. Ti_2CT_x (HF) with large $-\text{F}$ terminal groups shows inadequate CO_2 reduction, while Ti_2CT_x (KF-HCl) with smaller $-\text{F}$ terminal groups shows higher selectivity for CO_2 reduction and better efficiency. Chen *et al.* have investigated M_2XO_2 MXenes with carbon/nitrogen and transition metal vacancies. The vacancies present in the catalyst influence the CO_2 reduction by favouring a strong binding interaction of fragment type intermediates (e.g. $^*\text{COOH}$, $^*\text{CHO}$), allowing the tuning of overpotential.²⁶⁵ More research works are ongoing in this area to develop MXenes with acceptable cost for energy generation and conversion applications.

MOFs are another class of materials assembled by metal clusters/ions as nodes and ligands as linkers that have gained much attention for ECR to value-added chemicals. Permanent porosity, adjustable pore size, coordinatively

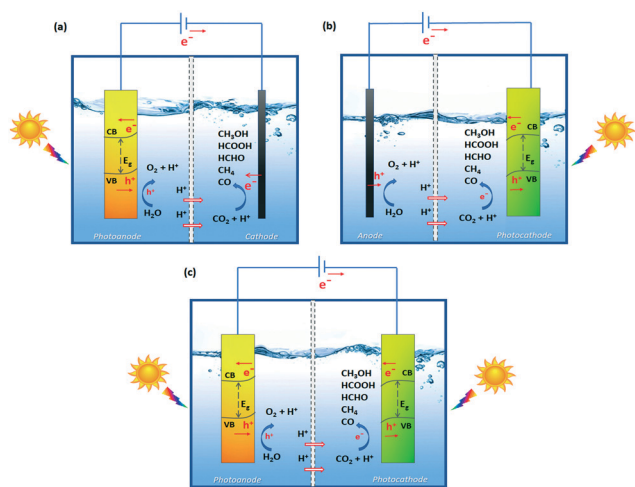


Fig. 17 Schematic representation of a PEC cell with a two-electrode system separated by an exchange membrane converting CO_2 to chemical fuels (a) with an illuminated photoanode and cathode, (b) with an anode and illuminated photocathode, and (c) when both the photocathode and photoanode are illuminated.

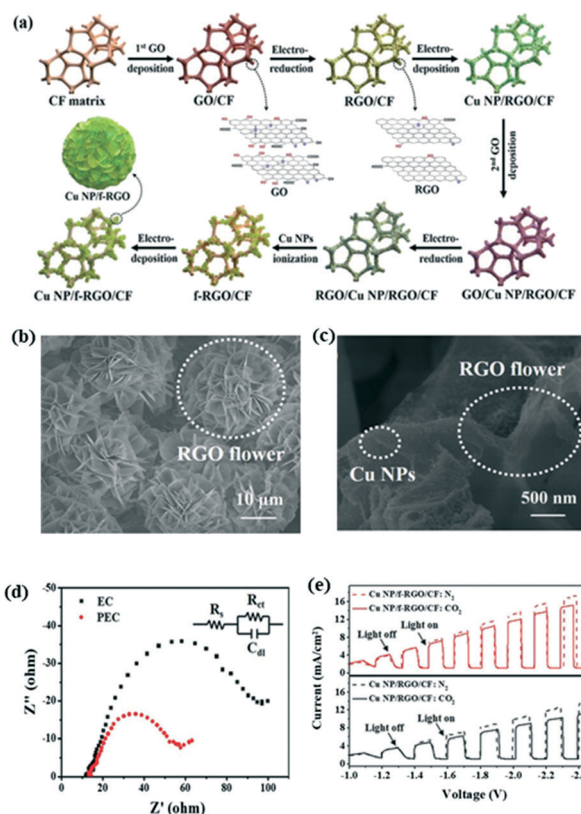


Fig. 18 PEC electrode based on graphene. (a) Schematic of the preparation of 3D flower-like reduced graphene oxide (f-rGO) modified with Cu NPs and deposited on Cu foam (Cu NP/f-rGO/CF electrode); SEM images of (b) f-rGO/CF and (c) Cu NP/f-rGO/CF electrodes; (d) EIS - Nyquist plots under PC, EC, or PEC conditions for the Cu NP/f-rGO/CF electrode in the Pt-TNT photoanode-driven PEC cell (inset shows the scheme for the circuit followed for fitting EIS); (e) linear sweep voltammetry curves of Cu NP/f-rGO/CF and Cu NP/rGO/CF. "Reproduced from ref. 304 with permission from Wiley-VCH, copyright 2020".

unsaturated metal sites, high surface area, *etc.* help to achieve free diffusion of reactants through MOF channels and readily facilitate the reaction over the open metal active sites. The efficiency of electrochemical reactions can be determined by the electron coupling interfacial interactions provided by the highly accessible metal–ligand junctions of MOFs.²⁶⁶ The possibility of electrochemical conversion of CO₂ to methanol using DFT combined with the computational hydrogen electrode model for the 2D Fe–hexaaminobenzene MOF was explored. They found that Fe₃(HAB)₂ containing Fe–N₄ sites is the most promising candidate for catalysing CO₂ into hydrocarbons through CO₂ → *COOH → *CO → *CHO → *CHOH → *CH₂OH with a free energy change of 0.69 eV, and the activation energy barrier is 1.36 eV.²⁶⁷ In a study, a bismuth-based metal–organic framework as a pre-catalyst, which undergoes structural changes to form bismuth-based nanoparticles for highly active and selective CO₂ reduction towards formate formation, was reported.²⁶⁸ The efficiency of CO₂ reduction can be enhanced by ligand doping. Zn-based MOFs of zeolitic imidazolate framework-8 (ZIF-8) are doped with a strong electron donating molecule, 1,10-phenanthroline. The electron-donating nature of the dopant enables the transfer of electrons from phenanthroline to the sp² C atoms of the imidazole ligand, and facilitates the formation of the COOH* intermediate, thus enhancing the faradaic efficiency.²⁶⁹ Cobalt porphyrin was anchored into the Zr-BTB MOF to increase the utilisation of active sites for CO₂ reduction and the catalyst shows ultrahigh turnover frequency. The post-modified electrocatalyst with *p*-(aminomethyl) benzoic acid (PABA), *p*-sulfobenzoic acid potassium (PSBA), and *p*-sulfamidobenzoic acid (PSABA) induces the steric effect and thereby reduces the activity of the HER. The modifiers attached to unsaturated Zr₆ sites with good coverage are responsible for the steric effect.²⁷⁰ A bimetallic layered MOF with copper-phthalocyanine as a ligand (CuN₄) and zinc-bis(dihydroxy) complex (ZnO₄) as a linkage (PcCu–O₈–Zn) was developed with a faradaic efficiency of 88% and high selectivity towards CO. Both experimental and theoretical calculations reveal that CuN₄ facilitates the protonation of adsorbed CO₂ while zinc-bis(dihydroxy) complexes act as the catalytic sites for the ECR process.²⁷¹ Overall, MOF-derived materials with a highly active metal site and good electrical conductivity are a good platform for electrocatalytic CO₂ reduction in the near future. COFs with tuneable catalytic centers provide a highly exposed surface area and active sites suitable for the CO₂ reduction reaction. A 2D layered structure with eclipsed stacking leads to insufficient use of active sites, thus leading to reduced activity towards CO₂ reduction. This problem can be avoided by exfoliating of the layered structure to a large surface area with high accessibility to more active sites. Zhu *et al.* designed covalent organic frameworks by the Schiff-base condensation reaction of metalloporphyrin and TTF. Remarkably, the FE was found to be 91.3% at –0.7 V and after exfoliation, the nanosheets with 5 nm thickness exhibit 100% FE at –0.8 V.²⁷²

Researchers have been focused on the development of non-noble earth-abundant catalysts for CO₂ reduction. In this regard, tin, lead, and bismuth have gained much attention due to their high stability and selectivity. Among these, bismuth possesses a wide bandgap, good electrical conductivity, rich valence electrons, and large theoretical capacity. Bismuth catalysts were developed by *in situ* restructuring of 2D bismuth oxyhalides. The electrocatalyst shows an FE of 90% for formate formation with a current density of 200 mA cm^{–2}.²⁷³ Yang *et al.* synthesised a stable free-standing Bi monolayer (bismuthene) to demonstrate high electrocatalytic CO₂ reduction activity towards formate formation. The thin monolayer of Bi (111) has a unique compressive strain that shows better catalysis activity than thicker nanosheets. The more exposed (011) facet of thicker Bi nanosheets strongly binds to intermediates and results in poisoning; this lowers the activity of the thick nanosheets of Bi.²⁷⁴ Another 2D material, black phosphorous, is used for electrocatalytic reduction of CO₂ to formic acid. The catalyst shows a FE of 25.8% at –1.3 V. The activity is enhanced to 92% at a lower potential of –1.0 V by loading Bi metal. The black phosphorous provides a large surface area and improves the kinetic activity for CO₂ reduction.²⁷⁵ Hexagonal boron nitride is a structural analogue of graphene widely used for oxygen reduction reactions due to its magnetic properties and wide and tuneable semiconducting band gaps. DFT calculations were carried out to investigate the reduction process of C-doped boron nitride nanoribbons (BNNRs) and line-defect (Ld)-embedded zigzag BNNRs with C₂ (Ld-C) and B₂ (Ld-B) dimers. Both boron and carbon atoms provide highly active sites for CO₂ reduction.²⁷⁶ In a study, the synthesis of Cu(I) supported BN sheets for CO₂ ECR to acetic acid was reported. The catalyst shows an FE of 80.3% with a current density of 1.39 mA cm^{–2}. The high activity can be attributed to the synergistic effect of BN, the copper metal centre and the N-based ligand.²⁷⁷ Pd catalysts are widely used for CO₂ reduction due to their distinguishable capability of converting CO₂ selectively into formate or CO. The selectivity depends on their surface binding abilities towards CO* or COOH*. The pristine Pd nanosheets possess a more exposed (111) facet, while reconstruction into a crumpled sheet-like structure results in a more exposed (100) facet with good electrocatalytic activity. The (100) facet exhibits a lower binding affinity to CO, facilitating the CO₂ reduction to CO.²⁷⁸ Metal oxides such as ZnO, TiO₂, RuO₂, Co₃O₄, SnO_x, *etc.* have been used as active electrocatalysts for CO₂ reduction. Among these, SnO_x is considered to be active in the reduction of CO₂ to HCOOH. Nanoflakes of amorphous SnO_x were fabricated by a mass production method from liquid metals. These nanoflakes were further modified with single atoms of Bi and show high selectivity of more than 90% towards HCOOH production.²⁷⁹

4.5 Photoelectrochemical conversion of CO₂

Conversion of CO₂ by photoelectrochemical (PEC) methods is a combination of photocatalytic and electrocatalytic conversions. This approach minimized the disadvantages of

both technologies, combined their advantages, and widened the range of catalysts. Compared to the particle suspension methodology in photocatalytic conversion, PEC reduction based on photoelectrodes has enhanced the charge separation and provided high solar conversion efficiency. Different research groups have proposed several hypotheses regarding PEC conversion of CO₂ that include complex multistep reaction pathways and shared intermediates.^{280–285}

On excitation of the photoelectrode with photons of suitable energy ($E_g \leq h\nu$), electron-hole pairs are generated which independently migrate to the cathode and anode to undergo redox reactions. Photogenerated electrons at the cathode are engaged in the reduction and conversion of CO₂ to solar fuels, while holes take part in the oxidative splitting of water (converting H₂O to O₂). A typical 2-e[−] reduction pathway initiates with the formation of the carbon dioxide anion radical (CO₂^{•−}) which gets adsorbed onto the electrode. H⁺ in the aqueous medium then reacts easily with the O atom of the adsorbed CO₂^{•−}, as the C atom is bonded to the electrode surface, leading to the formation of CO₂H_{ads}. The bond breaking in CO₂^{•−} is more facile due to its bent structure compared to the linear geometry of CO₂. CO₂H_{ads} formed thereafter gets reduced to CO, or may undergo successive reactions with e[−] or H⁺ to give other value-added products like CH₃OH, CH₄, *etc.*²⁸⁶ Hence effective photoconversion efficiency is highly required for effective PEC reduction of CO₂ due to the large consumption of electrons and holes. Henceforth, various strategies are conducted to modify the photoelectrodes, *viz.*, engineering of the band gap for effective light-harvesting, construction of hierarchical nanostructures, control of catalyst morphology, utilization of multi-functionalized homojunctions or heterojunctions, and co-catalyst loadings.^{287–291} Most of the PEC electrodes are prone to photo-corrosion which results in short-term usability. In most cases, catalytic layers of TiO₂ and noble metals like Pt, or Ir, usually fabricated by atomic layer deposition (ALD), are often complex and expensive for deployment.

4.5.1. Fundamentals of photoelectrochemical reduction.

PEC CO₂ fixation can be treated as an artificial photosynthesis strategy because it imitates the natural photosynthesis reaction.²⁵ Photosensitizers such as chlorophyll harness solar radiation and perform CO₂ fixation in natural photosynthesis, whereas in PEC CO₂ reduction, light radiation and electricity are used to drive the CO₂ transformation forward.^{292,293}

A schematic representation of a PEC cell having two compartments separated by a proton exchange membrane for CO₂ reduction is given in Fig. 17. In general, p-type semiconductors are used as photocathodes in a PEC system, and n-type semiconductors function as anodes.²⁹⁴ Upon light irradiation, electron-hole pairs are generated in the photocathode. The band bending phenomenon observed at the electrode-electrolyte interface is responsible for separating photogenerated electrons and holes. The application of an external potential to the system intensifies

the band bending and increases the electron-hole separation. The photogenerated electrons participate in the CO₂ reduction process at the electrode-electrolyte interface.²⁹⁵

The solar-to-fuel (STF) conversion efficiency of the PEC system is calculated as

$$\text{STF} = \frac{r_{\text{fuel}} (\text{mmol of fuel per s}) \times \Delta G^\circ (\text{kJ mol}^{-1})}{P_{\text{solar}} (\text{mW cm}^{-2}) \times \text{area} (\text{cm}^2)}$$

where r_{fuel} is the quantity of chemical fuel produced per second, and ΔG° is the Gibbs free energy associated with the conversion of CO₂ to fuels. P_{solar} is the power density of the light source used, and the area represents the photoelectrode area under light irradiation.²⁹⁶

4.5.2. 2D materials in the PEC reduction of CO₂. 2D materials can be effectively employed for the construction of stable, cost-effective, highly efficient catalytic layers. As a 2D material for photoelectrodes, graphene has received considerable attention for PEC reduction of CO₂ due to its π - π conjugation that promotes e[−] transfer and enhances CO₂ adsorption. A remarkably strong π - π interaction of CO₂ or CO₂^{•−} is established with graphene, as CO₂ contains a delocalized π - π conjugation, while graphene has an extensive 2D network of π conjugation.²⁹⁷ This synergistic interaction shows the more significant adsorption of CO₂ over the photoelectrode surface. Moreover, graphene has a large surface area of 2630 m² g^{−1}, thus providing many active sites for CO₂ adsorption and reduction.^{298,299} The availability of un-adsorbed CO₂^{•−} is reduced in the presence of the graphene photoelectrode, which would otherwise lead to the formation of formate ions by the action of the nucleophilic carbon atom of CO₂^{•−} as a Lewis base.³⁰⁰ The hydrophobic nature also makes the graphene surface more controllable to facilitate CO₂ reduction rather than transferring electrons to the H₂O molecule.³⁰¹ When a strongly coupled host-guest rGO/GO nanohybrid is fabricated by stacking the layers one above the other, the bandgap is lowered to 2.58 eV, enhancing the PEC performance.³⁰² While administering graphene to the electrode, usually using a polymeric binder, it often undergoes agglomeration due to the van der Waals forces acting between the layers.³⁰³ Recently, the self-agglomerating nature of graphene has been demonstrated to be suppressed by the design of a 3D flower-like reduced graphene oxide (f-rGO) modified with Cu NPs and deposited on Cu foam (Fig. 18).³⁰⁴ The so-formed CuNP/f-rGO/CF fabricated by electrochemical methods acted as a dual-role photoanode for PEC conversion of CO₂ to CO, C₂H₄, HCOOH, CH₃COOH, and C₂H₅OH. Decomposition of water at the photoanode delivers e[−] and H⁺, simultaneously with the anode's photovoltage compensation, which is reflected with a more negative cathode potential desirable for the conversion of CO₂. Due to its characteristic physicochemical properties, graphene, when integrated with other semiconductors such as TiO₂, Si, BiWO₆, Cu₂O, and other metal NPs, may form a Schottky barrier, leading to effective separation of charge carriers.^{305–307}

Replacing noble metal catalysts, 2D TMDCs such as MoS₂, MoSe₂, and WS₂ have gained considerable attention as PEC electrodes, due to their robust stability in acidic electrolytes, layered structure with basal planes being less permeable, and edges acting as active sites of PEC reductions.³⁰⁸ Also, monolayer and bulk MoS₂ have a bandgap of 1.88 eV and 1.29 eV, respectively,³⁰⁹ with the conduction band minimum higher than the redox potentials of most CO₂ conversions. Different defect sites of MoS₂ were analysed, and compared with the grain boundaries, edges and S vacancies (7–10% optimal density of vacancies) are the most catalytically active centers.³¹⁰ Simultaneously, Mo-terminated edges of layer-stacked vertically aligned bulk MoS₂ exhibited the highest rate of CO₂ reduction while as demonstrated for 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄), the IL is more selective for CO formation than water splitting.³¹¹ Due to significant variance in work functions, the deposition of n-type MoS₂ onto p-type semiconductors like Si results in high induced electric fields, thereby enhancing the charge transfer between the p-type semiconductor through MoS₂ and the solid/electrolyte interface.³⁰⁸ In addition to being an effective PEC catalyst, MoS₂ can also act as a protective layer stabilizing the photoelectrode. However, thin-film fabrication over the semiconductor electrode is rather tricky. It is usually achieved by the ALD technique, where the thickness/morphology is engineered by the number of cycles and deposition conditions. Jang *et al.* successfully introduced thermolysis as a fabrication method for developing thin films of MoS₂ over a Si substrate, using a precursor solution of (NH₄)₂MoS₄. The film thickness over the range of 5–29 nm was tuned by changing the precursor solution concentration. Moreover, among the different phases of 2D TMDCs, the 1T metallic phase usually exhibits enhanced PEC performance compared to 2H or 3R phases.³¹²

Inspired by graphene and various graphene analogs, the fabrication of photoelectrodes using 2D ultrathin van der Waals (vdW) heterostructures forming an ensemble of heterojunctions is also interesting and gaining attention. Such 2D vdW heterostructures have ultrafast transfer of charge carriers and robust carrier mobility. The MoS₂/graphene photoelectrode can have improved PEC performance when compared individually to MoS₂ or graphene.³¹³ Promoted PEC reactions due to enhanced charge transfer by reducing the potential barrier are observed when a heterojunction photoelectrode of MoS₂/monolayer O-g-C₃N₄ was developed.³¹⁴ An increase in the intrinsic activity with the enhancement in PEC active sites was reported through the formation of the graphene/h-BN heterostructure.³¹⁵ Furthermore, these 2D nanostructures can be combined with other 1D or 3D nanomaterials forming complex heterostructures, and accordingly can engineer the structural and functional designs for PEC cells and other optoelectronic devices.

Only a few reports have been focused on 2D materials for the PEC reduction of CO₂. The endless number of untested 2D nanomaterials and their heterojunctions, or functionalized 2D materials, infers that absolute materials are still waiting to be explored for PEC CO₂ conversion. An in-depth understanding of the adsorption of CO₂ at the active sites of the photoelectrode, the activity of these active surface sites to convert CO₂, and the effective transfer and utilization of charge carriers at the electrode interfaces is required to realize state-of-the-art PEC-based energy conversion systems. Even though there are such theoretical studies on 2D nanomaterials for PEC conversion of solar energy, they have usually employed ultrathin single-layer models, of which large-scale synthesis is highly challenging. MXenes, the new upcoming family of 2D transition metal carbides, nitrides, or carbonitrides, are the future two-dimensional materials for the PEC reduction of CO₂. Besides, until now, the PEC of CO₂ is still far from the requirements of being commercialized.

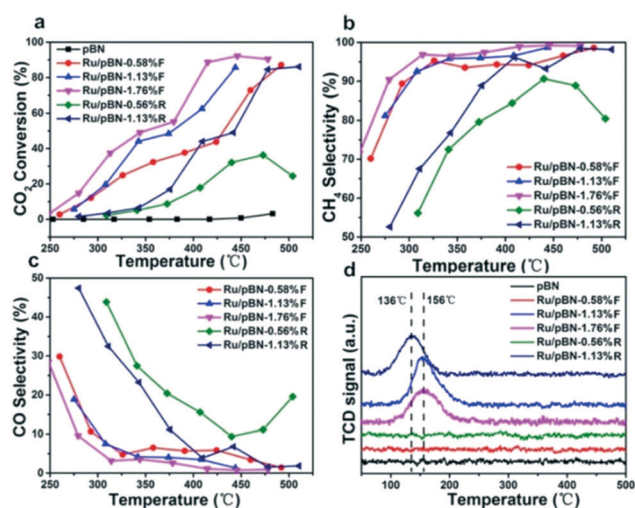


Fig. 19 Trend in CO₂ hydrogenation by Ru/pBN-*x*F and -*x*R (a); effect of temperature on CO₂ conversion (b); CO selectivity at varied temperatures (c); H₂-temperature-programmed reduction of all the samples (d). “Reproduced from ref. 330 with the permission from American Chemical Society, copyright 2019”.

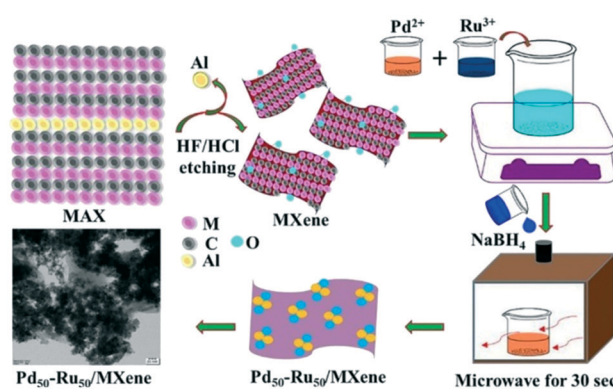


Fig. 20 Schematic illustration for the preparation of MXene from MAX and synthesis of Pd₅₀-Ru₅₀/MXene via a microwave process for 30 min. “Reproduced from ref. 331 with permission from Elsevier, copyright 2021”.

4.6 Thermal conversion of CO₂

Catalytic molecules can activate the unreactive CO₂ molecules and transform CO₂ into valuable chemicals by reducing the energy barrier for the reaction. In general, a thermocatalytic CO₂ conversion strategy involves the passing of a mixture of gases (CO₂, H₂ *etc.*) over the catalytic surface at higher temperatures and pressure to convert CO₂ into valuable products.³¹⁶ The CO₂ to CO conversion is achieved *via* a

reversible water gas shift reaction. Fischer–Tropsch synthesis performs the conversion of CO to hydrocarbon fuels *via* the water gas shift reaction. CO₂ reduction to CO in the presence of hydrogen is relatively easier to achieve with high selectivity and significant conversion efficiency. But the further conversion of CO to long-chain hydrocarbon fuels and alcohols with required selectivity is a challenging task.³¹⁷ To perform the thermocatalytic CO₂ conversion reaction, the active sites on the catalyst should be capable of injecting the

Table 3 Summary of different 2D nano-materials used for CO₂ conversion

Method	Catalyst/device structure	Reaction conditions	Products	Yield	Ref.
Photochemical conversion of CO ₂	ZnO/g-C ₃ N ₄ heterostructures	Cylindrical steel reactor, CO ₂ purge time: 20 min, rate: 20 mL min ⁻¹ , lamp: 5WUVC (254 nm)	CO, CH ₄	CO: 12.73 μmol g ⁻¹ CH ₄ : 3.99 μmol g ⁻¹	332
	Z-Scheme ZnO/g-C ₃ N ₄ photocatalyst	UV irradiation at 0.4 MPa, 25 °C	CO, CH ₄	CO: 70 μmol g ⁻¹ CH ₄ : 50 μmol g ⁻¹	333
	NH ₂ -MIL-101(Fe)/g-C ₃ N ₄	300 W xenon arc lamp; circular glass fiber membrane activated at 120 °C for 12 h	CO	132.8 μmol g ⁻¹	203
	Z-Scheme g-C ₃ N ₄ /FeWO ₄	Stainless steel photoreactor, Xe lamp of 300 W, He purging (20 mL min ⁻¹ for 1 h)	CO	6 μmol g ⁻¹ h ⁻¹	334
	Ti ³⁺ defective SnS ₂ /TiO ₂ photocatalyst	270 mL Pyrex reactor, simulated solar light irradiation for 4 h	CO	58 μmol g ⁻¹ h ⁻¹	335
Electrochemical conversion of CO ₂	Ultrafine CeO ₂ -decorated layered double hydroxide nanosheets	50 mL closed stainless reactor, 300 W Xe lamp	Syn gas	CO: 85 μmol g ⁻¹ h ⁻¹	336
	Copper immobilized MXene	Catalyst coated glass carbon electrode as working electrode, Ag/AgCl electrode as reference electrode and carbon rod electrode as counter electrode	CH ₃ OH	59.1% CO ₂ conversion	337
	Mo ₂ C and Ti ₃ C ₂ MXenes	Ionic liquid 1-ethyl-2-methylimidazolium tetrafluoroborate electrolyte, catalyst coated glassy carbon working electrode & Ag/Ag ⁺ reference electrode	CO	90% CO ₂ conversion	338
Photoelectrochemical conversion of CO ₂	g-C ₃ N ₄ /ZnTe heterojunction	Recorded in 2 mM K ₄ Fe(CN) ₆ with a scan rate of 50 mV s ⁻¹	C ₂ H ₅ OH	Generation rate of 7.1 μmol cm ⁻² h ⁻¹ at -1.1 V	339
	Cu NPs modified rGO flowers deposited on Cu foam (CuNP/f-rGO/CF)	Photoelectrode separated by Nafion membrane, 0.1 m H ₂ SO ₄ and 0.1 m NaHCO ₃ solutions were electrolytes, light source at 365 nm with intensity ≈100 mW cm ⁻²	CO, CH ₄ , C ₂ H ₄ , HCOOH, CH ₃ COOH, C ₂ H ₅ OH	Generation rate of HCOOH highest with ~12 μmol h ⁻¹	304
	Defect h-BN	—	CH ₃ OH	TOF of 1.52 × 10 ⁻² S ⁻¹	340
	Vertically aligned MoS ₂ in EMIM-BF ₄	Voltage swept between +1.0 and -0.764 V vs. RHE with a 15 mV s ⁻¹ scan rate	CO	CO ₂ reduction current density of 130 mA cm ⁻²	311
	MoSe ₂ thin films over Si substrate (MoSe ₂ /Si)	Scan rate of 10 mV s ⁻¹ from +0.2 V to -1.0 V voltage sweep, light irradiation with white LED USB flashlight (400–700 nm)	—	CO ₂ reduction activity (0.127 mA cm ⁻²) increased by 9.3 times on light irradiation	341
Thermal conversion of CO ₂	Cu–Zn supported on rGO	250 °C, 15 bar	CH ₃ OH	Space time yield: 424 mg g _{cat} ⁻¹ h ⁻¹ ; 26% CO ₂ conversion	322
	Ni/rGO	240 °C, 10 bar	CH ₄	Space time yield: 24.9 g kg _{cat} ⁻¹ h ⁻¹ ; 55.3% CO ₂ conversion	323
	Ni–SiO ₂ /GO–Ni-foam catalyst	470 °C, 1 bar	CH ₄	TOF of 0.3041 s ⁻¹ ; 83.7% CO ₂ conversion	324
	MoS ₂ /graphene hybrid	300 °C, 10 bar	CH ₄	33% CO ₂ conversion	326
	Pt/MoS ₂	210 °C, 30 bar	CH ₃ OH	TOF: 162.5 h ⁻¹	328
	MoS ₂ modified with porous activated carbon	200 °C, 20 bar	HCOOH	TOF: 510 h ⁻¹	329
	Ru/pBN	400 °C, 10 bar	CH ₄	81.1% CO ₂ conversion	330
	Pt loaded Ti ₃ -xC ₂ Ty MXene	Ambient conditions	Amides	~100% conversion	321
	Pd ₅₀ –Ru ₅₀ /MXene	150 °C, 10 bar	CH ₃ OH	78% CO ₂ conversion with TON 2932	331

electrons to the antibonding orbital of CO₂. In a thermocatalytic CO₂ conversion reaction, hydrogen is supplied as the reducing agent. The ability of the catalytic surface in dissociating the hydrogen molecule to atomic hydrogen (H*) is a critical parameter in evaluating the hydrogenation capacity of the catalyst.³¹⁸

4.6.1. Role of 2D materials in the thermocatalysis of CO₂.

Thermocatalytic conversion of CO₂ to valuable chemicals has received much attention because of its suitability for large-scale industrial applications.³¹⁹ The common thermocatalysis of CO₂ is based on the hydrogenation reaction to produce CO, CH₃OH, and CH₄. Due to the high thermodynamic and chemical stability of CO₂, a co-reactant such as H₂ with higher Gibbs free energy has been used for the facile progress of the reaction.³²⁰ Further, suitable catalysts can reduce the activation energy and make the bond cleavage easier during the hydrogenation process to yield selective products. In this context, the relevance of single-atom catalysts is significantly high due to their atomic dispersion and unsaturated coordination. However, due to the high surface energy, they tend to form aggregates. This can be remedied by using a suitable catalyst support and creating a good interaction between a single atom and the support.³²¹ The role of Cu–Zn supported on rGO in the catalytic hydrogenation of CO₂ to methanol was analysed. Zn oxide was used for the better dispersion of Cu particles, and the electron transfer from Zn oxide to Cu metal creates Cu⁰ and Cu⁺ species, promoting the hydrogenation process. Reduced graphene oxide was used as a support material to achieve better metal dispersion with an improved surface area. The effect of reaction temperature and percentage loading of Cu–Zn on rGO was analysed to optimize the reaction conditions to maximize methanol production. The hydrogenation was carried out in a tubular stainless steel fixed bed reactor after the *in situ* reduction of the catalyst at 350 °C for 2 h followed by treatment with the CO₂/H₂ mixture for the hydrogenation process. The Cu–Zn loading of 10 wt% at a temperature of 250 °C and 15 bar pressure was identified as the optimum condition for 26% CO₂ conversion with 424 (mg g_{cat}^{−1} h^{−1}) space time yield (STY) of methanol.³²² Similarly, a Ni/rGO hybrid was used for the catalytic hydrogenation of CO₂ to methane. Transition metal catalyst Ni was selected for the selective hydrogenation of CO₂ to methane and a Ni loading of 15% on rGO results in a 55.3% conversion of CO₂ to methane with 24.9 (g kg_{cat}^{−1} h^{−1}) STY³²³ at 240 °C and 10 bar pressure. In another study, a Ni–SiO₂/GO–Ni-foam catalyst was used for the hydrogenation of CO₂ to methane. The change in the electronic structures of Ni due to the presence of graphene or other metals could terminate the side reactions and avoid the formation of carbon deposition. Also, the incorporation of Ni into macro-mesoporous materials like silica was conducted to stabilize Ni by avoiding sintering during the process. By catalytic vapour deposition (CVD) followed by oxygen plasma treatment, GO was coated over

Ni foam, and on the top, this Ni–SiO₂ was deposited *via* sol–gel and hydrothermal methods. The intercalated GO layer could strengthen the interaction between Ni species and Ni-foam in the catalyst, and this helps Ni species to eliminate sintering on Ni foam. The intercalated GO layer could strengthen the interaction between Ni species and Ni-foam in the catalyst, and this helps Ni species to eliminate sintering on Ni foam. Ni–SiO₂/GO–Ni-foam with a surface area of 10.07 m² g^{−1} showed a CO₂ conversion of 83.7% with a TOF of 0.3041 s^{−1} at 470 °C and 0.1 MPa which was higher when compared to Ni–SiO₂/Ni-foam, GO–Ni-foam and Ni-foam.³²⁴ In another study, g-C₃N₄ was used as a single-atom catalyst supported for the hydrogenation of CO₂ to formic acid. The use of non-noble metal atoms such as Fe, Co, Ni, and Cu supported on g-C₃N₄ was highlighted using DFT calculations. The DFT calculations reveal that the reduction of CO₂ is a two-step reaction that consists of forming a formate (HCOO) intermediate and its subsequent transformation into a formic acid product. Based on activation barriers on the rate-determining steps, the catalytic activity for the CO₂ reduction to formic acid is found to be in the order of Fe-g-C₃N₄ > Co-g-C₃N₄ > Cu-g-C₃N₄ > Ni-g-C₃N₄.¹³⁶ Ag nanoparticle (NP) decorated porous C₃N₄ frameworks (PCNFs) prepared *via* the direct carbonization of the covalent triazine frameworks (CTFs) at different pyrolysis temperatures and used for carboxylation of CO₂ and terminal alkynes under mild conditions were reported. The catalyst Ag/PCNF-700, which was carbonized at 700 °C, showed better catalytic performance due to the presence of N atoms, porosity and the presence of well-dispersed Ag NPs in the catalyst.³²⁵

The potential of graphene as a support material for MoS₂ during the hydrogenation of CO₂ was examined using experimental and DFT calculations. Graphene grafted MoS₂ platelets were prepared by pyrolysis of natural polysaccharides containing the (NH₄)₂MoS₄ precursor at 900 °C for 2 h. Graphene grafted MoS₂ showed better catalytic activity than bare MoS₂ and the catalytic activity was analysed from the 300–600 °C temperature range. Carbon monoxide (CO) and methane were the two products detected in experiments carried out with different catalysts. CO was the major product when the catalyst used was pristine graphene or MoS₂, whereas methane was the major product while using MoS₂/graphene hybrid catalysts with more than 95% selectivity. However, desulfuration of MoS₂ and formation of less catalytically active MoO₃ were evidenced under the reaction conditions.³²⁶ In another study, the CO₂ reduction reaction of a Co atom supported on a MoS₂ monolayer was analysed by first principles simulation, and the preferred dispersion of Co on MoS₂ was evidenced. DFT calculations reveal that the CO₂ conversion to methanol proceeds through reverse water gas conversion with hydrogenation of CO to HCO as the rate limiting step. The predicted pathway for the methanol production is *CO₂ → *CO → *CHO → *CH₂O → *CH₂OH and *CH₃O → CH₃OH.³²⁷ Li *et al.* have studied the effect of neighbouring Pt on the hydrogenation of CO₂ in the

Pt anchored MoS_2 catalyst (Pt/MoS_2). The catalytic hydrogenation was carried out using Pt doped MoS_2 in 30 mL of DMF under a pressure of 30 bar. The effect of temperature on the yield and selectivity to the product was evidenced; for instance, the hydrogenation of CO_2 using the 7.5% Pt/MoS_2 catalyst yielded 0.2 mmol of HCOOH and 0.8 mmol of methanol at 150 °C, whereas 2.3 mmol of formic acid and 7.3 mmol of methanol were produced at 210 °C. The methanol selectivity got reduced during the reaction period from 95.4% to 81.3% at 150 °C and from 93.0% to 76.0% at 210 °C. Due to the quick drop in selectivity to formic acid from 70% to 30% during the initial time of the catalysis, formic acid was regarded as an intermediate product before the formation of methanol. Also, from DFT studies, it was observed that when compared to isolated Pt, neighbouring Pt monomers showed better catalytic activity due to their lower activation energy. By using isolated Pt, direct formation of methanol takes place making it the hydrogenation product; however, with the use of the neighbouring Pt monomer, methanol is generated *via* the formation of formic acid. Therefore, the study concludes that the catalyst (7.5% Pt/MoS_2) with a turnover frequency of 162.5 h^{-1} and activation energy of $124.7 \text{ kJ mol}^{-1}$ can be an ideal candidate for catalytic hydrogenation reactions.³²⁸ Recently, Bharath *et al.* have reported formic acid production from CO_2 hydrogenation using an economical and highly efficient MoS_2 modified with porous date seed derived activated carbon ($\text{MoS}_2/\text{f-DSAC}$). A turnover frequency of 510 h^{-1} was achieved by the $\text{MoS}_2/\text{f-DSAC}$ catalyst at 200 °C and 20 bar for 15 h during the formation of formic acid.³²⁹

In 2D h-BN, B and N atoms can act as ligands to the metals and so for the coordination of metals to the surface of h-BN, defect engineering can be adopted for creating B and N vacancies. The immobilisation of metal atoms on the surface of h-BN for effective hydrogenation of CO_2 was first reported in the year 2019 by Fan *et al.*³³⁰ The presence of numerous OH functional groups at the edges of h-BN (or in the porous pBN) facilitated the anchoring of Ru atoms due to electrostatic interactions.

The fixation of the Ru precursor on pBN was achieved by simple vacuum filtration of the mixture of the solution containing pBN and $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$. Further, the immobilization of Ru on pBN was carried out by annealing at 750 °C in a 50:50 Ar/NH_3 atmosphere for 1 h. The effect of Ru loading on pBN was analysed and Ru/pBN 1.76% F with 81.1% CO_2 conversion efficiency and 98.8% CH_4 selectivity at 400 °C was obtained (Fig. 19a and b). The higher Ru loading leads to better catalytic performance like CO_2 conversion efficiency and CH_4 selectivity due to the availability of active sites in the catalyst. On the other hand, $\text{Ru}/\text{pBN-xR}$ samples prepared *via* rotary evaporation showed decreased catalytic activity when compared to $\text{Ru}/\text{pBN-xF}$ prepared by the filtration process due to the formation of large metal particles and showed better selectivity towards CO (Fig. 19c). The reduction temperature

measured for $\text{Ru}/\text{pBN-xF}$ is ~ 156 °C, and that for the $\text{Ru}/\text{pBN-xR}$ catalyst is ~ 136 °C (Fig. 19d), which indicates the presence of RuOx in $\text{Ru}/\text{pBN-xR}$. Apart from this, DFT calculations hint that the presence of low valence Ru atoms on pBN can selectively hydrogenate CO_2 to methane.³³⁰

Another type of 2D material used as a catalytic support for single metal atoms is MXenes. Due to their surface defects and significantly high reducing ability, $\text{Ti}_{3-x}\text{C}_2\text{T}_y$ MXenes are supposed to be an ideal choice as a support for single-atom catalysts.³²¹ Pt loaded $\text{Ti}_{3-x}\text{C}_2\text{T}_y$ MXene ($\text{Pt}_1/\text{Ti}_{3-x}\text{C}_2\text{T}_y$) was synthesized through a room temperature self-reduction and stabilization process. In the Pt anchored MXene sheets, the strong bond between Pt and C has been achieved due to the occupancy of Pt atoms in Ti-deficit defect sites in the MXene. The as-prepared Pt/MXene catalyst could catalyse the formylation reaction of amine in the presence of CO_2 at room temperature and ambient pressure to yield amides with a higher turnover number and high selectivity towards amides as compared to Pt particles alone as the catalyst.³²¹ Very recently a bimetallic $\text{Pd}_{50}\text{-Ru}_{50}$ loaded 2D MXene was synthesized *via* a microwave process for the selective catalytic hydrogenation of CO_2 to form methanol. The scheme for the preparation of $\text{Pd}_{50}\text{-Ru}_{50}/\text{MXene}$ is shown in Fig. 20. By removing the interlayered Al from MAX (Ti_3AlC_2) through etching with HF, MXenes ($\text{Ti}_3\text{C}_2\text{T}_x$) were prepared, and the etching process provides the sites for $\text{Pd}_{50}\text{-Ru}_{50}$ alloy nanoparticles to get anchored on the MXene surface. The nanoparticle precursors (RuCl_3 and PdCl_2 in 1:1 ratio) were introduced to the system, and the released Pd^{2+} and Ru^{3+} ions electrostatically anchored on the MXene surface. The reduced nanoparticle alloy can prevent the re-stacking of MXene layers and lead to a high surface area system formation. The hydrogenation process involved the hydrolysis of NaBH_4 for facilitating hydrogen with ethylene glycol solution as the capture agent. The higher product selectivity and total turnover number (TON) were observed for $\text{Pd}_{50}\text{-Ru}_{50}/\text{MXene}$ (99%, 2932) when compared to unmodified MXene (88%, 120) and $\text{Pd}_{50}\text{-Ru}_{50}$ (87%, 1810) catalysts under the reaction conditions of 150 °C and 10 bar pressure for 12 h. The high TON (2932), product selectivity (99%), CO_2 conversion efficiency (78%) and methanol production efficiency (76%) of the $\text{Pd}_{50}\text{-Ru}_{50}/\text{MXene}$ catalyst are due to the adequate amount of highly dense basic sites with a good surface area which in turn can enhance the hydrogenation of CO_2 . Even after several cycles of hydrogenation, the good stability and intact morphology hint at the practical utility of the proposed catalyst.³³¹ To conclude, the usage of single atom catalysts is more significant in the case of thermo-catalysis and the major role of 2D materials is to act as catalyst supports and to improve the conversion rate by enhancing the surface area and availability of reactive sites of the catalyst. The 2D catalysts used for the various catalytic conversions of CO_2 are summarized in Table 3.

4.7 Defect engineering in 2D catalysts for effective CO₂ conversion

Defect engineering has been claimed to be an effective tactic that enriches photocatalytic surfaces of 2D materials with exposed active sites that align every photoinduced charge carrier into the photoreduction process directly without leaving any room for exciton recombination. Defect engineering at both the surface and at the atomic level, such as creating anion/cation vacancies, crystal distortions, pits and pores, grain boundaries, stacking faults, *etc.* directly influences the optoelectronic properties of 2D nanomaterials. Moreover, the active sites optimize the reaction rate of adsorption, activation and conversion of CO₂ to corresponding products. Recently, defect concocted 2D atomic level materials including TMDCs, LDHs, *etc.* have drawn much attention in the arena of photocatalytic CO₂ reduction. In a recent study, Li *et al.* have fabricated CuIn₅S₈ ultrathin photocatalysts covered with sulfur defects that excelled with nearly 100% methane selectivity owing to the active sites that surfaced on Cu and In.³⁴² Substantially, simple metal sulfides configured into special morphologies including hierarchical, hollow or other dimensional structures which offer more specific surface areas and pore size have proved to contribute to the augmentation of active site formation.³⁴³ Wang's group exploited this possibility to achieve 100% CO selectivity without any cocatalyst support, by means of a hollow multi-shelled system of SnS₂/SnO₂ composed of lattice distortions. The hollow structure, apart from enabling an efficient light harvest despite the absence of any sensitizers, apparently promotes CO₂ adsorption.³⁴⁴ Moreover, introduction of a non-metallic dopant and defect engineering bring about a bridge between photoinduced charge carriers and surface reactions owing to the modulation of the electronic structure. Sun *et al.* addressed the fundamental challenges in photocatalysis including poor efficiency, weak charge carrier transport, *etc.* by establishing phosphate and oxygen vacancies in the Bi₂WO₆ atomic layer and explored the fine connection between the electronic structures and output of the engineered atomic layered photocatalyst which realised a better methanol formation rate.³⁴⁵ Furthermore, Xie *et al.* unveiled the facts behind the bond between defect sites and CO₂ photoreduction by designing a freestanding single-unit-cell o-BiVO₄ layer enriched with vanadium vacancies which created more new defect levels, resulting in the highest methanol production rate of 398.3 μmol⁻¹ h⁻¹ *via* defective layered photocatalysts.³⁴⁶ Nevertheless, introduction of active sites is important in the case of LDH photocatalysts. Besides the possibility of tuning the catalytic electronic structure in accordance with the given metal cations, thickness reduction of LDHs can result in the formation of more surface-active sites. The work put forward by Zhang and co-workers confirmed the versatile path to enhance the photocatalytic performance by thinning ZnAl-LDH nanosheets to less than 5 nm to harvest CO in the presence of water vapour at a rate of

7.6 μmol g⁻¹ h⁻¹ on account of the abundant oxygen vacancies and unsaturated Zn⁺ cation sites which also enabled the activation of adsorbed CO₂ molecules.³⁴⁷

Chemically stable electrocatalysts with good performance are necessary to improve the CO₂ reduction efficiency. Defect engineering in 2D materials is an obvious way to enhance the ECR process. For the first time, in 2020 Chen *et al.* employed DFT calculations for thorough analysis of defect engineering in 16 different types of O-terminated MXenes. They found that Hf₂NO₂ with Hf vacancies is the most promising defective MXene showing a low overpotential of 0.45 V. A significant change in the Fermi level created upon generation of vacancies shows a linear relationship with the binding energy change of ECR intermediates.²⁶⁵ Defective graphene act as an excellent electrocatalyst in the ECR process. Han *et al.* synthesised defective graphene by the N-removal method.³⁴⁸ They first synthesised N-doped graphene by annealing of pristine graphene under NH₃. The obtained N-doped graphene is again annealed at 1150 °C to get the defective graphene. They observed that the catalytic activity of the graphene was enhanced with the increase in defect concentration. The presence of defects also helps to create abundant catalytic sites and facilitates the strong adsorption of CO₂. The defect engineering in graphene improves the affinity for the reaction of intermediates by distributing local charge density uniformly. Defect engineering of 2D materials for electrolytes can also show enhanced performance for photoelectrochemical reduction of CO₂. Similar works were developed in many other fields such as water splitting and N₂ fixation, following innovative tracks on CO₂ photoreduction. However, an insightful study is yet to be carried out to expose the obscure facts on the influence of defects on photophysical properties like carrier lifetime, diffusion length, and PL intensity; photocatalytic activity and selectivity; interaction of electrolytes on the defects, to identify and quantify the exact defect among many if present, which contributes to the catalytic conversion, *etc.*

5. Challenges and prospects

5.1 Challenges and future prospects

In general, the CO₂ adsorption capacities of adsorbents are evaluated gravimetrically, which is based on the mass of the adsorbate per unit mass of the adsorbent. However, for more precise evaluation, the volumetric CO₂ adsorption capacities should be reported. Physisorption of CO₂ on an adsorbent with weak van der Waals interactions is not enough to hold the adsorbed gases due to the possibility of desorption by a minimal thermal distortion. However, very strong chemisorption of CO₂ can reduce the reusability of the material because of the requirement of tedious gas removal procedures of the sorbed gas. Therefore, materials with suitable adsorption-desorption characteristics should be developed. Even though the chemisorption or physisorption of CO₂ on 2D materials has been identified *via* spectral techniques (FTIR), detailed kinetic studies on the adsorption

and desorption of CO₂ on 2D adsorbent surfaces are rare. Hence the parameters such as the rate of adsorption, adsorption half time, adsorption isotherms, *etc.* are yet to be identified in various systems. Even though theoretical correlations supported many experimental studies, the analysis of CO₂ adsorbed samples *via* nuclear resonance spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, *etc.* can deliver more information related to the species formed on the adsorbent. Since these studies are meagre, the molecular level understanding of adsorbent–adsorbate interactions is limited. Another major challenge is the inadequacy of direct capture of CO₂ from the atmosphere. This is due to low partial pressure of CO₂ in the atmosphere compared to post and pre-combustion capture processes. Hence the development of an ideal sorbent to be used under different reaction conditions is still a concern. Therefore, to commercialize these promising 2D nanomaterials, researchers should pay immense attention to filling the research gaps and rectifying the technical challenges.

Although enormous efforts have been dedicated in developing a better photocatalyst, the key to ultimate stability and durability, a cure to photodecomposition, *etc.* are still unknown. The production of low-cost earth-abundant elements and their mechanistic insight as co-photocatalysts for forming an efficient 2D photocatalyst are also among the many challenges, including poor yield, photoexcited charge carrier kinetics, active sites, recyclability, *etc.* The implementation of advanced tailoring strategies for the development of electronic and chemical structures, for instance, homogeneous doping in 2D material semiconductor photocatalysts, has been among the few successful attempts in the long run.^{349,350} However, it is still difficult to track the particular dopant-induced electronic states in the system. Moreover, the effects of these dopants on photocatalyst stability during the reaction process remain a puzzle. Therefore, a novel doping policy should be assigned to steer its distribution, homogeneity, and composition which goes along with the surface state traits of photocatalysts so as to realize a functional design. Furthermore, the role of inherent or intrinsic defects, structural design, number of 2D layers, and lateral interface dimensions in the output catalytic performance, particularly in a composite photocatalyst, is yet to be investigated. A comprehensive study regarding the charge transfer process and pathways, charge carrier migration diffusivity, and fast recombination reasons should be conducted while considering practical issues regarding recyclability and device design for the establishment of an advanced ideal photocatalyst.³⁵¹

For commercial CO₂ electrocatalysis applications, researchers still face some challenges. Firstly, it is difficult to produce 2D nanomaterials on a large scale while maintaining well-controlled uniform structures due to their electrostatic interaction, strong in-plane bonds and π – π stacking within the atomic layers, resulting in agglomeration and low yield.

Another problem is the analysis of the 2D structures at the atomic level to optimise the catalytic factors such as catalytic activity, selectivity, and stability which further leads to enhanced CO₂ ECR current density, reduction of CO₂ to C₂ and C₂₊ chemicals, and large cyclability for industrial application. The in-depth understanding of the reaction mechanisms limits the future commercialisation of the ECR process.

The major challenge of PEC conversion of CO₂ is its large scale production. Even though electrocatalytic conversion is commercialized, PEC conversion of CO₂ is still at the laboratory scale and needs to be developed and upgraded for pilot-scale production. One of the most challenging tasks in PEC conversion is its high consumption of energy and its meager product yield. The cost of electricity for biasing the photoelectrodes may sometimes be greater than the cost of products yielded. The research on PEC conversion without external bias should be developed and investigated for practical viability. PEC cells are still ambiguous for their long-term usability. Also, the present photoelectrode materials exhibit high overpotential with low product selectivity. Moreover, theoretical studies should surpass the present gap between kinetic and thermodynamic factors for CO₂ binding and bond-breakage by different photocatalytic materials for their bandgap engineering and tuning of reduction potentials to enhance CO₂ affinity and conversion.

Industrially, the thermocatalytic conversion of CO₂ to value-added products is possible under the influence of medium to high pressure, using liquid and gas phase reactors. The requirements of pure CO₂ gas, high temperature and pressure, and the lack of utility of direct intake of atmospheric CO₂ make thermocatalysis uninteresting compared to other catalytic conversion techniques. In most of the studies, 2D materials have been used as supporting materials for single-atom catalysts. The properties of 2D materials such as high electrical conductivity, high surface area, photogeneration of charge carriers, *etc.* make them attractive in photoreduction, electroreduction and photoelectroreduction of CO₂. However, these properties of 2D materials do not contribute to the thermal reduction of CO₂; therefore, the studies focused on the thermocatalysis of CO₂ by 2D materials are generally rare.

5.2 Techno-economic analysis

Along with developing laboratory-scale techniques for capturing and converting CO₂, performing techno-economic analysis of those methodologies is inevitable in identifying the economically viable technologies. Among the different strategies for CO₂ conversion to valuable products, electrochemical CO₂ reduction is close to commercialisation by companies such as Mitsui Chemical and Carbon Recycling International.^{352–354} Economic analysis performed on electrocatalytic CO₂ reduction to produce carbon monoxide and formic acid (100 tons per day) revealed end-of-life net present values (NPV) of \$13.5 million and \$39.4 million,

respectively.³⁵⁵ Because of the market potential associated with higher-order alcohols such as ethanol and *n*-propanol, the profitability analysis for producing these liquid fuels is also indispensable. The techno-economic model mentions that reaching a target of 70% faradaic efficiency at 0.5 V overpotential can achieve profitable ethanol and propanol production *via* electrocatalytic CO₂ reduction. In a similar study, researchers analyse the possibility of cost-effective production of ethylene glycol by CO₂ reduction.³⁵⁴ By performing various cost analyses, the study concluded that ethylene glycol is an economically viable target if the electrocatalytic system can be coupled with a cheap renewable source of electricity.

Integrating the methodologies for CO₂ capture and conversion is projected to be a cost-effective strategy. When the captured CO₂ is directly utilised for a conversion reaction, an extra step of desorption can be eliminated. A recent study showed that an integrated CO₂ capture conversion process could save 8% cost while converting a mixture of CO₂ and methanol to methyl formate.³⁵⁶ Further studies on economic analysis are required to identify and explore the economically viable CO₂ capture and conversion strategies.

6. Conclusions

2D nanomaterials with a good surface area, porosity, and unique and tuneable topography, or textures can be widely used for CO₂ adsorption and conversion. The analysis of various 2D nanomaterials for CO₂ adsorption reveals that a substantial improvement in CO₂ adsorption was observed using nitrogen-doped or nitrogen functionality incorporating adsorbents. The chemisorption of the adsorbate along with physisorption leads to enhanced CO₂ uptake in the N doped systems. In comparison to other gases such as N₂ or H₂, CO₂ molecules with a high EQM value would get adsorbed, leading to the selective adsorption of CO₂. On the other hand, with the help of computational tools, many researchers could accelerate the research on CO₂ adsorption on 2D nanomaterials. Though theoretical studies have proven the importance of defect engineering towards enhanced CO₂ adsorption in 2D materials, more experimental analyses in the area are to be explored for developing highly efficient CO₂ adsorbents. Through the current examination, we can understand that N doped (PPy or PANI) aerogels or porous adsorbents based on 2D materials, especially graphene or MXenes, are promising towards CO₂ adsorption applications.

In the photocatalytic reduction of CO₂, the thermodynamic hindrance of the stable CO₂ molecule was remedied by a semiconducting photocatalyst with light energy driving force under ambient conditions. Several 2D materials based on graphene, g-C₃N₄, metal oxides in thin atomic layers, LDHs, TMDCs, h-BN, *etc.* have been utilised for photocatalytic conversion of CO₂ to value added products. A deeper understanding of the mechanism in 2D materials is still unclear, and this is due to the unawareness of contributions from photoinduced carriers generated under

light irradiation. By finding suitable remedies to the issues mentioned above, the future developments of photocatalytic CO₂ reduction *via* 2D materials are expected to be tremendous. With the help of an electrochemically active catalyst and external potential, the stable chemical environment of CO₂ can be disturbed for the ECR of CO₂. The design of electrolytes and potential play a vital role in the process of electro-reduction. The high CO₂ conversion efficiency, selectivity, and high TON and TOF make them more attractive for CO₂ reduction. Recently, a wide variety of 2D nanostructures were designed as efficient electrocatalysts for the CO₂ ECR process. The presence of edge sites or edge dopants and the high surface area of 2D structures enable the generation of abundant reactive sites, promoting selective CO₂ reduction with high faradaic efficiency. Most of the research works are supported by theoretical calculations to understand the mechanism of reduction and product selectivity. The tuning of surface, electronic, and structural properties of 2D materials could lead to a suitable electrocatalyst for producing high hydrocarbon value-added fuels in the near future.

The studies on the PEC of CO₂ are in their beginning stage, and significant number of 2D nanomaterials need to be explored for PEC CO₂ conversion. A deeper understanding of the PEC conversion process mechanism is to be accomplished or research in this field should be pursued. The thermocatalytic conversion of CO₂ requires thermal energy and suitable catalysts to disrupt the stable molecular state of carbon dioxide to form products. Facile implementation for scaled-up production, versatility in the products, easy recovery of the catalyst, and high CO₂ conversion rate are the significant advantages. However, in the thermal reduction of CO₂, 2D nanomaterials are widely used as catalyst supports, especially for single-atom catalysts.

Conflicts of interest

There are no conflicts to declare.

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