Two-dimensional materials: synthesis and applications in the electro-reduction of carbon dioxide

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Abstract

The emission of CO\textsubscript{2} has become an increasingly prominent issue. Electrochemical reduction of CO\textsubscript{2} to value-added chemicals provides a promising strategy to mitigate energy shortage and achieve carbon neutrality. Two-dimensional (2D) materials are highly attractive for the fabrication of catalysts owing to their special electronic and geometric properties as well as a multitude of edge active sites. Various 2D materials have been proposed for synthesis and use in the conversion of CO\textsubscript{2} to versatile carbonous products. This review presents the latest progress on various 2D materials with a focus on their synthesis and applications in the electrochemical reduction of CO\textsubscript{2}. Initially, the advantages of 2D materials for CO\textsubscript{2} electro-reduction are briefly discussed. Subsequently, common methods for the synthesis of 2D materials and the role of these materials in the electrochemical reduction of CO\textsubscript{2} are elaborated. Finally, some perspectives for future investigations of 2D materials for CO\textsubscript{2} electro-reduction are proposed.
**INTRODUCTION**

The concentration of greenhouse gas CO$_2$ has risen by 100 ppm since the industrial revolution. The average temperature has been rising at an average rate of 0.1 °C per decade for nearly half a century, which results in serious global warming [1-3]. From another perspective, CO$_2$ is an abundant, clean, and cheap feedstock for the production of value-added chemicals. Hence, it is of great ecological and social significance to utilize and convert CO$_2$ into high-value-added chemical products [4-6]. Nonetheless, CO$_2$ has thermodynamically stable and chemically inert properties, and thus its conversion is highly energy intensive. Considering the prominent role of CO$_2$ in global warming and the chemical characteristics of CO$_2$, numerous chemical technologies have been developed for CO$_2$ conversion, including thermal catalysis [7-9], photocatalysis [10-12], and electrocatalysis [13-15]. The development of highly effective catalysts and related equipment for CO$_2$ transformation has boomed in recent years [16]. Among them, the electro-reduction of CO$_2$ to value-added chemicals benefits from low investment in equipment, high efficiency, and environmental acceptance [17-20].

The electrochemical reduction of CO$_2$ is a multi-electron transfer process, which mainly occurs at the electrode and the electrolyte interface. This process consists of four steps: (i) CO$_2$ is chemically adsorbed on the electrode surface; (ii) CO$_2$ is converted into CO$_2$$^•$ by one-electron attacks; (iii) Multiple electrons and protons are transferred to CO$_2$$^•$ for the construction of C-H and C-C bonds; and (iv) Products are released from the electrode [21]. The half-reactions and corresponding standard reduction potentials for the electro-reduction of CO$_2$ to various products have been elucidated through thermodynamic studies, as illustrated in Figure 1.

The electro-reduction of CO$_2$ to related products is a multi-step reduction. In spite of the low chemical reactivity of CO$_2$, the theoretical potential required for products is not a large negative value [22]. In fact, the first hurdle of CO$_2$ electro-reduction is the potential barrier for CO$_2$ activation (CO$_2$ + e$^-$ = CO$_2$$^•$), which is -1.90 V vs. the standard hydrogen electrode (SHE). Because different products require similar thermodynamic potentials, it is challenging to obtain the desired product with high selectivity [23,24]. Accordingly, the development of electrode materials is significant to realize efficient electro-reduction with high selectivity toward target products.

Current density and selectivity are two evaluation indicators in CO$_2$ electro-reduction. A large current density indicates a fast reaction rate to provide a high yield of products from CO$_2$, and high selectivity can ease separation to reduce cost. Electrode materials play a decisive role in electrocatalytic performance. Hence, the design and synthesis of electrode materials with high activity, selectivity, and stability are significant for highly efficient CO$_2$ electro-reduction. 2D materials are defined as a type of nanomaterials with a layer-like morphology and small thickness (normally 1-100 nm) in which electrons move on the nanoscale in two dimensions [25]. 2D materials have been developed for various applications, such as energy conversion [26-28], catalysis [29-31], sensing [32-34], photodetector [35-37], and memristor [38-40], owing to their unique 2D geometry, nanoscale thickness, and high surface-to-volume ratio. 2D structures, such as nanoplates, nanosheets, and nanoflakes, have been using for preparation of various materials, including metals, metal oxides, metallic sulfides, and carbon materials [41-44]. Until now, numerous 2D materials have been designed and prepared for CO$_2$ electro-reduction [45-47]. For commercial applications of electrocatalysts, high yield and controllable fabrication techniques are essential. Versatile methods for the preparation of 2D materials, such as exfoliation, extraction, chemical or physical vapor deposition, and wet-chemical synthesis, have been developed. Different synthesis routes have different advantages. These strategies determine the morphology...
Figure 1. Half reactions and corresponding standard reduction potentials vs. reversible hydrogen electrode (RHE) ($E^0$/V vs. RHE) for the electrochemical reduction of CO$_2$ to various products.

of materials and further affect their properties, providing opportunities for their utilization in electrocatalysis.

This review covers the current progress on CO$_2$ electro-reduction using 2D material electrodes with a focus on the (i) advantages of 2D materials for CO$_2$ electro-reduction, (ii) strategies for 2D nanomaterial synthesis, and (iii) catalytic performance of 2D materials in the electrochemical reduction of CO$_2$.

ADVANTAGES OF 2D NANOSTRUCTURES FOR CO$_2$ ELECTRO-REDUCTION

Electrochemical reduction of CO$_2$ is a process involving gas-solid-liquid interactions$^{[48,49]}$, and its current density and Faradaic efficiency (FE) are largely affected by the specific surface area of electrode materials. Generally, a higher specific surface area guarantees more adsorption and active sites, leading to better catalytic performance. In addition, the concentration gradient of CO$_2$ and reaction intermediates are related to CO$_2$ diffusion on the electrode surface. The adsorption/desorption thermodynamics and kinetics of intermediates determine the selectivity and production rate of target products. Thus, materials with special morphologies and structures play a crucial role in catalyzing this process.

The electrochemical reduction of CO$_2$ is surface reaction, and thus 2D materials are suitable as catalysts because of the following advantages. First, 2D materials have a unique planar structure, which promotes interactions with the substrate or active components as well as the formation of heterojunctions to realize comprehensive regulation of electrocatalysis$^{[50]}$. Second, 2D materials have enhanced electronic properties, such as high electron mobility and carrier concentration$^{[51,52]}$, which increase electron transfer from the electrode to CO$_2$. Third, 2D materials have a high proportion of uncoordinated sites and large specific surface areas, which increases interactions between CO$_2$ and the catalyst$^{[53]}$. Exposed surface atoms in 2D materials can escape from their respective lattices to form defect sites, and these thermodynamically
unstable sites can trap electrons and shorten electron transport and ion diffusion distances\cite{54,55}. Owing to the low atomic coordination number at the edge, the activity at the edge is higher than that at the basal plane in 2D materials\cite{56}. Fourth, a multi-layer or single-layer structure increases the confinement effect, which improves the catalytic performance\cite{57,58}. The surface of 2D materials can be modified to produce special gas trapping cavities, where interactions between the electrode, electrolyte, and CO$_2$ gas are enhanced\cite{59,60}. Fifth, pores in 2D materials are fully exploited owing to the ultrathin structure. Porous structures in 2D materials can effectively amplify the differences in mass transfer efficiency as well as intermediate diffusion during CO$_2$ reduction.

In summary, 2D materials have geometries, electronic structures, and defects that are suitable for CO$_2$ electro-reduction. Owing to their large specific surface area, 2D materials can serve as supports for hybrid materials. In addition, the unique atomic-layer-thick structure provides an ideal platform for revealing atomic-scale mechanisms. The rational development and exploitation of distinct structural and electronic properties of 2D materials endow 2D materials with more opportunities for broad applications in the field of CO$_2$ electro-reduction.

**SYNTHESIS OF 2D NANOSTRUCTURES**

The electrocatalytic performances of 2D materials are mainly determined by the morphology, structure and chemical properties of the materials, which in turn are closely related to the synthesis methods. Since the discovery of graphene, many efficient routes have been developed for the synthesis of 2D materials, allowing researchers to design more promising 2D materials. Top-down and bottom-up routes are commonly used for the synthesis of 2D materials\cite{61-63}. Top-down routes, such as exfoliation and extraction procedures, are easily performed without special equipment, and thus they are effective for the synthesis of inorganic materials, such as graphene and metal dichalcogenides. Bottom-up routes, including chemical/physical vapor deposition and wet-chemical syntheses, provide 2D materials with accurately controlled morphologies and structures, and thus they are frequently used to prepare materials with unique structures. In this section, several typical routes for the fabrication of 2D materials are briefly described.

**Exfoliation**

Exfoliation requires external mechanical forces to peel off 2D materials with a single or few layers from bulk objects. This method relies on driving forces, such as mechanical and ultrasonic forces, to overcome intermolecular interactions, such as the van der Waals force, between atomic layers. This process is simple to operate and produces few defects in the resulting material, although it suffers from low effectiveness and poor repeatability, which limits its practical applications.

Mechanical exfoliation has been a common method for the fabrication of emergent 2D materials [Figure 2A] since Geim obtained graphene by tearing off graphite from tape\cite{64}. Other research groups have since developed similar methods for producing high-quality 2D materials. Li et al. used bulk materials to isolate desired products and prepare various single- and few-layer transition-metal dichalcogenide nanosheets with high crystallinity, including WSe$_2$, TaS$_2$, and TaSe$_2$\cite{65}. However, the yield is low and the thickness and size of as-prepared materials are difficult to control using this strategy, thus inhibiting large-scale production. Huang et al. used a universal, one-step method via Au-assisted mechanical exfoliation to address the above problem [Figure 2B] and synthesize a series of 2D materials such as BP, RuCl$_3$, Fe$_3$GeTe$_2$, FeSe, MoS$_2$, and WSe$_2$\cite{66} [Figure 2C]. This environmentally compliant route meets the requirements of green chemistry. Field-effect transistor devices have been fabricated using 2D MoS$_2$ and WSe$_2$. However, the use of noble metals undoubtedly increases the cost, thus hampering the implementation of this route for the fabrication of large devices.
Figure 2. Synthesis of 2D materials by exfoliation. (A) Graphene films synthesized by mechanical exfoliation\[64\]. (B) Schematic diagram of Au-assisted mechanical exfoliation. (C) 2D materials synthesized by Au-assisted mechanical exfoliation\[66\]. (D) Schematic diagram of CTAB-assisted material swelling\[69\]. 2D: 2-dimensional; CTAB: hexadecyl trimethyl ammonium bromide.

Ultrasonic exfoliation in the liquid phase relies on the cavitation effect. When bulk materials are subjected to an ultrasonic wave in a suitable solvent, micro-gas core cavitation bubbles produced in the solvent expand the space between the layers of the material, thus producing the 2D material. Coleman et al. reported in detail that ultrasonic exfoliation of transition metal dichalcogenides, such as BN, MoS\(_2\), WS\(_2\), MoSe\(_2\), MoTe\(_2\), TaSe\(_2\), NbSe\(_2\), NiTe\(_2\), and Bi\(_2\)Te\(_3\), in organic solvents can be used to produce 2D materials with few layers\[67\]. Metal oxide and hydroxide with limited layers can also be produced by ultrasonic exfoliation. Compared with transition metal dichalcogenides, which are stabilized by weak intermolecular interactions, such as the van der Waals force, metal oxides and hydroxides are stabilized by strong ionic interactions, which makes exfoliation difficult\[68\]. Although ultrasonic exfoliation is the most promising strategy for the industrial production of 2D materials, this strategy has fatal defects. For example, (i) the number of layers and thickness are difficult to control and (ii) the recovery rate is low, which confines the method to the laboratory.

Intercalation-based exfoliation has been widely explored owing to the unique characteristics of high-yield monolayers. Suitable intercalation species are vital for effective intercalation and determine whether intercalation proceeds. For example, surfactants are often used for the production of 2D nanosheets. Dakhchoune et al. reported that intercalation of surfactant hexadecyl trimethyl ammonium bromide (CTAB) into sodalite precursors leads to material swelling\[69\]. Consequently, the lattice spacing increases from 1.4 nm to 3.1 nm [Figure 2D], indicating that interlayer interactions are weakened by the intercalation of CTAB.

Chemical vapor deposition
Chemical vapor deposition (CVD) is one of the most commonly used methods for the synthesis of 2D materials\[70\]. In this technique, a thin solid layer is deposited on the surface of a substrate through vapor-
phase chemical reactions in a high-temperature gas. Various solid-state layers (e.g., single crystals, continuous thin films, and heterojunctions) can be produced on substrates by adjusting the operating temperature, flow gas species, phase composition, and substrate. Numerous functional van der Waals heterostructures can also be created by this method\cite{71} [Figure 3A-D]. In contrast to exfoliation and extraction, CVD allows control of the number of layers as well as the density and purity of products through changes in the synthesis conditions.

CVD has become an important method for the preparation of 2D materials since it was used to prepare graphene in 2009\cite{72,73}. Browne et al. synthesized MoS$_2$ and WS$_2$ materials to serve as electrodes\cite{74}. The surface of as-prepared MoS$_2$/WS$_2$ is rougher than that of commercial materials. Li et al. used methane to prepare graphene films with a large surface area on a copper substrate by CVD\cite{75}. The as-prepared graphene film can be easily transferred to alternative substrates for the fabrication of functional devices. Yin et al. synthesized high-quality nonlayered Fe$_2$O$_3$ nanosheets with a thickness of 1.95 nm, which exhibit lattice relaxation owing to the ultrathin structure\cite{76}. Although the growth of 2D materials on substrates is rapid, the direct growth of 2D metal/metal oxides onto substrates is restricted because of the high melting point of metals/metal oxides. Introducing molten salts as additives can effectively reduce the reaction temperature and promote the growth of high-quality 2D materials. For instance, Zhou et al. reported a new method to synthesize 47 compounds by adding NaCl and KI as adjuvants\cite{79}. Despite various efforts focused on synthesizing 2D materials by CVD, poor repeatability and unscalable production restrict the industrial application of CVD.

As mentioned above, the thickness and size of 2D materials can be precisely controlled by adjusting the working temperature, carrier gas rate, and chamber pressure. Space-confined CVD can be used to achieve the growth of high-quality 2D materials. Recently, Li et al. used Te-assisted CVD to precisely synthesize 2D Fe single-crystal nanoflakes with different thicknesses\cite{77} [Figure 3E-G]. Xu et al. used space-confined CVD to grow homogeneous 1T'-MoTe$_2$ monolayers with a lateral size of 100 μm in batches, demonstrating that the confined space can increase the vapor pressure of sulfur to extend the lifetime of monolayer tellurides from several minutes to at least 24 h\cite{78}.

**Hydrothermal and solvothermal methods**

Hydrothermal and solvothermal methods are widely used to prepare various 2D materials with high yields. Both methods are based on heterogeneous chemical reactions occurring at high temperature and pressure during which substances are dissolved and recrystallized. The difference between the two methods is the solvent. Water is used as the solvent in hydrothermal methods, while non-aqueous organic solvents are used in solvothermal methods. Materials prepared by hydro/solvothermal methods have advantageous characteristics, such as high crystallinity, small particle size, and uniform distribution.

Among various 2D materials, metal oxides have attracted considerable attention in the fields of catalysis, energy conversion, and electronics owing to their low cost and large surface area. Sun et al. developed a general solvothermal method to prepare various transition metal oxides nanosheets, such as ZnO, WO$_3$, Co$_3$O$_4$, and TiO$_2$, [Figure 4] in different solvents (water/ethanol/glycol) for use in photoelectric or photochemical devices\cite{79}. The thickness of as-prepared nanosheets ranges from 1.6 nm to 5.2 nm. Metal-organic frameworks (MOFs) represent a class of hybrid materials comprising ordered networks formed by combining metal ions with organic ligands\cite{80-82}. MOFs have been explored extensively to prepare 2D structures. As a bottom-up synthesis method, the templated hydrothermal strategy induces the confined growth of 2D MOF materials. Zheng et al. synthesized ultrathin 2D Co-MOF with a thickness of 2 nm by reacting precursors and polyvinyl pyrrolidone in DMF/C$_2$H$_5$OH solution at 80 °C for 80 h\cite{83}. Moreover,
Figure 3. Synthesis of 2D materials by CVD. (A) Schematic diagram of the CVD method. (B-D) Schematic diagram and TEM images of graphene/hBN heterostructures. Here, carbon atoms are represented by blue spheres, boron is shown in yellow, and nitrogen is in purple. (E-G) Synthesis of 2D Fe single-crystal nanoflakes by space-confined CVD. 2D: 2-dimensional; CVD: chemical vapor deposition; TEM: transmission electron microscopy.

Figure 4. Synthesis of 2D metal oxide nanosheets by the hydrothermal method. (A) Schematic diagram of the synthesis route. TEM images of (B) Co$_3$O$_4$, (C) TiO$_2$, (D) ZnO, and (E) WO$_3$. 2D: 2-dimensional; TEM: transmission electron microscopy.

various novel 2D materials, such as MoP@In-PC, Mo-Bi bimetallic, Sn$_4$P$_3$/rGO, have been synthesized by hydro/solvothermal methods.

Electrodeposition
Electrochemical deposition is a liquid-phase process based on redox reactions by which 2D materials are easily formed. This method has numerous advantages, including mild conditions, low cost, high safety, easy operation, and high controllability. The morphology, structure, and physicochemical property of products
can be controlled by adjusting various conditions, including the pH of the solution, potential, time, and temperature, during electrodeposition.

Electrodes prepared by electrodeposition have very low contact resistance, which promotes electron transfer in functional devices. Rabiee et al. grew uniform Bi-based nanosheets on a substrate by pulse electrodeposition\(^{[87]}\). In contrast, a Bi-based bulk material was obtained by continuous electrodeposition. Abdelazim et al. reported the lateral growth of MoS\(_2\) on an insulating surface\(^{[88]}\). The highly anisotropic growth rate of MoS\(_2\) can be controlled by simple electrodeposition to obtain a lateral to vertical growth ratio exceeding 20. This paves a new pathway to precisely control the growth direction to obtain 2D materials. Polymetallic alloys have shown great potential in various applications, and co-deposition of versatile metals can be realized with electrodeposition by adjusting the pH of the solution or applied voltage. For example, Feng et al. used electrodeposition in a solution of pH 10 to obtain an active borate-intercalated NiCoFe-LDH, which is susceptible to redeposition to recover catalytic activity, further confirming the advantage of electrodeposition\(^{[89]}\). Shen et al. synthesized amorphous 2D FeMn by electrodeposition using sodium citrate as a structure-directing agent\(^{[90]}\) [Figure 5A-C]. OH\(^-\) is produced near the surface of the cathode, and metal ions are deposited with OH\(^-\) at the cathode to form hydroxides.

Despite recent achievements in the electrodeposition of 2D materials, the mechanism remains difficult to demonstrate. Tan et al. used transmission electron microscopy (TEM) to visualize material synthesis, including nucleation sites, growth mechanisms, and structures formed during electrochemical reactions\(^{[91]}\). This promising technology can be used to observe an electron beam-stable and low-contrast extended electrode area with high resolution [Figure 5D].

**Extraction**

To date, many new types of 2D materials have been developed for functional devices. 2D transition metal carbides and nitrides (MXenes) have good electrical properties owing to the inner conductive carbide layer and hydrophilic transition metal oxide surface, and thus they are promising materials for the fabrication of batteries and catalysts.

The most effective synthesis route of MXenes is the selective etching of “A” layers from an Al-containing MAX phase, where A represents a III A or IV A element (e.g., Al, Ga, Si, or Ge) and X represents either C or N. Lukatskaya et al. and Ghidiu et al. synthesized various MXenes by selective extraction, electrochemical etching, and ion intercalation\(^{[92-94]}\). The as-prepared 2D materials are applied in Li-ion batteries, which acquire excellent electricity performance.

In addition to the methods above, researchers have explored many other routes for the synthesis of 2D materials. Among the multitude of strategies, templated synthesis can easily and directly realize 2D materials with controlled structures. For example, Liu et al. synthesized a series of mesoporous materials with a single-layer structure\(^{[95]}\). Phenolic formaldehyde resin, a flexible template, is beneficial for the adsorption and subsequent confinement of inorganic precursors on the salt surface. Surface-limited cooperative assembly allows for large-scale production, and 14.1 g of mesoporous TiO\(_2\) with single-layer structure can be synthesized per batch. Although templated synthesis has been extensively explored for the preparation of 2D materials, the long preparation time and high cost restrict its wide application in industry. Developing template-free preparation methods is of significance for the mass production of 2D materials. Zhang et al. developed a general method for control-oriented growth of MOF nanosheets with ultrathin thicknesses and abundant unsaturated coordination metal sites using CO\(_2\) as a capping agent\(^{[96]}\). The process is template-free and CO\(_2\) can be easily removed by depressurization after synthesis. Atomic
layer deposition has emerged as a powerful technique to prepare nanofilms with a thickness approaching the Debye length. Ko et al. reported the preparation of a large-area WS$_2$ nanosheet with a precisely controlled number of layers by atomic layer deposition$^{[97]}$. These methods can be used for reference and guidance in the development and application of 2D materials for CO$_2$ electrocatalytic reduction.

**ELECTROCHEMICAL REDUCTION OF CO$_2$ OVER 2D NANOSTRUCTURES**

Various 2D nanostructures have been extensively explored for the electro-reduction of CO$_2$ owing to their unique structure and properties. Versatile electrode materials, including metals, metal oxides, metal dichalcogenides, and carbon-based nanomaterials, have shown potential in CO$_2$ electrocatalytic reduction$^{[98-100]}. In this section, advances in 2D materials for CO$_2$ electrocatalytic reduction are reviewed and the related mechanism is discussed.

**Metal materials**

Zero-valence metals are the most popular electrode materials for CO$_2$ electro-reduction owing to their high conductivity, high stability, controllable crystal faces, and ease of CO$_2$ activation.

**Noble metals**

Noble metals are considered the most effective catalysts$^{[114,115]}$, and electrochemical reduction of CO$_2$ over noble metal-based electrodes has been extensively studied in recent years$^{[116,117]}$. The particle size determines the catalytic performance because larger particles have fewer active sites, whereas smaller particles favor H$_2$ evolution over CO$_2$ reduction. Noble metal nanosheets exhibit excellent catalytic performance in CO$_2$
Table 1. Summary of 2D-based materials developed for CO₂ electrocatalytic reduction

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Electrolyte</th>
<th>Products</th>
<th>FE</th>
<th>Potential</th>
<th>(j) (mA cm(^{-2}))</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag nanosheet</td>
<td>0.5 M NaHCO(_3)</td>
<td>CO</td>
<td>95</td>
<td>-0.8 V vs. RHE</td>
<td>10</td>
<td>[98]</td>
</tr>
<tr>
<td>Ag foil</td>
<td>0.5 M NaHCO(_3)</td>
<td>CO</td>
<td>75</td>
<td>-1.13 V vs. RHE</td>
<td>6</td>
<td>[99]</td>
</tr>
<tr>
<td>Zn nanosheet</td>
<td>0.5 M NaHCO(_3)</td>
<td>CO</td>
<td>9.5</td>
<td>-1 V</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Sn sheet confined in graphene</td>
<td>0.1 M NaHCO(_3)</td>
<td>formate</td>
<td>89</td>
<td>-1.8 V vs. SCE</td>
<td>21.1</td>
<td>[100]</td>
</tr>
<tr>
<td>Bulk Sn</td>
<td>0.1 M NaHCO(_3)</td>
<td>formate</td>
<td>44.5</td>
<td>-1.8 V vs. RHE</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Cu nanosheet</td>
<td>0.1 M K(_2)SO(_4)</td>
<td>ethylene</td>
<td>83.2</td>
<td>-2.18 V vs. RHE</td>
<td>58.8</td>
<td>[101]</td>
</tr>
<tr>
<td>Cu nanoparticles</td>
<td>0.5 M NaHCO(_3)</td>
<td>formate</td>
<td>37.2</td>
<td>-0.9 V vs. RHE</td>
<td>36.4</td>
<td></td>
</tr>
<tr>
<td>Sn nanoparticles</td>
<td>0.1 M KHCO(_3)</td>
<td>CO</td>
<td>25</td>
<td>-1.0 V vs. RHE</td>
<td>14</td>
<td>[102]</td>
</tr>
<tr>
<td>Cu plates</td>
<td>0.1 M KHCO(_3)</td>
<td>CO</td>
<td>70</td>
<td>-1.0 V vs. RHE</td>
<td>50</td>
<td>[103]</td>
</tr>
<tr>
<td>Bulk Co</td>
<td>0.1 M KHCO(_3)</td>
<td>CO</td>
<td>70</td>
<td>-1.0 V vs. RHE</td>
<td>50</td>
<td>[104]</td>
</tr>
<tr>
<td>Co nanoparticles</td>
<td>0.1 M Na(_2)SO(_4)</td>
<td>formate</td>
<td>25</td>
<td>-0.85 V vs. SCE</td>
<td>10.59</td>
<td>[105]</td>
</tr>
<tr>
<td>Bi nanosheet</td>
<td>0.1 M KHCO(_3)</td>
<td>formate</td>
<td>70</td>
<td>-0.88 V vs. SCE</td>
<td>0.68</td>
<td>[106]</td>
</tr>
<tr>
<td>Bi nanoparticles</td>
<td>0.1 M KHCO(_3)</td>
<td>formate</td>
<td>18.5</td>
<td>-0.88 V vs. SCE</td>
<td>0.034</td>
<td>[107]</td>
</tr>
<tr>
<td>ZnO nanosheet</td>
<td>0.5 M KHCO(_3)</td>
<td>formate</td>
<td>18.5</td>
<td>-0.74 V vs. SHE</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Bi(_2)WO(_3) nanosheet</td>
<td>0.5 M BmimPF(_6)/MeCN</td>
<td>CO</td>
<td>70</td>
<td>-0.4 V vs. Ag/Ag(^+)</td>
<td>43</td>
<td>[108]</td>
</tr>
<tr>
<td>N-codoped graphenes nanosheet</td>
<td>0.5 M KHCO(_3)</td>
<td>formate</td>
<td>64</td>
<td>-2.4 V vs. Ag/Ag(^+)</td>
<td>4</td>
<td>[109]</td>
</tr>
<tr>
<td>SnS(_2)</td>
<td>0.5 M BmimPF(_6)/MeCN</td>
<td>CO</td>
<td>91</td>
<td>-0.8 V vs. SHE</td>
<td>4</td>
<td>[110]</td>
</tr>
<tr>
<td>InN nanosheet</td>
<td>0.1 M KHCO(_3)</td>
<td>formate</td>
<td>91</td>
<td>-0.9 V vs. RHE</td>
<td>46</td>
<td>[111]</td>
</tr>
<tr>
<td>Mo-Bi bimetallic chalcogenide nanosheet</td>
<td>0.5 M BmimBF(_4)/MeCN</td>
<td>methanol</td>
<td>71.2</td>
<td>-0.7 V vs. SHE</td>
<td>12.1</td>
<td>[85]</td>
</tr>
<tr>
<td>FeTPP(Cl)/Cu</td>
<td>1 M KHCO(_3)</td>
<td>ethanol</td>
<td>41</td>
<td>-0.82 V vs. SHE</td>
<td>124</td>
<td>[113]</td>
</tr>
</tbody>
</table>

2D: 2-dimensional; FE: Faradaic efficiency.

electro-reduction compared with their nanoparticles. For instance, Lee et al. prepared Ag nanosheets [Figure 6A] using a self-organized method and obtained an FE\(_{CO}\) of 95% over the Ag nanosheets at an overpotential of only 0.29 V\(^{[18]}\) [Figure 6B and C]. The current density and surface area of the Ag nanosheets are 37 and 17 times higher than those of polycrystalline Ag, indicating that both the enlarged surface area and high current density promoted by the 2D structure determine the catalytic performance. According to scanning transmission electron microscopy (STEM) images, numerous twin crystals exist between and within individual grains of the Ag nanosheets, and these grain boundaries are considered active sites for CO₂ electro-reduction.

Different crystal planes exhibit different catalytic activities for the conversion of CO₂ to products, and thus regulation of the crystal planes of nanosheet is an effective strategy to obtain high current density and FE for certain products. For example, Zhao et al. demonstrated that Pd nanosheets prepared by co-precipitation exhibit excellent catalytic activity in the electro-reduction of CO₂ to CO at the moderate overpotential of 590 mV\(^{[18]}\) [Figure 6D-F]. Pd nanosheets with dominant (111) facet sites are transformed into more active (100) sites after 1 h of electrolysis. The reconstruction of crystal planes not only increases the density of active sites but also reduces the binding energy with CO intermediates, leading to high CO selectivity [Figure 6G].
Figure 6. Electrochemical reduction of CO$_2$ over 2D noble metals. (A) Plot of current density vs. potential over Ag electrodes. (B) $\text{FE}_{\text{CO}}$ and $\text{FE}_{\text{H}_2}$ vs. potential over Ag electrodes. (C) Tafel plots$^{[98]}$. (D) Plot of current density vs. potential over Pd electrodes. (E) $\text{FE}_{\text{CO}}$ vs. potential over Pd electrodes. (F) Electrochemical active surface area of different catalysts. (G) Schematic illustration of different Pd materials$^{[118]}$. 2D: 2-dimensional.

It is worth mentioning that noble metal nanosheets favor CO over other carbon products of CO$_2$ electro-reduction because noble metals can strongly adsorb the *COOH intermediate, which is further reduced to CO* on the electrode surface. In addition, CO* is weakly adsorbed on the surface of noble metals, and thus CO easily desorbs from the surface of noble metal nanosheets.

**Transition metals**

Noble metals are expensive, and thus cost-effective transition metals are increasingly used for CO$_2$ electro-reduction$^{[119]}$. For example, Zn nanosheets prepared by the hydrothermal method perform better than Zn-foil in the electro-reduction of CO$_2$ and show high selectivity toward CO$^{[99]}$. 2D nanostructures exhibit high catalytic activity in CO$_2$ electro-reduction owing to the high density of edge sites. Xiao *et al.* reported that hexagonal Zn nanoplates prepared by cathodic electrochemical deposition [Figure 7A and B] are suitable for the electrochemical reduction of CO$_2$ to CO at a wide potential range$^{[120]}$. $\text{FE}_{\text{CO}}$ over Zn nanoplate can reach 94.2%, which is 2.2 times higher than that over Zn foil [Figure 7C]. The high catalytic performance of Zn nanoplates is attributed to the exposed Zn (100) facets and edges, where COOH* can form more easily than at any other facet, indicating that an increased edge-to-corner ratio can enhance the reactivity.
Figure 7. Electrochemical reduction of CO₂ over 2D transition metals. (A) SEM image of hexagonal Zn nanoplates. (B) TEM image of Zn nanoplates. (C) Plot of FE\textsubscript{CO₂} vs. potential over different Zn electrodes\cite{120}. (D) Schematic diagram of the partially oxidized and pure Co 4-atomic-layer. (E) Plot of FE\textsubscript{formate} vs. potential over different Co electrodes\cite{105}. (F) Plot of current density vs. potential over different Cu electrodes. (G) Plot of FE\textsubscript{C₂H₄} vs. potential over different Cu electrodes. (H) Plot of j\textsubscript{C₂H₄} vs. potential over different Cu electrodes\cite{101}. 2D: 2-dimensional; TEM: transmission electron microscopy.

Co is the first transition metal used in CO₂ electro-reduction. Gao \textit{et al.} prepared a 4-atomic-thick Co sheet with and without surface Co oxide for CO₂ electro-reduction [Figure 7D], achieving a high FE\textsubscript{formate} of 90.1% at a low overpotential of 0.85 V vs. SCE\cite{105} [Figure 7E]. Moreover, the catalyst exhibits long-term stability, and FE\textsubscript{HCOOH} remains at a high level of approximately 90% within 30 h. Volumetric CO₂ adsorption measurements were used to demonstrate that changes in the oxidation state of Co and increases in the surface area synergistically favor CO₂ adsorption, thereby enhancing catalytic performance. Porphyrin Co is one of the most efficient species for CO₂ electro-reduction because of the strong interaction between the metal and ligand. Han \textit{et al.} prepared Co single-site catalysts by assembling Co-porphyrin molecules\cite{121}. The catalyst can promote the conversion of CO₂ to CO with an FE of 96% at an overpotential of 500 mV. This outstanding catalytic performance is attributed to the increase in the energy of d orbitals originating in the strong repulsive force between the ligand and electrons in the z-direction. Yin \textit{et al.} recently prepared Co nanosheets for the conversion of CO₂ to C₂ products\cite{122}. Co nanoparticles were first prepared by a hydrothermal reaction and then converted to Co nanosheets by exfoliation in formamide. Remarkably, ethanol is the main product of the Co nanosheet electrode with an FE\textsubscript{ethanol} of 60%. Ultraviolet photoelectron
spectroscopy was used to show that Co nanosheets have a wide electronic distribution near the Fermi level, resulting in rapid electron transfer. The electron-rich environment around Co 3d of Co nanosheets is beneficial for CO-CO coupling.

Bi is cheap and environmentally acceptable because of its low toxicity. Bi precursors are used to prepare Bi nanosheets in situ by a hydrothermal method\cite{123}, during which O is introduced into the Bi nanosheets. The as-prepared electrode can achieve an FE$_{\text{formic acid}}$ of $>90\%$ with a current density of approximately 200 mA cm$^{-2}$ in a flow cell. The catalytic performance remains unchanged when the Bi nanosheets are applied to a long-term test at -0.52 V vs. RHE for 10 h. Density functional theory (DFT) calculations suggest that the free energy for $^\ast\text{CO}_2 \rightarrow ^\ast\text{OCHO}$ is respectively 0.46 eV and 0.17 eV over Bi and Bi-O, indicating that in situ construction of Bi nanosheets during electrode fabrication promotes the conversion of CO$_2$ to formic acid. Yang et al. prepared a Bi nanosheet-based catalyst by a solvothermal method, and the as-prepared electrode can achieve an FE$_{\text{formate}}$ of nearly 100\% over a broad potential range\cite{124}. Moreover, this electrode exhibits long-term stability at -0.8 V vs. RHE for 12 h. DFT calculations demonstrated that Bi(101) and Bi(111) planes can significantly stabilize the COOH$^\ast$ intermediate to promote the formation of formate.

Sn is another transition metal that can be used to convert CO$_2$ into valuable formate by electrochemical methods. A series of Sn nanosheets have been designed and synthesized for the electro-reduction of CO$_2$. Wu et al. prepared a very sensitive Sn nanosheet with a layer thickness of approximately 9.2 μm by directly spraying Sn catalyst ink onto a gas diffusion layer\cite{125}. The Sn nanosheet electrode exhibits a high FE$_{\text{formate}}$ owing to the desirable proton concentration, electronic conduction, and gas diffusion of the 2D structure. The thickness of Sn nanosheets also influences the current density, FE, and operating potentials. An ultrathin Sn layer can significantly enhance these reduction-related properties, but an excessively thin layer may increase the oxidation rate of Sn, leading to poor stability. This problem can be resolved by confining metal layers into carbon materials\cite{126,127}. Lei et al. reported a method to prepare Sn quantum sheets confined in graphene\cite{100}. The confined nanostructure enhances CO$_2$ adsorption and rate-limiting electron transfer and stabilizes the CO$_2$$^\ast$ intermediate. As a result, the graphene confined Sn quantum sheet displays a current density of 21.1 mA cm$^{-2}$ and FE$_{\text{formate}}$ of 89\% at -1.8 V versus SCE, which is higher than that of the mixture of Sn nanoparticles and graphene. Electrochemical impedance spectroscopy was used to confirm the very low interfacial charge-transfer resistance, suggesting that the existence of 2D graphene can improve the conductivity of the electrocatalyst. Moreover, the electronic state of the complex interface can stabilize reaction intermediates, reducing the free energy barrier for the formation of products.

Among the elements, Cu is the most effective in harvesting various products, such as CO, HCOOH, and C$_2$ products, because Cu has a suitable binding energy between products and the surface of catalysts according to the Sabatier principle\cite{128}. Thus, exploring Cu-based electrodes for CO$_2$ electro-reduction has become a vigorous research topic. Recently, numerous efforts have been dedicated to developing 2D Cu materials for the electro-reduction of CO$_2$ to hydrocarbons and alcohols\cite{129}.

In a pioneering work, Hori et al. reported the efficient electro-conversion of CO$_2$ to hydrocarbons and alcohols over an electrodeposited Cu sheet electrode in aqueous inorganic salt solutions\cite{130}. KCl, K$_2$SO$_4$, KClO$_4$ and dilute HCO$_3^-$ electrolytes favor the formation of ethylene and alcohols, while concentrated HCO$_3^-$ and phosphate solutions prefer the generation of methane. Zhang et al. demonstrated that nanodefective Cu nanosheets (n-CuNS) effectively reduce CO$_2$ into C$_2$ products\cite{101}. FE$_{\text{C}_2\text{H}_4}$ over n-CuNS electrode is 83.2\%, which is higher than that over Cu nanosheets with a smooth surface (CuNS, 45.7\%) and Cu nanoparticles (CuNP, 37.2\%). The current density and FE$_{\text{C}_2\text{H}_4}$ over different electrodes at different applied potentials are shown in Figure 7F-H. Interestingly, n-CuNS does not produce CO, while CuNS and
CuNP convert CO$_2$ into CO in high quantities. Therefore, nano defects in Cu nanosheet significantly improve the current density because CO$_2$ adsorption and C-C coupling are boosted by the enrichment and confinement of reaction intermediates and OH. Chen et al. investigated the effects of grain boundary (GB) density and Cu$^+$/Cu$^0$ ratio during CO$_2$ electro-reduction$^{[131]}$. As the GB density increases, FE$_{C_2H_4}$ first increases and then decreases, which is related to the content of Cu$^+$ in the catalyst during the reaction. Therefore, the GB density can activate CO$_2$ molecules, and Cu$^+$ can promote selectivity toward C$_2$H$_4$ products.

2D metal nanomaterials have highly anisotropic characteristics, abundant coordination sites, and a special electronic structure. Moreover, 2D metals have a unique structure in the absence of external fields, which leads to special properties that can be exploited for electrocatalysis.

**Metal oxide materials**

Since the pioneering report on the catalytic behaviors of metal oxide semiconductor powders in the 1970s$^{[132]}$, the past decades have witnessed great progress in the fundamental study of metal oxide catalysts. Semiconductor metal oxides for CO$_2$ electro-reduction offer several advantages, including low cost, easy maintenance, and the potential to generate C$_2$H$_4$ products. At present, many kinds of metal oxides have been used for CO$_2$ electro-reduction. It is worth pointing out that metal oxides are usually unstable and partially or entirely convert to low-valence metal oxide or zero-valence metallic species under negative potentials. Moreover, the final state and reconstruction of electrodes during electrolysis play important roles in CO$_2$ conversion$^{[133,134]}$.

Different ZnO nanosheets have been synthesized and employed as excellent electrodes for CO$_2$ electro-reduction$^{[135,136]}$. A series of strategies, such as hydrothermal method, spray-coating, and electrodeposition, was used by Luo et al. to prepare ZnO precursors with different morphologies$^{[137]}$. ZnO is reconstructed to a porous sheet-like structure, specifically hexagonal Zn crystals, regardless of the initial morphology and reduced to the metallic state during the electrochemistry process. ZnO nanosheets exhibit an FE$_{CO}$ of 91.6% with a current density of 200 mA cm$^{-2}$ at -0.62 V vs. RHE in a flow reactor. Overall, the reconstruction provides a high surface area, which enhances the catalytic activity and potentially promotes gas diffusion.

In addition to ZnO nanosheets, a number of other 2D metal oxide nanostructures, such as SnO$_2$, Co$_3$O$_4$, and CuO, have been tested for CO$_2$ electro-reduction. Han et al. synthesized porous SnO$_2$ nanosheets by a two-step method$^{[102]}$. A precursor of SnS$_2$ nanosheets is first obtained by a hydrothermal method and subsequently annealed to obtain SnO$_2$ nanosheets with a highly porous architecture. The calcination step increases the surface area and active sites of SnO$_2$, resulting in a small onset potential, large current density, high FE$_{HCOOH}$, and high stability. Gao et al. prepared Co$_3$O$_4$ nanolayers for the selective electro-reduction of CO$_2$ to formate$^{[138]}$. The catalyst exhibits good stability, and the current density negligibly changes within 40 h. The materials have abundant oxygen vacancies, which serve as active sites to stabilize reduction intermediates and reduce the activation energy barrier. Moreover, the valence of Co$_3$O$_4$ is retained, although the crystal structure is destroyed after the reaction owing to the existence of oxygen vacancies.

CuO is widely used in electro-reduction of CO$_2$ to C$_2$, products. CuO is reduced to Cu$^+$ and metallic Cu during CO$_2$ electro-reduction$^{[139,140]}$. Liu et al. prepared an oxygen-rich ultrathin CuO nanoplate for the electro-reduction of CO$_2$ to C$_2$H$_4$ with an FE$_{C_2H_4}$ of 84.5%, which can be maintained for at least 55 h$^{[103]}$ [Figure 8A]. At the optimal current density of 75 mA cm$^{-2}$ and a full-cell voltage of -3.1 V, the FE$_{C_2H_4}$ is 77.3% and the energy efficiency of C$_2$H$_4$ is 28.9% [Figure 8B and C]. Cu/Cu$_2$O heterogeneous interfaces are formed through the self-evolution of CuO nanoplate arrays during electrocatalysis. The impressive
Figure 8. Electrochemical reduction of CO₂ over 2D metal oxides. (A) Schematic illustration of the electrochemical reconstruction of CuO nanosheets. (B) Plot of FE of various products vs. potential over the CuO electrode. (C) Plot of full cell potential and FECH₄ vs. current density over the CuO electrode.[103] (D) Schematic illustration of the BiCuSeO superlattice. (E) EDS mapping images of BiCuSeO. (F) Chronoamperometric curves at different potentials over the BiCuSeO electrode. (G) FEformate, FEH₂, and FEH₂O vs. potential over the BiCuSeO electrode.[142] 2D: 2-dimensional; FE: Faradaic efficiency; EDS: energy dispersive spectroscopy.

performance is derived from Cu/Cu₂O interfaces. The enhanced adsorption of the *OCCOH intermediate on the surface of Cu(110)/Cu₂O(110) facilitates the production of C₂H₄. A network comprising Ag and S-Cu₂O/Cu is also formed by the reduction of CuO in Na₂S solution, followed by immersion in AgNO₃ solution[141]. The as-prepared catalyst exhibits an FECH₃OH of 67.4% with a current density of approximately 122.7 mA cm⁻² in a typical H-cell at -1.2 V vs. RHE using an ionic liquid (IL)-based electrolyte. Synergistic interaction of multiple atoms in the 2D nanostructure facilitates the practical electro-reduction of CO₂ to methanol. S can control the spatial position of adsorption to accommodate and stabilize the *CHO intermediate, while Ag supresses the hydrogen evolution reaction (HER) to provide a high FECH₃OH.

Recently, polymetallic oxides have been developed for CO₂ electro-reduction owing to their structural flexibility. A tangible superlattice model of metal oxide and selenide for CO₂ electro-reduction was demonstrated by Duan et al.[142]. The as-prepared BiCuSeO (layer stacked superlattices) [Figure 8D and E] shows an FEformate of > 90% at a low overpotential [Figure 8F]. The outstanding catalytic activity is attributed to the active 2D Bi₂O₂– sublayer. It is worth pointing out that the layer-stacked superlattices can inhibit the reduction of metal oxide and HER, resulting in long-term stability and a high FEformate over electrocatalysts [Figure 8G]. Zhao et al. reported that 2D ZnGa₂O₄ nanoplates prepared by an ion-exchange method can reduce CO₂ into CO at the relatively low applied potential of -1.4 V vs. Ag/AgCl, with a high FECO of 96%, owing to the high specific area of the nanoplates.[143] During CO₂ electro-reduction, partial Zn²⁺ reduces to Zn⁺, and the Zn⁺/Zn²⁺ redox couple favors the activation of CO₂.

2D transition metal oxides have a large specific surface area, atomic-scale thickness, and abundant dangling bonds, leading to high catalytic performance in CO₂ electro-reduction. In principle, metal oxides are first reduced to the corresponding metals, and the as-reduced metal oxides become the active species for CO₂ electro-reduction. Defects and other active components are introduced into the final electrocatalysts during the reduction of metal oxides.
2D metal dichalcogenides
Transition metal dichalcogenides, such as MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$, are common 2D nanostructures and can be easily prepared by simple exfoliation and CVD methods. These materials have a high surface-to-volume ratio and rich active sites, and thus they have the potential to convert CO$_2$ into valuable products.

During the past decades, MoS$_2$ has attracted considerable attention owing to its special 2D structure and property. Asadi et al. reported that excess d electrons on Mo-edge atoms and a low work function result in high catalytic performance$^{[144]}$ [Figure 9A and B]. The catalyst shows a current density of 65 mA cm$^{-2}$ at -0.764 V vs. RHE, at which FE$_{CO_2}$ reaches 98%. In contrast to bulk MoS$_2$, the edges of 2D MoS$_2$ are exposed to the electrolyte, leading to enhanced catalytic effectiveness. Additionally, by tailoring the edge structure of MoS$_2$, a low onset potential of 31 mV for CO$_2$ electro-reduction is achievable. 2D VA-Mo$_{1-x}$M$_x$S$_2$ (M = Nb and Ta) materials were prepared by a CVD method and applied as electrodes for CO$_2$ electro-reduction in an IL-based electrolyte$^{[145]}$. The current density of Nb-doped MoS$_2$ is 50 times higher than that of pristine MoS$_2$ because doped Nb can shift the center of the d orbitals of Mo edge atoms, leading to weaker binding of CO. However, excessive Nb doping can increase the work function of MoS$_2$, which has a negative influence on the catalytic performance. Mao et al. demonstrated that modulating the MoS$_2$ edge structure by V, Zr, and Hf can promote the desorption of CO$^{[146]}$. It is worth pointing out that dopants located close to the active Mo sites influence the catalytic activity.

Asadi et al. also synthesized a series of 2D transition metal dichalcogenides, including MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$, by a chemical vapor transport method for CO$_2$ electro-reduction$^{[147]}$. Among the as-prepared materials, WSe$_2$ shows the best catalytic performance, leading to an FE$_{CO_2}$ of 24% with a current density of 18.95 mA cm$^{-2}$ at -0.164 V vs. RHE (overpotential of 54 mV) in EmimBF$_4$/H$_2$O (1:1) solution. The calculated work functions of the four catalysts decrease in the following sequence: MoS$_2$ > WS$_2$ > MoSe$_2$ > WSe$_2$, in agreement with experimental results.

In addition to 2D transition metal dichalcogenides, other 2D metal sulfides, such as SnS$_2$, also promote efficient electrochemical reduction of CO$_2$. Zheng et al. prepared SnS$_2$ nanosheets by an atomic layer deposition method$^{[111]}$. Using over 2D SnS$_2$, the current density and FE$_{formate}$ at -0.75 V vs. RHE are 55 mA cm$^{-2}$ and 93%, respectively. The catalyst also shows excellent stability, with FE$_{formate}$ decreasing by less than 2% after 40 h of electrolysis. The excellent catalytic performance is attributed to the presence of sulfur atoms on the catalyst surface, which increase the number of undercoordinated sites. A hybrid nanosheet consisting of SnS$_2$ and H [Figure 9C-F] was investigated by Zhang et al.$^{[148]}$. The H-SnS$_2$ catalyst achieves a high FE$_{formate}$ of 93% at -0.9 V vs. RHE in 0.1 M KHCO$_3$ [Figure 9G-I], making it competitive in activity with pristine 2D metal dichalcogenides. The introduction of H onto the surface of the catalyst optimizes the structure of SnS$_2$ and increases the electron density in adjacent atoms, resulting in a lower reaction barrier for the formation of the HCOO$^*$ intermediate.

Transition metal dichalcogenides present a typical sandwich structure in which the metal atomic layer is sandwiched between two layers of sulfur atoms. Although the van der Waals force between each layer is very weak, strong covalent bonds in the plane ensure the stability of the 2D nanostructure. Therefore, 2D transition metal dichalcogenides exhibit excellent stability for long-term CO$_2$ electro-reduction.

2D carbon-based materials
Carbon-based materials represent a class of submetallic materials owing to the sp$^2$ hybrid state and the existence of metallized electrons on the surface. In the past decade, carbon-based materials have received increasing attention for electrocatalysis owing to their active edges, large surface area, and high charge carrier mobility$^{[150-151]}$. The ultrahigh surface area and high electron transport along the carbon base plane...
make 2D carbon-based materials suitable for the electrochemical reduction of CO₂.

Graphene is a representative of the carbon family and has been extensively explored in different research fields. Neither pure graphene nor graphene oxide (GO) is active in the electrochemical reduction of CO₂ because the π-π framework cannot effectively activate CO₂. The electronic structure, physical structure, and morphology of graphene materials can be adjusted by heteroatom doping. N-doped carbon has been widely studied because N is more electronegative than C. Four types of N exist in N-doped graphene: basal plane quaternary N, edge pyrrolic N, pyridinic N, and nitrilic N. Wang et al. prepared a nitrogen-doped graphene by high-temperature pyrolysis. The nitrogen-doped graphene shows high catalytic...
activity in the electrochemical conversion of CO\textsubscript{2} to formate, leading to an FE\textsubscript{formate} of 73%. Recently, many groups have reported that N-doped carbon materials can promote the conversion of CO\textsubscript{2} to C\textsubscript{2} products. For example, Song \textit{et al.} developed a novel method to synthesize nitrogen-doped mesoporous carbon using a copolymer as the template\cite{156} [Figure 10A]. Pyridinic N sites in this material facilitate the formation of CO*, which is subsequently coupled. Thus, an FE\textsubscript{ethanol} of 77\% at -0.56 V vs. RHE is obtained [Figure 10B-D]. Hao \textit{et al.} also confirmed that pyridinic N promotes efficient CO\textsubscript{2} electro-reduction\cite{157}. DFT calculations showed that the catalytic activity of different N species in CO formation decreases according to the following sequence: pyridinic N > graphitic N > pyrrolic N [Figure 10E]. Moreover, pyridinic N can also induce C-C coupling\cite{156}, thus boosting the generation of C\textsubscript{2+} products.

N-doped carbon hybrid nanosheets, normally prepared by wet chemical synthesis, have the advantages of feasible operation, low cost, and large-scale synthesis, and thus they are widely employed as electrodes for the electro-reduction of CO\textsubscript{2}. Genovese \textit{et al.} demonstrated that iron (III) oxyhydroxide on nitrogen-doped graphene exhibits an FE\textsubscript{CH\textsubscript{3}COOH} of 61\% at -0.5 V vs. Ag/AgCl\cite{158}. The N-doped graphene not only boosts the activation of CO\textsubscript{2}, but also stabilizes Fe(II) species to suppress HER. Lu \textit{et al.} reported that pyridinic N-rich carbon layers encapsulating Ni nanoparticles prepared by a hydrothermal method and pyrolysis exhibit a high FE\textsubscript{CO} of 95\% and long-term stability of 92 h at -1.05 V vs. RHE\cite{159}. The excellent catalytic performance is attributed to the core-shell structure, which promotes mass transfer and the synergistic effect of N-C and metal oxides, while pyridinic-N increases the CO\textsubscript{2} adsorption capacity and decreases the reaction energy barrier for *COOH formation, the rate-determining step.

Single-atom loaded carbon-based materials are also attractive for CO\textsubscript{2} electro-reduction. Guo \textit{et al.} reported that atomic indium on carbon (In/NC) exhibits a current density of 39.4 mA cm\textsuperscript{-2} and FE\textsubscript{CO} of 97.2\% in 0.5 M BmimPF\textsubscript{6}/MeCN\cite{160}. N-coordinated atomic indium catalysts [Figure 10F] can effectively activate CO\textsubscript{2} and hinder the formation of formic acid. In-N coordination is dominant in In/As [Figure 10G], indicating that atomic In is stabilized by the surrounding N. Owing to the high double-layer capacitance, large CO\textsubscript{2} adsorption capacity, and low interfacial charge transfer resistance, In/NC achieves a turnover frequency of approximately 40,000 h\textsuperscript{-1} without appreciable decrease during 24 h of electrolysis [Figure 10H]. DFT results show that the centers of the s and p orbitals of atomic In (In-N) downshift significantly compared with bulk In. A local alkaline environment is produced as the electron density reconfigures because of N coordination. Shi \textit{et al.} reported that Cu single-site in graphdiyne enhances the electro-reduction of CO\textsubscript{2} to methane, with an FE\textsubscript{CH\textsubscript{4}} of 81\% and high stability in 1.0 M KOH at -1.2 V vs. RHE\cite{161}. The acetylenic bond in the catalyst suppresses the formation of multi-carbon products, and the as-constructed Cu-C bond favors the formation of the *OCHO intermediate, resulting in the high FE\textsubscript{CH\textsubscript{4}}.

2D carbon materials, such as graphene, have unique electronic properties, including the ambipolar electric field effect and quantum Hall effect. These unique electronic properties enable carbon materials to exhibit metal-like behaviors, which is beneficial for CO\textsubscript{2} electro-reduction. Moreover, 2D carbon materials are often used as substrates for doping or decoration, broadening their utilizations in CO\textsubscript{2} electro-reduction. Nevertheless, developing highly efficient 2D carbon based materials for CO\textsubscript{2} electro-reduction still has a long way to go.

Other 2D materials

In addition to traditional 2D materials, many other 2D nanostructures are potential candidates to realize highly efficient electro-conversion of CO\textsubscript{2} to valuable products. Recently, a series of novel 2D materials was applied to the electrochemical conversion of CO\textsubscript{2} to various products, and their special structure determines the catalytic performance.
Figure 10. Electrochemical reduction of CO$_2$ over 2D carbon-based materials. (A) TEM images of nitrogen-doped mesoporous carbons. (B) FEs of various products vs. potential over nitrogen-doped mesoporous carbon electrodes. (C) Schematic illustration of CO$_2$ electro-reduction over nitrogen-doped mesoporous carbon electrodes. (D) DFT calculations of the electro-reduction of CO$_2$ to ethanol over different pyrrolic N sites.$^{[156]}$ (E) Free-energy diagrams of CO$_2$ electro-reduction over different N species.$^{[157]}$ (F) Magnified high-angle annular dark-field scanning transmission electron microscopy image of In/NC. (G) Fourier transform of In K-edge extended X-ray absorption fine structure spectra of different In-based catalysts. (H) Long-term stability of CO$_2$ electro-reduction over In/NC.$^{[160]}$ 2D: 2-dimensional; TEM: transmission electron microscopy; FE: Faradaic efficiency; DFT: density functional theory.

MOFs have attracted considerable attention in the field of catalysis and energy conversion owing to their
rich active sites, diverse structure, and controllable morphology. Kang et al. designed and synthesized a highly efficient MOF catalyst [Cu(L)-e/Cu] by in situ growth on Cu-foam substrates in IL-based solutions\(^\text{[162]}\). MOF particles with assemblies of approximately 50 nm on the surface of the Cu-foam form a thin film [Figure 11A-D]. The MOF thin film contains 15.3% of uncoupled Cu(II) sites, which are considered active sites for the electro-reduction of CO\(_2\) to formic acid. The as-prepared catalyst achieves a high current density of 65.8 mA cm\(^{-2}\) and FE\(_{\text{formic}}\) of 90.5% at -1.8 V vs. Ag/Ag\(^+\) in an IL-based electrolyte [Figure 11E and F]. DFT calculations showed that free Cu(II) centers in defect Cu(L) are produced by the rupture of Cu-O bond to promote CO\(_2\) binding.

With their specific layered structure, 2D transition metal carbides and nitrides (MXenes) show high conductivity, high chemical stability, and multiple catalytic sites. Li et al. calculated the catalytic activity of single-component MXenes by DFT, and the results showed that Cr\(_x\)C\(_2\)T\(_x\) and Mo\(_x\)C\(_x\)T\(_x\) are the best candidates for the electrochemical reduction of CO\(_2\) to CH\(_2\)O\(_2\)\(_n\)\(_2\)\(_f\). These two materials favor the activation of CO\(_2\) rather than H\(_2\)O, resulting in highly efficient CO\(_2\) electro-reduction and HER suppression. Qu et al. prepared N-doped Ti\(_x\)C\(_x\) MXene nanosheets with abundant titanium vacancies (V\(_\text{Ti}\)) by a facile NH\(_2\)-etching pyrolysis approach to achieve an FE\(_{\text{CO}}\) of 92% and current density of 10 mA cm\(^{-2}\) at -0.7 V vs. RHE in seawater as the electrolyte\(^\text{[164]}\). The coexistence of N and V\(_\text{Ti}\) modulates the electronic structure, leading to a decrease in the reaction energy barriers for *COOH formation.

Molecule-metal catalysts are molecular adsorbates that can accumulate intermediates during CO\(_2\) electro-reduction. Li et al. immobilized FeTPP[Cl] onto a Cu substrate to produce a molecular metal catalyst [Figure 11G-I], which was used as an electrode for the electrochemical reduction of CO\(_2\)\(^\text{[113]}\). FeTPP[Cl] does not reduce into iron nanoparticles or nanoclusters under the operating conditions, and the electrode can achieve an FE\(_{\text{ethanol}}\) of 41% with a current density of 124 mA cm\(^{-2}\) at -0.82 V vs. RHE [Figure 11J and K]. In situ surface-enhanced Raman spectroscopy and DFT calculations were used to reveal that a local high concentration of CO induced by the electrode promotes C-C coupling to ethanol. Han et al. deposited N-substituted pyridinium additives as a film on a Cu electrode for the electro-reduction of CO\(_2\) into C\(_2\), products and, furthermore, demonstrated that the film promotes C-C coupling and impedes HER\(^\text{[165]}\).

Substrates functionalized by molecular monolayers are considered a type of 2D electrodes, which have been extensively studied for CO\(_2\) electro-reduction\(^\text{[166-169]}\). For instance, Fang et al. reported that a Au electrode modified with 4-pyridinylethanemercaptan(4-PEM) exhibits high CO\(_2\) selectivity toward formate compared with pristine Au electrode\(^\text{[170]}\). The high surface concentration of H\(^+\) impedes the first electron transfer to CO\(_2\)\(^-\). Moreover, the organometallic complex was also modified as a gas diffusion layer to fabricate a 2D electrode, which was employed as a cathode in a flow cell microreactor for CO\(_2\) electro-reduction. The electrode exhibits an FE\(_{\text{HCOOH}}\) of 76% and FE\(_{\text{CO}}\) of 10%\(^\text{[171]}\).

Covalent organic frameworks (COFs), composed of organic monomers and hybrid atoms, are new porous organic materials with high crystallinity. Covalent bonds are formed through reversible chemical reactions. COFs have gradually been applied to CO\(_2\) electrocatalysis owing to their designable structure, low density, adjustable pore structure, and easily modified structure. Bandomo et al. synthesized Mn\(^{\text{II}}\) tricarbonyl-based 2D COFs for CO\(_2\) electro-reduction\(^\text{[172]}\). The as-prepared 2D COFs exhibit a low onset potential of 190 mV, at which a current density of 12 mA cm\(^{-2}\) and FE\(_{\text{CO}}\) of 72% are achieved, and the catalyst remains active even after 16 h. Zhu et al. developed metalloporphyrin-tetrathiafulvalene-based COFs (M-TTCOFs), which have impressive catalytic performance, achieving an FE\(_{\text{CO}}\) of > 90% and high cycling stability (> 40 h)\(^\text{[172]}\). Tetrathiafulvalene in the 2D nanostructure serves as an electron donor to construct an efficient pathway to accelerate electron transfer and obtain a low activation energy for CO\(_2\) reduction.
To understand the catalytic nature of 2D materials, the electrochemical properties of the same material with various nanostructures are summarized in Table 1. In general, 2D catalysts exhibit excellent catalytic performance compared with the corresponding bulk catalysts.

**SUMMARY AND OUTLOOK**

This review summarizes the progress on various 2D materials with a focus on preparation methods and applications to CO$_2$ electro-reduction. Without any doubt, advances in the synthesis of 2D materials over...
the past decade have produced 2D materials that markedly enhance the efficiency of CO$_2$ electro-reduction.

Methods based on different principles for the preparation of 2D nanostructures have been reviewed. Wet-chemical synthesis and CVD are still the dominant methods for the mass production of 2D materials. It remains urgent to understand how to control the number of layers, flake dimensions, defect levels, and yield of 2D materials. Surface decoration is very important to broaden the application of 2D materials, and it is also an effective way to realize high catalytic performance for CO$_2$ electro-reduction. Selecting the electrode material is the first step of catalysis. The distribution and production rate of products are determined by the thermodynamic and kinetic energy barriers of reaction pathways. In principle, the electron distribution and the charge density of the catalyst surface affect the kinetic energy barriers. Therefore, selecting electrode materials with appropriate electronic properties can enhance the efficiency of CO$_2$ electroreduction.

Selectivity is an essential evaluation indicator of the catalytic performance of 2D materials. Although great progress has been made, the reaction pathway determined by the 2D structure is still unclear. In other words, catalytic performance as a function of structural parameters remains unexplored. Strategies such as morphology modification, doping, and surface decoration have been developed to achieve high catalytic performance of 2D materials. Nevertheless, designing in situ characterization techniques and developing theoretical calculations to unveil the effect of the structure of 2D materials on CO$_2$ electro-reduction are highly significant.

Nowadays, high current density can be easily realized by potential increase, structure design, surface functionalization, and cell modification. However, high potentials require high energy consumption, which is inconsistent with the concept of sustainable development. High potentials also influence the long-term stability and promote HER. The surface structure and activity of 2D materials also change under extremely negative potentials. Additionally, most cases of CO$_2$ electro-reduction over 2D materials are currently being investigated in laboratories owing to the high cost, difficulties in scale-up, and uncontrollable operation. Large-scale synthesis of 2D materials and the preparation of stable and large 2D material-based electrodes are the first important steps into industrialization. We believe that 2D nanostructures will gradually prevail in CO$_2$ electro-reduction and contribute to carbon neutrality worldwide.

DECLARATIONS

Authors’ contributions
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Conflict of interest
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