

---

# Progress in Raman Spectroscopy and Reduction of Carbon Dioxide

Adil Emin<sup>1</sup>, Tursunay Mamtimin<sup>2,\*</sup>

<sup>1</sup>School of Physical Science & Technology, Lanzhou University, Lanzhou, P. R. China

<sup>2</sup>School of Life Sciences, Lanzhou University, Lanzhou, P. R. China

## Email address:

adl19@lzu.edu.cn (A. Emin), tuexay18@lzu.edu.cn (T. Mamtimin)

\*Corresponding author

## To cite this article:

Adil Emin, Tursunay Mamtimin. Progress in Raman Spectroscopy and Reduction of Carbon Dioxide. *Advances in Materials*.

Vol. 9, No. 6, 2021, pp. 135-144. doi: 10.11648/j.sjc.20210906.12

**Received:** October 8, 2021; **Accepted:** October 25, 2021; **Published:** November 23, 2021

---

**Abstract:** The metal catalyst has good electrical conductivity, is simple to prepare and easy to be applied in practice. It is currently the most in-depth researched catalyst for electrochemical reduction of carbon dioxide. In recent decades, metals such as copper, cobalt, tin, and gold have been used as electrode catalysts for reducing carbon dioxide. From the perspective of the reduction mechanism of carbon dioxide, it is generally believed that the formation of C intermediate is the rate-determining step of the entire reduction reaction. One of the main functions of metal catalysts is to enable the corresponding reaction intermediates to exist stably, thereby improving the energy efficiency of the reaction. According to the combination with different intermediates and the different products obtained, the metal electrode catalysts can be divided into three categories. In this paper, the current research status of electrocatalytic and photocatalytic reduction of carbon dioxide and carbon dioxide under Raman spectroscopy are introduced. Also elaborate, the Raman spectroscopic characterization of carbon dioxide has been introduced in this paper with emphasis on the changes of Fermi resonance peaks of CO<sub>2</sub> with temperature and pressure. The advantages and disadvantages of using metal and metal complexes, carbon materials, composite materials and MOF materials to reduce CO<sub>2</sub> are introduced. The method was improved, and finally focused on the core issues of improving reactivity and product selectivity, and analyzed the shortcomings of current electrocatalytic processes extended to large-scale production applications from surface engineering, chemical modification, nano or composite materials. There are other ways to improve the activity of the catalyst from these aspects, as well as the prospects for future research.

**Keywords:** Carbon Dioxide, Electrocatalytic Reduction, Photocatalytic, Raman Scattering

---

## 1. Introduction

Since the industrial revolution, the large-scale application of fossil fuels has brought convenience to people, and it has also caused excessive emissions of CO<sub>2</sub> [1-5]. Researchers believe that the concentration of CO<sub>2</sub> in the atmosphere and ocean is the main cause of the destruction of the natural carbon cycle, and the resulting changes in global ecological environment, such as the greenhouse effect and ocean acidification, will greatly affect human survival and development [1, 2]. On the other hand, fossil fuels, as non-renewable energy sources, have limited reserves, so people are trying to develop a variety of new and renewable energy sources to reduce their dependence on fossil fuels.

Because CO<sub>2</sub> is rich in reserves, cheap and non-toxic on the earth, if it is used as a carbon and oxygen source to synthesize various chemicals and materials, it can simultaneously alleviate the two major environmental and energy crises, so it has application prospects [3, 4]. If renewable energy is used to drive the process, the impact on the environment and energy of the production process can be reduced, in line with the goal of sustainable human development [1, 4, 5]. The development of catalytic science and technology is inextricably linked to the development of catalytic research methods. New characterization techniques play an important role, especially in the continual exploration of new materials and new reactions. Over the past few decades, especially since the 1960s, a new series of catalytic research has developed. The characterization method uses

almost all new technologies derived from the development of modern science, including modern physics based on the principles of photo acoustics, electricity, magnetism, electronics, atoms, ions and heat [1, 4-8].

The discovery of Raman spectroscopy has been around for more than 80 years. The rise of laser technology has made Raman spectroscopy one of the most active research fields in laser analysis. Various spectral analysis methods, from different angles to different expressions, further study the purity of the sample, surface composition, surface structure, sample morphology versus other physicochemical properties, sample internal atom distribution rules, atomic molecular structure information, chemical bonds and combining electron spectroscopy, etc. Laser Raman and infrared spectroscopy complement each other and become a powerful force for molecular vibration and molecular structure identification tool [1, 2, 4-7].

In recent years, with the sharp improvement of detector sensitivity and the improvement of spectrometer which is the signal-to-noise ratio of Raman spectroscopy is greatly improved. That is to say, with the significant advances in materials science, laser and synchrotron technology, and nanotechnology, there are more and more opportunities and possibilities for Raman spectroscopy in catalytic research [4, 7-9]. Especially in the field of catalysis, Raman spectroscopy in the research of supported metal oxides, molecular sieves, in-situ reaction and adsorption, the results have been achieved. The reason why Raman spectroscopy has developed rapidly in the application of catalytic research is mainly as follows:

Firstly, Raman spectroscopy can provide the catalyst itself and the structural information of the species on the surface, which is the most important information to understand the catalyst and catalytic reaction; Secondly, Raman spectroscopy is easier to achieve catalytic research under in situ conditions (high temperature, high pressure, complex system). Thirdly, Raman spectroscopy can be used in the preparation of catalysts, especially in the real-time study of the catalyst preparation process from the aqueous phase to the solid phase, which is difficult to achieve in many other spectroscopy techniques; [2-4, 9]. However, there are some difficulties in the application of Raman spectroscopy. Among them, the low fluorescence interference and low sensitivity are the most important problems that hinder its wide application. The developed UV Raman spectroscopy technology effectively solves the above problems encountered in catalysis research and greatly expands the application range of Raman spectroscopy. Electrochemical research originated from the "animal electricity" phenomenon discovered by Oalvani in 1791 [1, 2, 4, 7]. With electronics, quantum chemistry, structural chemistry, spectroscopy, catalytic chemistry, solid physics, fluids-new achievements in various disciplines such as mechanics and computer science are constantly applied to electrochemistry, making this ancient science alive. Machine and broad development prospects. Greenhouse gases CO<sub>2</sub> is a major cause of global warming. The use of solar energy or other

effective catalytic materials to reduce CO<sub>2</sub> and other organic matter such as hydrocarbons will benefit environmental protection and energy use [2-5, 7, 9-13]. This paper focuses on the research of carbon dioxide in Raman spectroscopy, photocatalytic reduction and its electrocatalytic process.

## 2. Raman Spectroscopy of Carbon Dioxide

The development of catalytic science and technology is inextricably linked to the development of catalytic research methods. Using almost all new technologies derived from the development of modern science, including optics, acoustics, electricity, magnetism, electrons, atoms, ions and the discovery of Raman spectroscopy has been around for more than 80 years. The rise of laser technology has made Raman spectroscopy one of the most active research fields in laser analysis.

For any molecule with a number of atoms N, the degree of molecular vibration has a degree of freedom of 3N-6, and CO<sub>2</sub> is a linear molecule. Therefore, the vibrational freedom of the CO<sub>2</sub> molecule is 3N-5, that is, there are four vibration modes. The four vibration modes include symmetric tensile vibration  $\nu_1$ , asymmetric tensile vibration  $\nu_3$ , and two bending vibrations  $\nu_2$  and  $\nu_4$  with the same frequency. The symmetric tensile vibration mode has almost the same energy as the infrared active second level of  $\nu_2$ , which is composed of two sub-levels, namely  $2\nu_2^0$  and  $2\nu_2^2$  [2, 6-9, 14-16].

Since the energy levels  $2\nu_2^0$  and  $\nu_1$  are two different vibrations with similar energies, the so-called degenerate energy levels are formed; therefore, these degenerate energy levels have the same form of vibration. Because they occasionally have the same energy and the same form of vibration, they interfere with each other in the excited state, and at the same time, Raman activity occurs, which is often called Fermi resonance [7, 9, 16]. The symmetric tensile vibration mode has almost the same energy as the infrared active second level of  $\nu_2$ , which is composed of two sub-levels, namely  $2\nu_2^0$  and  $2\nu_2^2$ . Since the energy levels  $2\nu_2^0$  and  $\nu_2$  are two different vibrations with similar energies, the so-called degenerate energy levels are formed; therefore, these degenerate energy levels have the same form of vibration. Because they occasionally have the same energy and the same form of vibration, they interfere with each other in the excited state, and at the same time, Raman activity occurs, which is often called Fermi resonance [7].

Garrabos et al. [7] have shown that Fermi resonance causes mixing excited state splitting, showing two strong CO<sub>2</sub> characteristics in Raman spectroscopy sign line. As shown in Figure 1, they are  $\nu_1$ - $2\nu_2$  Fermi resonance double peaks frequencies are 1388.2 cm<sup>-1</sup> (high frequency) and 1285.4 cm<sup>-1</sup> (low frequency). There is a small peak on the side of the Fermi formant (Figure 1), which the peak is called the hot peak (hot band) and is generated by a transition state because the molecular thermal energy causes excitation vibration dynamics.

The energy is higher than the ground state. The positions of the heat peaks are 1264.8 cm<sup>-1</sup> and 1409.2 cm<sup>-1</sup>

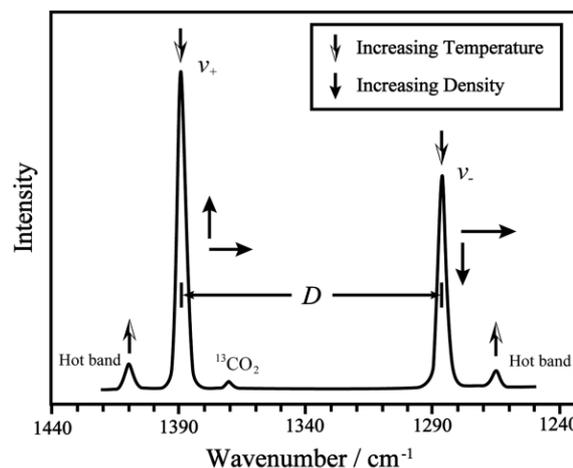
respectively. The intensity of a peak at  $1370\text{ cm}^{-1}$  is very weak, which is due to the isotope splitting of  $^{13}\text{CO}_2$  crack produced.  $^{13}\text{CO}_2$  content in natural  $\text{CO}_2$  (volume fraction) is 1.1%,  $^{13}\text{CO}_2$  can be detected in the experiment only when the gas density is particularly large [4, 7].

(Figure 1) are reprinted with permission from Ref. [7], Copyright 1995. *Geochimica et Cosmochimica Acta*. 2.2 Relationship between  $\text{CO}_2$  Fermi resonance peak and temperature and density.

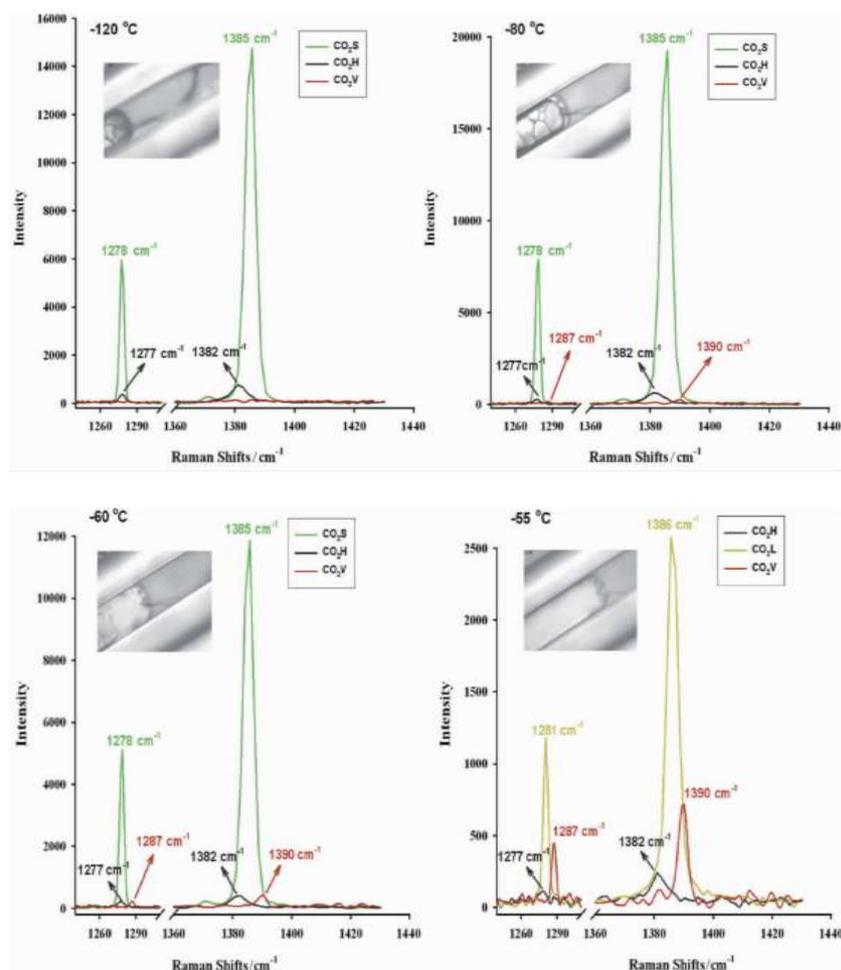
The characteristics of the Raman peak frequency, peak shape and intensity depend on the vibration dynamic mode molecular polarizability changes. Rosso et al [7] study shows that the intensity and position of  $\text{CO}_2$  Raman peaks tend to vary with gas density and temperature. Change with other parameters, as shown in Figure 1.

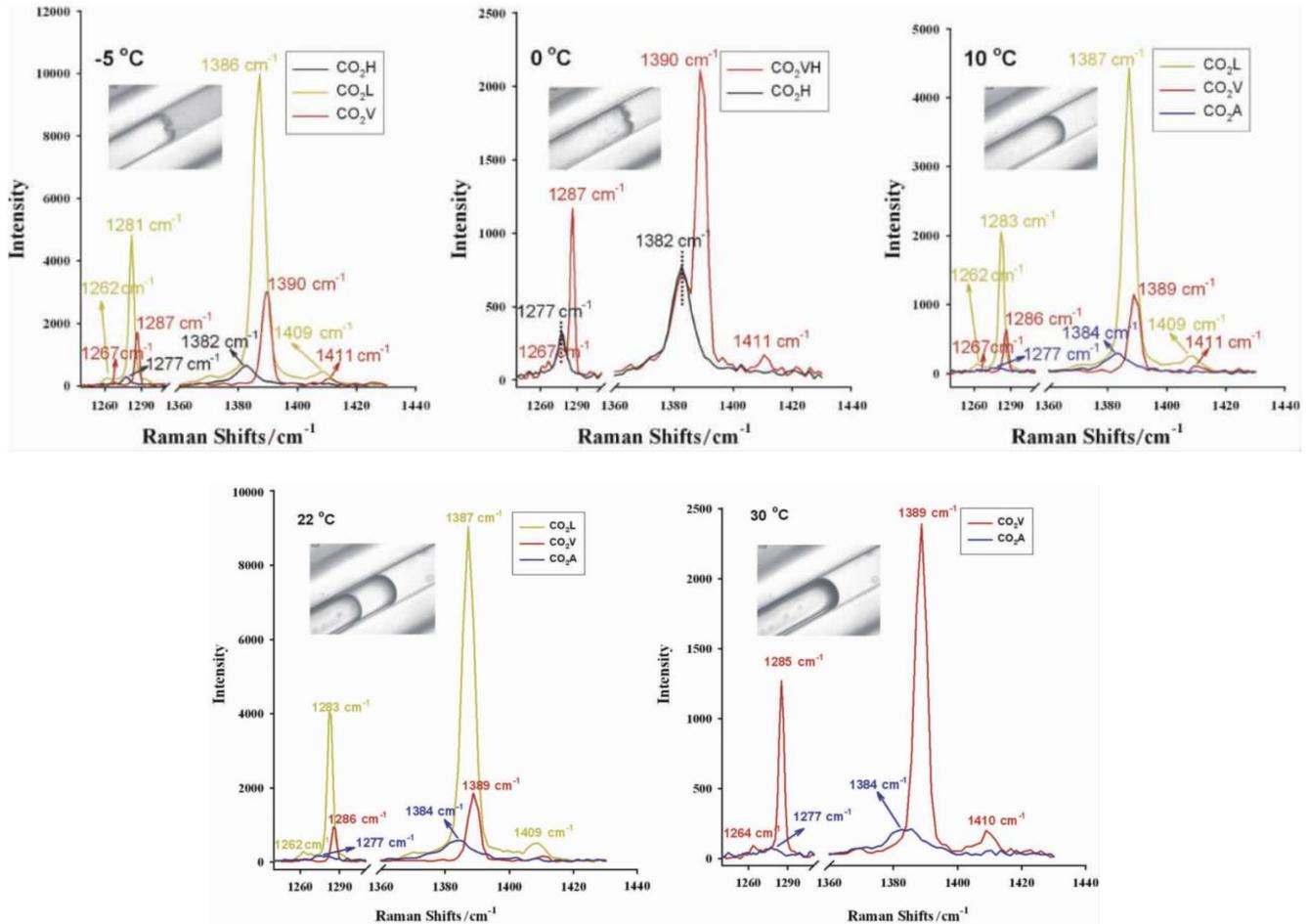
Garrabos et al. [17] studies have shown that as the density increases, the Fermi doublet shifts to a low wavenumber and the moving speed of the low frequency peak is faster than the high frequency peak; Moreover, the high frequency peaks the intensity ratio of the low frequency peak increases as the density increases; With the increase of temperature, the Fermi resonance peak intensity decreases, and the thermal (hot) peaks intensity increases, that is, the ratio of the thermal peak to the Fermi resonance peak increases with increasing temperature [4, 7, 9, 10]. Given therefore, it can be determined according to the position and relative intensity of

the  $\text{CO}_2$  Raman peak. The relative size and temperature of the gas density in the inclusions. Since under normal conditions, the movement of the peak position is related to changes in the environment in which the molecule is located, such as the number of molecular collisions. In view of this, the relative size and temperature of the gas density in the inclusions can be determined based on the position and relative intensity of the  $\text{CO}_2$  Raman peak.



**Figure 1.** A typical Raman spectrum of  $\text{CO}_2$  with the effects of density and temperature.





**Figure 2.** Raman spectra acquired respectively from each phase in capillary at  $-120^{\circ}\text{C}$ – $30^{\circ}\text{C}$ .

(Figure 2) are reprinted with permission from Ref. [7], Copyright 1995. *Geochimica et Cosmochimica Acta*.

For this experiment, refer to Chou et al. [10]. By rapidly freezing the sample, and then during the temperature recovery process, refer to the microscopic thermometric phase transition temperature at  $-120$ ,  $-80$ ,  $-60$ ,  $-55$ ,  $-10$ ,  $-5$ ,  $0$ ,  $10$ ,  $22$ , and  $30^{\circ}\text{C}$ , respectively. Observing the experimental results, it was found that the peak position of the Fermi resonance peak of  $\text{CO}_2$  in each phase at a temperature of  $-120$  to  $30^{\circ}\text{C}$  has such characteristics as temperature changes.  $\text{CO}_2$  solid phase and hydrate peaks remain unchanged; The peaks of  $\text{CO}_2$  gas phase, liquid phase and aqueous solution change; As the temperature increases, the two peaks of the gas phase shift toward the low wavenumber as a whole, and  $1285\text{ cm}^{-1}$  Peak shift ( $2\text{ cm}^{-1}$ ) is greater than  $1390\text{ cm}^{-1}$  peak ( $1\text{ cm}^{-1}$ ); The two peaks of the phase shift to a high wavenumber as the temperature increases, and the offsets are the same; The  $1278\text{ cm}^{-1}$  peak of the aqueous phase rises with temperature to low wavenumber shift, while the  $1383\text{ cm}^{-1}$  peak is reversed, and the offsets are the same. The results show that in the temperature range of  $-120\sim 30^{\circ}\text{C}$ ,  $\text{CO}_2$  gas phase,  $\text{CO}_2$  the characteristic spectra of liquid phase and  $\text{CO}_2$  aqueous phase have variability with temperature. The reason is that  $\text{CO}_2$  changes in the fluid inclusions between the phases due to temperature changes, which directly leads to changes in  $\text{CO}_2$  pressure or density in

these phases, thus affecting the characteristic peaks the  $\text{CO}_2$  solid phase and hydrate characteristic spectra are stable, and their fixed characteristic peaks contribute to the Raman spectroscopy identification of  $\text{CO}_2$  solid phase and hydrate phase in fluid inclusions. It is well known that in fluid inclusion analysis, for fluid inclusions such as rich gas and small size, it is difficult to identify the fluid phase transition in the inclusion during microscopic temperature measurement, and the composition of fluid inclusions in nature is diverse, and the microscopic temperature measurement process The phase transition of the fluid is complicated, and it is difficult to understand the phase transition process under simple microscopic observation and define the phase transition temperature. Raman results at different temperatures change due to fluid phase transitions: The characteristics of  $\text{CO}_2$  solid phase, gas phase and hydrate are shown on the spectra collected below the initial melting temperature ( $-56.6^{\circ}\text{C}$ ) (Figure 2). Subsequently, the  $\text{CO}_2$  solid phase disappears and the  $\text{CO}_2$  liquid phase appears (Figure 2). After freezing point ( $-1.5^{\circ}\text{C}$ ), the liquid phase water continues to combine with the adjacent  $\text{CO}_2$  liquid phase to form a hydrate due to the melting of all the ice, so only the  $\text{CO}_2$  gas phase and hydrate, and the  $\text{CO}_2$  hydrate signal is enhanced (Figure 2). Next, the hydrate disappears ( $10^{\circ}\text{C}$ ) and returns to the  $\text{CO}_2$  gas phase and liquid phase. Simultaneous detection of  $\text{CO}_2$  aqueous phase (Figure

2). Finally, in the CO<sub>2</sub> phase, the gas-liquid two phases are uniform to the gas phase (23°C), and the Raman results show a CO<sub>2</sub> gas phase and a CO<sub>2</sub> aqueous phase (Figure 2). Therefore, by collecting characteristic spectra of fluids at different temperatures, laser Raman spectroscopy combined with microscopic temperature measurement technology can effectively identify different fluid phases, obtain phase transition processes, and determine phase transition temperatures [1, 5, 7, 9-11, 14].

### 3. Summary of Catalytic Materials

#### 3.1. Metal Catalyst

Metal catalysts have good electrical conductivity and are simple and easy to prepare. Inter-application, is the most in-depth research on carbon dioxide electrochemistry chemical agent. In the last few decades, copper, cobalt, tin, and gold have been used. It is used as an electrode catalyst for reducing carbon dioxide. Reduction from carbon dioxide-in terms of mechanics, it is generally considered that the formation of the C<sub>2</sub><sup>\*</sup> intermediate is the entire reversion reaction. The quick step [11, 17-20]. One of the main functions of metal catalysts is to-the intermediate energy of the reaction can be stabilized, thereby increasing the energy efficiency of the reaction rate. According to different intermediates combined with different intermediates, in order to classify metal electrode catalysts into three categories [2, 11, 19, 21]. The first category includes tin, mercury, lead, indium, etc. They have a high hydrogen potential (that is, they need to be at a more negative potential). Only hydrogen can be produced underneath), but the carbon dioxide adsorption capacity is weak, so CO<sub>2</sub> tends to combine with protons to form HCOO<sup>-</sup> and then leaves the surface of the electrode. The original product is formic acid or formate; the typical representative of the second type is gold, silver, zinc and palladium, the hydrogen evolution potential is moderate, but the ability to adsorb carbon monoxide is weak, Once produced, it tends to be directly off the surface of the electrode, so it can be acid Basically, CO<sub>2</sub> is restored to CO; copper is classified into the third category. The only metal. Its CO combination can be bigger, which is beneficial to CO growth. A hydrogen reaction that converts CO<sub>2</sub> into more industrially valuable products such as hydrocarbons and ethyl alcohol. In addition to this, for nickel, iron, platinum, titanium, their hydrogen evolution potential is low. And it has strong adsorption capacity for the original carbon monoxide, which is strongly adsorbed on electricity. The surface of the surface is poisoned by the catalyst, so the product is hydrogen gas. Classify these metals into the fourth category, which will be introduced separately.

##### 3.1.1. Copper (Cu)

The copper reductive product is dominated by hydrocarbons. In the 80s of the last centuries, there was a text it is reported that the method of producing hydrocarbons in the conversion of polycrystalline Cu to catalytic C the

Faraday Efficiency (FE) is over 50%. Although copper-based catalysts are very good Faraday electrolysis efficiency and high added value of electrochemical reductive products, some of its problems have limited its use and development: First, copper is an active metal that dissolves during electrolysis, so the high-index crystal surface of copper with better catalytic activity is quickly deactivated during the reaction. Cause irreversible loss of catalyst, unable to balance the activity and stability of the catalyst. Secondly, the electrochemical reduction products of copper carbon dioxide are still complicated, and the products include CO, HCOOH, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and various alcohols, aldehydes, acids and the like. In addition, the overpotential required for polycrystalline Cu to catalytically reduce CO<sub>2</sub> in the aqueous phase is high, so that the potential for negative shifting and hydrogen evolution reaction of the reaction is large. Serious accumulation, resulting in the latter's competition to dominate. The problem of copper-based catalysts, there are mainly methods such as alloying method, oxidizing method, surface active agent method, surface finishing method, Nano metering method and metal covering method to improve performance [11, 18, 22].

##### 3.1.2. Silver (Ag)

Silver has become a more common catalyst for the reduction of carbon dioxide due to its relatively low overpotential and high selectivity. It is a more commonly used catalyst for the reduction of carbon dioxide. Recent research on silver-reduced carbon dioxide has recently made a new development. Lu et al. have discovered a Nano-silver catalyst, [11-13, 22] which can reduce carbon dioxide to carbon monoxide with 92% selectivity at a voltage of 0.6 V. The 1.1% Faraday current efficiency of nano silver is far less than that of the commonly used polycrystalline silver catalyst, but the deposition density of the product carbon monoxide on nano silver is about 3,000 times that of polycrystalline silver. Since the specific surface area of nano-silver is 150 times that of polycrystalline silver, the catalytic activity of nano-silver is about 20 times that of polycrystalline silver.

##### 3.1.3. Gold (Au)

Gold, like silver, is a more active catalyst in the reduction of carbon dioxide, but due to its higher price, it is not as good as gold. In Chen and Kannan's experiments, [21-24] they passed the reduction of gold oxides. The membrane method obtained the gold nanoparticle, and the nanoparticle made the electrode pair. The catalytic effect of oxidized carbon reduction is much better than the commonly used polycrystalline gold, and its Faraday current efficiency is as high as 96%. In the gold-catalyzed reduction of carbon dioxide, the initial conversion of carbon dioxide requires a higher overpotential, so it is the final step of the reaction. the test shows that the catalytic effect of nanogold is better than that of ordinary gold, which is similar to silver. Except this, it is more effective in stabilizing the free radical of carbon dioxide.

##### 3.1.4. Other Metals

In addition to the metals mentioned above, there are some

studies showing that certain metals and their oxidants have a good catalytic effect on the reduction of carbon dioxide.

#### Tin (Sn)

The research shows that when Sn is used as the electrode, SnO can be better catalyzed. Reductive reaction of oxidized carbon, but related to the reversion of tin dioxide to carbon dioxide there should be very little research, but the reason is that tin dioxide is easy to be reverted to metal tin. However, Lee [25] recently researched the use of nano tin dioxide. A method of reducing carbon dioxide. At a potential of -1.8 V, 5 nm of tin dioxide nanoparticle as a catalyst can make the reversion Faraday's current efficiency is 86%.

#### Molybdenum (Mo)

Recently, Oh's [26] research shows that there is an organic solvent solution of molybdenum oxide. It is also an excellent catalyst for electrocatalytic reduction of carbon dioxide. Its reductive product at room temperature is more complex, but at -20° C, it will mainly produce carbon monoxide. The presence of water will also make the reaction of the product and the catalyst the activity changes. In addition, Mo's sulfur compound MoS<sub>2</sub> is unexpectedly a very good catalytic effect. It can highly specifically reduce carbon monoxide at a voltage of -0.764 V in the tetrafluoroborate solution of the 3-methyl-1-ethylimidazolium cation mentioned above, and the Faraday current efficiency is as high as 98%. The scientists also developed a nanosheet of MoS<sub>2</sub> to increase its specific surface area and obtain better catalytic effects. The success of MoS<sub>2</sub> has also led scientists to focus on substances of similar structure, such as MoSe<sub>2</sub>, WS<sub>2</sub>, etc. Although no new research results have emerged, but there is no doubt that this is a development direction full of prospects [12, 22, 26, 27].

#### Gallium (Ga)

Sekimoto [27] found that gallium trioxide is also a catalyst for carbon dioxide reduction. Unlike most of the metals mentioned above, it is more selective in reducing carbon dioxide to formic acid and has a Faraday current efficiency of up to 80%. The reaction mechanism indicates that the selectivity to formic acid is higher due to the presence of the more stable intermediate HCOOGa<sub>2</sub>O<sub>3</sub>.

### 3.2. Non-metallic Catalyst

Relative to the high price and low reserves of metals, non-metallic, especially carbon materials, the source is wider, the price is much cheaper, and the environment is friendly, because many researchers are trying to load metal on non-metallic substrates. That is say, the metal is supported on a non-metallic substrate to electrochemically catalyze the reduction of CO<sub>2</sub>. Non-metallic bases can help reduce metal usage, increase metal utilization, stabilize, Dispersing the metal nanoparticles, through the electron cloud structure of the support effect metal catalyst, thereby increasing the activity and selectivity of the catalyst. At present, the nanocarbon substrate is the object of research by the researcher because of its unique ability to assemble carbon atoms into nanomaterials with different dimensions and structures. The unique ability of nanomaterials has become the focus of research, such as one-dimensional carbon

nanotubes (CNT), carbon nanofiber (CNF) and two-dimensional graphite [16, 22, 27]. These nano carbons the material has a high surface area, strong electrical conductivity, and good chemical stability and higher mechanical strength metal material, it is not fully equipped with the advantages.

### 3.3. Carbon Material

Studies have shown that under high pressure, the surface of the glassy carbon electrode can directly produce CO<sub>2</sub>, its products include CO, HCOOH and a small number of hydrocarbons. In the study related to carbon nanomaterials, 500 nm diameter CNF obtained by carbonization of polyaniline, compared with nanometer metal, it has a higher current density and can be used at an overpotential of 0.17 V, the catalytic CO<sub>2</sub> is reduced to CO. Researchers believe that its active site is still carbon atoms and nitrogen doping can enhance the catalytic performance of carbon materials. Sharma et al. Use nitrogen-doped carbon nanotubes (N-CNTs) as catalysts, but also at lower levels the overpotential (-0.18 V) efficiently restores CO<sub>2</sub> to CO. Theoretical calculation the lone pair of pyridinium and pyrrole N can be bonded to C to make it alive. Wu et al. carried out different kinds of nitrogen doping on the graphite. This 3D graphene material can reduce CO<sub>2</sub> to CO at an overpotential of -0.19 V, and Faraday effect (FE) can be as high as about 85% [11, 28].

### 3.4. Carbon-based Composite Materials

The copper that was discussed before is a kind of high added value that can be obtained. The original product, its shortcomings are too bad in response efficiency and selectivity, it is difficult to get dedicated product. For this question, Song et al. [17] Through the analysis of the reaction mechanism, it was found that the graphene-based nanopolycrystalline Cu interacted with graphene through the defect sites, which stabilized the intermediate of the CO<sub>2</sub> reduction reaction and improved at a lower overpotential. For the selectivity for products such as methane and methanol. The authors used a nano-Cu particle on the N-doped carbon layer (CNS, length about 50-80 nm) to catalyze the reduction of CO<sub>2</sub> at room temperature. The main product was ethanol, the Faraday effect (FE) was 75%, and the highest efficiency of ethanol conversion was 63%. The innovation of this research is to combine the traditional advantages of the metal catalyst with the characteristics of the carbon material and use the interaction to achieve the purpose of improving the selectivity of the reaction.

### 3.5. Metal Framed Material

MOF, Metal-Organic Frameworks, refers to a metal organic framework material, which is a porous material formed by a self-assembly process of a metal node structure or a cluster structure and an organic ligand [22, 29]. This kind of material is a combination of metal and organic ligand, so it has many unique properties, such as large specific

surface area and high porosity, which makes it better deoxidized carbon is combined to form a good carbon dioxide reduction catalyst. Zhang et al. [29]. used metal and porphyrin through an organic frame combined to form a multiphase catalyst, the experiment shows that the catalyst can be specialized reducing carbon dioxide to carbon monoxide in one place, and Faraday's current efficiency higher up to 90%. At the same time, it also has the advantages of long life and low voltage. Li et al. [30] and other researchers used  $\text{Ni}^{2+}$  and using azo-4,4-pyridine as a ligand, self-assembled and washed into a nitrogen-rich MOF material COF due to its. It has a good adsorption and fixation effect on carbon dioxide, so it is also a kind a better carbon dioxide reductive catalyst.

#### 4. Photocatalytic Reduction

Hydrocarbon fuels have the stability and high energy and become the most important energy source in today's society. However, the combustion of hydrocarbon fuels produces a large amount of  $\text{CO}_2$  gas, resulting in an increase in the greenhouse effect. Photocatalytic reduction of  $\text{CO}_2$  can produce hydrocarbons such as formic acid, formaldehyde and methanol, which are of great significance for environmental protection and energy reuse.

In recent years, a lot of exploration and research on photocatalytic reduction of  $\text{CO}_2$  has been carried out internationally. In order to improve the conversion rate of  $\text{CO}_2$ , a photocatalyst with high catalytic activity and high selectivity has been sought. At present, photocatalysts mainly study  $\text{TiO}_2$  and some metal oxides, and improve the catalytic activity of photocatalysts by modification methods such as metal or non-metal doping. This paper mainly introduces the types and catalytic reaction characteristics of photocatalysts used in photocatalytic reduction of carbon dioxide in recent years.

$\text{TiO}_2$  has rutile, anatase and titanium in nature. The three crystal forms of the ore type are mainly anatase type used as a photocatalyst.  $\text{TiO}_2$  has high photocatalytic activity, strong corrosion resistance, stability, and non-toxicity. The relatively low price is a commonly used photocatalyst. Different experimental conditions, photocatalytic reduction of  $\text{CO}_2$  products is very different, the products are mainly carbon monoxide, formic acid, formaldehyde, methanol, methane and other carbon compounds and acetic acid, ethane, ethylene and other two carbon compounds.

Tan et al. [31]. studied photocatalytic reduction of  $\text{CO}_2$  using particulate  $\text{TiO}_2$  as a photocatalyst. The experimental results show that under room temperature conditions,  $\text{CO}_2$  and saturated water vapor are continuously reacted under different wavelengths of ultraviolet light for 48 hours, and the reduction product is mainly  $\text{CH}_4$ . Gas chromatographic analysis revealed that a small amount of  $\text{H}_2$  and  $\text{CO}$  were formed in the reduced product, and  $\text{H}_2/\text{CH}_4$  was about 0.6  $\text{CO}/\text{CH}_4$  of about 1. The study found that the methane concentration in the product was about 200 ppm under 253.7 nm ultraviolet light, and the methane concentration was less than 100 ppm under

365 nm ultraviolet light. Granular  $\text{TiO}_2$  has a better catalytic effect than film-like  $\text{TiO}_2$ .

Vijayan et al. [32] conducted photocatalytic reduction of  $\text{CO}_2$  using different sizes of  $\text{TiO}_2$  nanotubes as catalysts. The experimental results show that when the calcination temperature is between 200 and 800°C, different sizes of  $\text{TiO}_2$  nanotubes are synthesized by hydrothermal oxidation method, with diameters between 8 and 12 nm and lengths between 50 and 300 nm. between. When the catalyst calcined at 400°C was subjected to a catalytic reaction, the methane yield was the highest; when the catalyst calcined at 600°C was subjected to a catalytic reaction, the acetaldehyde yield was the largest. When the calcination temperature is higher than 400°C, the specific surface of the catalyst is small as the calcination temperature is increased. The nanotube-type  $\text{TiO}_2$  has better catalytic effect than the P25-type  $\text{TiO}_2$  [31, 33, 34].

Wang et al. [34] used  $\text{CdSe}/\text{Pt}/\text{TiO}_2$  as a catalyst. Photocatalytic reduction of  $\text{CO}_2$  was carried out. The experimental results show that the reaction product is more than 4h under the irradiation of visible light with  $\lambda > 420$  nm with water as solvent. The main products are  $\text{CH}_4$ ,  $\text{CH}_3\text{OH}$  and a small amount of  $\text{CO}$  and  $\text{H}_2$ . The methane yield was 48 ppm/g·h, and the methanol yield was 3.3 ppm/g·h. The XPS characterization shows that the doping amounts of Pt and Cd in the catalyst are 0.5% and 1%, respectively [35].

Schulte et al. [33] used photocatalytic reduction of  $\text{CO}_2$  using  $\text{TiO}_2$  nanotubes as a catalyst. The experimental results show that methanol is formed in the reduced product under 365 nm ultraviolet light irradiation. The nanotube-type  $\text{TiO}_2$  catalyst has a large surface area, and the  $\text{TiO}_2$  nanotubes composed of anatase phase and rutile phase have stronger catalytic activity than single-phase  $\text{TiO}_2$  nanotubes. Under ultraviolet light irradiation, as the ratio of rutile phase increases, the photocatalytic reaction rate slows down. Under the irradiation of visible light or light near the visible wavelength, the reaction rate increases as the ratio of the rutile phase increases [33, 36-38]. It has been found that by adjusting the calcination temperature, the composition of the catalyst can be adjusted to adjust the catalytic activity of the catalyst and to expand the absorption range of the catalyst for visible light. The  $\text{TiO}_2$  nanotube catalyst calcined at 480°C has the highest photocatalytic activity and the strongest absorption of ultraviolet light.

Wu Shuxin et al. [39] carried out photocatalytic reduction of  $\text{CO}_2$  by using copper-doped titanium dioxide as a photocatalyst. The experimental results show that the photocatalytic reduction performance of titanium dioxide is the best when the amount of copper doping is 0.2%. For the undoped copper  $\text{TiO}_2$  catalyst, the photocatalytic reduction products are only formic acid and formaldehyde; the copper-doped  $\text{TiO}_2$  catalyst, photocatalytic reduction products not only have formic acid and formaldehyde, but also methanol [28, 39-41].

Fan Jun et al. [42] used  $\text{Fe}^{3+}$  doped nano  $\text{TiO}_2$  as a catalyst. Study on photocatalytic reduction of  $\text{CO}_2$ . Catalyst characterization results show that the dispersion of  $\text{Fe}-\text{TiO}_2$  catalyst is good. The average particle size is 9.37 nm and the

specific surface area is 85.46 m<sup>2</sup>/g. The doping of Fe<sup>3+</sup> not only reduces the average particle size of TiO<sub>2</sub>, but also effectively inhibits the phase transition of TiO<sub>2</sub>, so that the catalyst maintains a single anatase phase structure. When the Fe<sup>3+</sup> doping amount is 4.0 % (relative to the mass fraction of TiO<sub>2</sub>), The yield of methanol in photocatalytic reduction products when Fe-TiO<sub>2</sub> catalyst dosage is 1.0 g/L, reaction time is 8h, CO<sub>2</sub> flow rate is 200 mL/min, reaction temperature is 90°C, and the concentration of NaOH and Na<sub>2</sub>SO<sub>3</sub> in the reaction solution are both 0.10 mol/L. Up to 308.76 μmol/g (based on the amount of material that produces methanol per gram of catalyst) [18, 32, 43, 44].

Kocia et al. [45] Photocatalytic reduction of CO<sub>2</sub> using silver-doped TiO<sub>2</sub> as a catalyst. The experimental results show that the photocatalytic reduction of CO<sub>2</sub> products is mainly methane and methanol under 254 nm ultraviolet light irradiation. When the amount of silver doping is 5%, the forbidden band width of TiO<sub>2</sub> is lowered. When the amount of silver doping is more than 5%, silver polymerizes on the surface of the semiconductor catalyst, which reduces the probability of the combination of photogenerated electrons and holes, and improves the service life of the catalyst. XRD characterization shows that as the amount of silver doping increases, the forbidden band width gradually decreases. When the doping amount of silver is 7%, the yield of methane and methanol is the highest [36, 46-49].

In summary, the catalysts used are mainly powdered TiO<sub>2</sub>, TiO<sub>2</sub> nanotubes and metal or non-metal doped TiO<sub>2</sub> powder. TiO<sub>2</sub> can only absorb ultraviolet light with a wavelength of less than 387.5 nm. After doping with metal and non-metal, the photocatalytic activity is improved and the visible light response can be achieved.

## 5. Summary and Perspectives

In recent years, the topic of electrochemical reduction of carbon dioxide has attracted a lot of research. The researcher's attention is mainly due to the following reasons:

1) The reduction of CO<sub>2</sub> can be reduced CO<sub>2</sub> in low gas, so as to relieve a series of warming caused by global warming unfavorable effects; 2) The chemical products of the chemical recovery are all about valuable raw materials or fuels can alleviate the energy crisis; 3) This is a convenient way to store reusable electrical energy in a chemical form with high energy density. By rational (reasonable) design and selection of the catalyst, the desired reduction product can be obtained with high selectivity. According to the species composition of the element, the inorganic multiphase electrode catalysts currently studied can be classified into metal, metal oxide, metal sulfur and non-metal (Mainly carbon-based materials). Difficulties encountered in the design and selection of catalytic materials include the overpotential too high or low catalytic activity, poor product selection, and insufficient catalyst stability and many more. Next, this overview mainly provides boosting power from the following aspects. Possible recommendations and methods for polar catalyst performance:

**Surface engineering:** The surface properties of the catalyst to the final catalytic effect, there is a significant impact (especially for metal catalysts). We know that the smooth surface of the metal is compared with the rough surface of the metal. Rough surface metals have larger electrochemically active surface areas and higher current densities. More importantly, the rough surface has more low coordination sites (surface steps, surface defects) than the smooth surface, which can improve the reaction activity of CO<sub>2</sub> reduction. In order to improve catalyst performance, in addition to surface effects, surface impurities and metal coatings should also be considered. In summary, although the exact reaction mechanism has not been proved, the experimental results show that there are more active reaction sites on the high-density grain boundaries, which can promote the improvement of reduction activity.

**Chemical modification:** The active group or the catalytic substance is attached to the surface of the electrode by adsorption, coating, polymerization, chemical reaction, etc., thereby improving the characteristic function of the electrode catalyst. Surface modification of copper-based catalysts, such as the addition of other metal elements or sulfur ions, can improve their catalytic performance. For pure carbon catalysts with low catalytic activity, can be hybrid N and other miscellaneous atoms to improve performance.

**Nano array materials:** The structure of the nano array of catalytic materials, that is an independent structural element with a nanometer size, such as a nanometer rod, a nanometer tube, etc. ordering to obtain microscopic array materials. The current method of constructing nano arrays is the hydrothermal synthesis method.

**Composite materials:** There are special interactions between two or more composite materials, thereby achieving the purpose of improving the activity of the catalyst while ensuring its stability. Such as Cu, CNS, Sn and stilbene the combination also has an unmistakable effect. From this, metal-carbon materials, metal-metal oxides, metal sulphide-carbon materials, etc. a composite material with practical potential for electrocatalytic reduction of CO<sub>2</sub>.

**Others:** In addition to the nature of the catalyst itself, other influencing factors also have some room for improvement. In the process of electrochemical reduction, the efficiency of CO<sub>2</sub> transport to the surface of the cathode catalyst is not high, resulting in low current density. Therefore, this problem can be solved by improving the design of the electrolytic cell. For example, changing the material of the gas diffusion layer and the liquid flow layer; A solid polymer electrolyte is used; an ionic liquid or the like is used. Compared with the aqueous solution, the ion liquid has an unparalleled advantage of high CO<sub>2</sub> solubility and potential window width. More importantly, ionic liquids can greatly inhibit the side reactions that generate hydrogen, which is worthy of further attention. From the perspective of materials science, many relatively less popular inorganic materials (metal nitrides, metal phosphides, metal carbides, metal borides, etc.) have yet to be developed and explored. While most of the researchers are paying attention to the performance of the cathode catalyst, the selection of the

anode material also affects the overall response efficiency. Parameters such as CO<sub>2</sub> pressure, reaction temperature, pH, and the occurrence of catalyst poisoning and deactivation also affect the final reaction results.

All in all, with the continuous development of the international economy and the large-scale application of industrial fuels, the content of carbon dioxide in the atmosphere continues to increase. Catalytic reduction of carbon dioxide to produce hydrocarbon fuels is of great significance for environmental protection and renewable energy use. The use of eternal solar energy to catalytically reduce CO<sub>2</sub>, its system is simple and easy to control, and pollution is becoming an important direction for researchers. Develop environmental protection, economy, high activity, high lifetime catalysts will be the key to industrialization.

## Data Availability

This study is available from the corresponding author upon reasonable request.

## Acknowledgements

This work is financially supported by the Doctoral Startup Funding.

## References

- [1] P. A. H. Christensen, A., Techniques and mechanisms in electrochemistry [M], Chapman & Hall, London, 1993.
- [2] Z. Q. T. A. L. J. L. M. Fleischmann, Raman spectroscopy of adsorbates on thin film electrodes deposited on silver substrates, *J. Electroanal. Chem*, 217 (1987) 397-410.
- [3] M. Berkesi, K. Hidas, T. Guzmics, J. Dubessy, R. J. Bodnar, C. Szabó, B. Vajna, T. Tsunogae, Detection of small amounts of H<sub>2</sub>O in CO<sub>2</sub>-rich fluid inclusions using Raman spectroscopy, *Journal of Raman Spectroscopy*, 40 (2009) 1461-1463.
- [4] W. A. Ed., Interfacial electrochemistry [M], VCH, New York, 1999.
- [5] A. Emin, A. Hushur, T. Mamtimin, Raman study of mixed solutions of methanol and ethanol, *AIP Advances*, 10 (2020) 065330.
- [6] V. L. Furer, A. E. Vandyukov, J. P. Majoral, A. M. Caminade, V. I. Kovalenko, Comparative DFT study of Raman spectra of phosphorus-containing dendrimers built from thiophosphoryl, cyclotriphosphazene and phthalocyanine cores, *Vibrational Spectroscopy*, 70 (2014) 78-88.
- [7] K. M. R. A. R. J. Bodnar, Microthermometric and Raman spectroscopic detection limits of CO<sub>2</sub> in fluid inclusions and the Raman spectroscopic characterization of CO<sub>2</sub>, *Geochimica et Cosmochimica Acta*, 59 (1995) 3961-3975.
- [8] H. H. W. Yoshio Hori, Toshio Tsukamoto and Osamu Koga, Electrochemical process of CO selectivity in electrochemical reduction of CO<sub>2</sub> at metal electrodes in aqueous media, *Electrochimica Acta*, 39 (1994) 1833-1839.
- [9] X. M. Lin, Y. Cui, Y. H. Xu, B. Ren, Z. Q. Tian, Surface-enhanced Raman spectroscopy: substrate-related issues, *Anal Bioanal Chem*, 394 (2009) 1729-1745.
- [10] J. Bonin, M. Robert, M. Routier, Selective and efficient photocatalytic CO<sub>2</sub> reduction to CO using visible light and an iron-based homogeneous catalyst, *J Am Chem Soc*, 136 (2014) 16768-16771.
- [11] M. Gattrell, N. Gupta, A. Co, A review of the aqueous electrochemical reduction of CO<sub>2</sub> to hydrocarbons at copper, *Journal of Electroanalytical Chemistry*, 594 (2006) 1-19.
- [12] C. W. Li, M. W. Kanan, CO<sub>2</sub> reduction at low overpotential on Cu electrodes resulting from the reduction of thick Cu<sub>2</sub>O films, *J Am Chem Soc*, 134 (2012) 7231-7234.
- [13] M. Liu, Y. Pang, B. Zhang, P. De Luna, O. Voznyy, J. Xu, X. Zheng, C. T. Dinh, F. Fan, C. Cao, F. P. de Arquer, T. S. Safaei, A. Mepham, A. Klinkova, E. Kumacheva, T. Filleter, D. Sinton, S. O. Kelley, E. H. Sargent, Enhanced electrocatalytic CO<sub>2</sub> reduction via field-induced reagent concentration, *Nature*, 537 (2016) 382-386.
- [14] M. S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Raman spectroscopy of carbon nanotubes, *Physics Reports*, 409 (2005) 47-99.
- [15] T. Kume, Y. Ohya, S. Sasaki, H. Shimizu, Raman study of carbon dioxide up to 80 GPa, *High Pressure Research*, 26 (2006) 309-312.
- [16] J. Norooz Olliaee, M. Dehghany, M. Rezaei, A. R. McKellar, N. Moazzen-Ahmadi, Five intermolecular vibrations of the CO<sub>2</sub> dimer observed via infrared combination bands, *J Chem Phys*, 145 (2016) 174302.
- [17] S. Gao, X. Jiao, Z. Sun, W. Zhang, Y. Sun, C. Wang, Q. Hu, X. Zu, F. Yang, S. Yang, L. Liang, J. Wu, Y. Xie, Ultrathin Co<sub>3</sub>O<sub>4</sub> Layers Realizing Optimized CO<sub>2</sub> Electroreduction to Formate, *Angew Chem Int Ed Engl*, 55 (2016) 698-702.
- [18] F. Cai, D. Gao, R. Si, Y. Ye, T. He, S. Miao, G. Wang, X. Bao, Effect of metal deposition sequence in carbon-supported Pd-Pt catalysts on activity towards CO<sub>2</sub> electroreduction to formate, *Electrochemistry Communications*, 76 (2017) 1-5.
- [19] C. Cometto, L. Chen, P. -K. Lo, Z. Guo, K. -C. Lau, E. Anxolabéhère-Mallart, C. Fave, T. -C. Lau, M. Robert, Highly Selective Molecular Catalysts for the CO<sub>2</sub>-to-CO Electrochemical Conversion at Very Low Overpotential. Contrasting Fe vs Co Quaterpyridine Complexes upon Mechanistic Studies, *ACS Catalysis*, 8 (2018) 3411-3417.
- [20] Y. Zhou, F. Che, M. Liu, C. Zou, Z. Liang, P. De Luna, H. Yuan, J. Li, Z. Wang, H. Xie, H. Li, P. Chen, E. Bladt, R. Quintero-Bermudez, T. K. Sham, S. Bals, J. Hofkens, D. Sinton, G. Chen, E. H. Sargent, Dopant-induced electron localization drives CO<sub>2</sub> reduction to C<sub>2</sub> hydrocarbons, *Nat Chem*, 10 (2018) 974-980.
- [21] R. Kamata, H. Kumagai, Y. Yamazaki, G. Sahara, O. Ishitani, Photoelectrochemical CO<sub>2</sub> Reduction Using a Ru(II)-Re(I) Supramolecular Photocatalyst Connected to a Vinyl Polymer on a NiO Electrode, *ACS Appl Mater Interfaces*, 11 (2019) 5632-5641.
- [22] D. D. Zhu, J. L. Liu, S. Z. Qiao, Recent Advances in Inorganic Heterogeneous Electrocatalysts for Reduction of Carbon Dioxide, *Adv Mater*, 28 (2016) 3423-3452.

- [23] L. He, Z. Tong, Z. Wang, M. Chen, N. Huang, W. Zhang, Effects of calcination temperature and heating rate on the photocatalytic properties of ZnO prepared by pyrolysis, *J Colloid Interface Sci*, 509 (2018) 448-456.
- [24] B. Wetzel, P. Rosso, F. Hauptert, K. Friedrich, Epoxy nanocomposites – fracture and toughening mechanisms, *Engineering Fracture Mechanics*, 73 (2006) 2375-2398.
- [25] Y. -I. Lee, J. -S. Lee, E. -S. Park, D. -H. Jang, J. -E. Lee, K. Kim, N. V. Myung, Y. -H. Choa, Effect of Calcination Temperature on the Photocatalytic Properties of Electrospun TiO<sub>2</sub> Nanofibers, *Journal of Nanoscience and Nanotechnology*, 14 (2014) 8005-8009.
- [26] Y. Oh, H. Vrabel, S. Guidoux, X. Hu, Electrochemical reduction of CO<sub>2</sub> in organic solvents catalyzed by MoO<sub>2</sub>, *Chem Commun (Camb)*, 50 (2014) 3878-3881.
- [27] T. Sekimoto, H. Hashiba, M. Deguchi, S. Yotsuhashi, T. Masui, A. Kuramata, S. Yamakoshi, Electrochemical application of Ga<sub>2</sub>O<sub>3</sub> and related materials: CO<sub>2</sub>-to-HCOOH conversion, *Japanese Journal of Applied Physics*, 55 (2016).
- [28] J. -P. Jones, G. K. S. Prakash, G. A. Olah, Electrochemical CO<sub>2</sub> Reduction: Recent Advances and Current Trends, *Israel Journal of Chemistry*, 54 (2014) 1451-1466.
- [29] T. Zhang, W. Lin, Metal-organic frameworks for artificial photosynthesis and photocatalysis, *Chem Soc Rev*, 43 (2014) 5982-5993.
- [30] J. Li, M. Zhang, X. Li, Q. Li, J. Yang, Effect of the calcination temperature on the visible light photocatalytic activity of direct contact Z-scheme g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> heterojunction, *Applied Catalysis B: Environmental*, 212 (2017) 106-114.
- [31] S. S. Tan, L. Zou, E. Hu, Photocatalytic reduction of carbon dioxide into gaseous hydrocarbon using TiO<sub>2</sub> pellets, *Catalysis Today*, 115 (2006) 269-273.
- [32] V. Krishnaraj, A. Prabukarthi, A. Ramanathan, N. Elanghovan, M. Senthil Kumar, R. Zitoune, J. P. Davim, Optimization of machining parameters at high speed drilling of carbon fiber reinforced plastic (CFRP) laminates, *Composites Part B: Engineering*, 43 (2012) 1791-1799.
- [33] K. L. Schulte, P. A. DeSario, K. A. Gray, Effect of crystal phase composition on the reductive and oxidative abilities of TiO<sub>2</sub> nanotubes under UV and visible light, *Applied Catalysis B: Environmental*, 97 (2010) 354-360.
- [34] Z. Wang, F. F. Li, C. Yang, W. Y. Zhang, J. H. Wu, Photocatalytic Reduction of CO<sub>2</sub> Using Cu/S-TiO<sub>2</sub> Prepared by Electroless Plating Method, *Advanced Materials Research*, 233-235 (2011) 589-595.
- [35] X. Jiang, F. Cai, D. Gao, J. Dong, S. Miao, G. Wang, X. Bao, Electrocatalytic reduction of carbon dioxide over reduced nanoporous zinc oxide, *Electrochemistry Communications*, 68 (2016) 67-70.
- [36] J. Low, B. Cheng, J. Yu, Surface modification and enhanced photocatalytic CO<sub>2</sub> reduction performance of TiO<sub>2</sub>: a review, *Applied Surface Science*, 392 (2017) 658-686.
- [37] Q. Lu, J. Rosen, Y. Zhou, G. S. Hutchings, Y. C. Kimmel, J. G. Chen, F. Jiao, A selective and efficient electrocatalyst for carbon dioxide reduction, *Nat Commun*, 5 (2014) 3242.
- [38] K. K. Shan Jiang, Chiara Pasquini, and Holger Dau, New aspects of operando Raman spectroscopy applied to electrochemical CO<sub>2</sub> reduction on Cu foams, *J. Chem. Phys.*, 041718-12 (2019) 13.
- [39] P. Li, S. Ouyang, G. Xi, T. Kako, J. Ye, The Effects of Crystal Structure and Electronic Structure on Photocatalytic H<sub>2</sub> Evolution and CO<sub>2</sub> Reduction over Two Phases of Perovskite-Structured NaNbO<sub>3</sub>, *The Journal of Physical Chemistry C*, 116 (2012) 7621-7628.
- [40] Y. Hermans, A. Klein, K. Ellmer, R. van de Krol, T. Toupance, W. Jaegermann, Energy-Band Alignment of BiVO<sub>4</sub> from Photoelectron Spectroscopy of Solid-State Interfaces, *The Journal of Physical Chemistry C*, 122 (2018) 20861-20870.
- [41] H. Takeda, O. Ishitani, Development of efficient photocatalytic systems for CO<sub>2</sub> reduction using mononuclear and multinuclear metal complexes based on mechanistic studies, *Coordination Chemistry Reviews*, 254 (2010) 346-354.
- [42] X. Chang, T. Wang, J. Gong, CO<sub>2</sub> photo-reduction: insights into CO<sub>2</sub> activation and reaction on surfaces of photocatalysts, *Energy & Environmental Science*, 9 (2016) 2177-2196.
- [43] K. K. Hiroyuki Takeda, Haruo Inoue, and Osamu Ishitani, Development of an Efficient Photocatalytic System for CO<sub>2</sub> Reduction Using Rhenium(I) Complexes Based on Mechanistic Studies, *American Chemical Society*, 130 (2008) 2023-2031.
- [44] B. I. a. D. Uner, Artificial Photosynthesis from a Chemical Engineering Perspective, *Artificial Photosynthesis*, (2012) 13-36.
- [45] I. Ciereszko, A. Janonis, M. Kociakowska, Growth And Metabolism of Cucumber In Phosphate-Deficient Conditions, *Journal of Plant Nutrition*, 25 (2002) 1-1.
- [46] L. Liu, H. Zhao, J. M. Andino, Y. Li, Photocatalytic CO<sub>2</sub> Reduction with H<sub>2</sub>O on TiO<sub>2</sub> Nanocrystals: Comparison of Anatase, Rutile, and Brookite Polymorphs and Exploration of Surface Chemistry, *ACS Catalysis*, 2 (2012) 1817-1828.
- [47] Y. X. Pan, Y. You, S. Xin, Y. Li, G. Fu, Z. Cui, Y. L. Men, F. F. Cao, S. H. Yu, J. B. Goodenough, Photocatalytic CO<sub>2</sub> Reduction by Carbon-Coated Indium-Oxide Nanobelts, *J Am Chem Soc*, 139 (2017) 4123-4129.
- [48] Y. Yamazaki, H. Takeda, O. Ishitani, Photocatalytic reduction of CO<sub>2</sub> using metal complexes, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 25 (2015) 106-137.
- [49] C. -C. Wang, Y. -Q. Zhang, J. Li, P. Wang, Photocatalytic CO<sub>2</sub> reduction in metal-organic frameworks: A mini review, *Journal of Molecular Structure*, 1083 (2015) 127-136.