

Review

# Conversion of Carbon Dioxide: Opportunities and Fundamental Challenges

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**Abstract:** The rising atmospheric levels of carbon dioxide is one of the most urgent challenges facing societies nowadays. There is also great potential in energy carriers and other materials from CO<sub>2</sub>, with many challenges to overcome. The way to reduce greenhouse gas emissions should be using carbon free sources that do not generate carbon dioxide to the atmosphere. This article reviews recent developments, remaining challenges and novel approaches of CO<sub>2</sub> reduction for the efficient and sustainable production of fuels and valuable chemicals. It has been suggested that the CO<sub>2</sub> reduction and conversion may provide promising solutions for energy resource scarcity as well as reduction of greenhouse gas emissions. Hence, this paper discusses novel technologies and approaches to reduce carbon dioxide to produce energy and chemicals through heterogeneous catalysis, electrocatalysis and photocatalysis, which will contribute to the economic growth and mitigate the hazardous emissions for cleaner environment. A review of the state-of-the-art of various technologies for carbon dioxide reduction was carried out aiming to demonstrate the advances in this area and provide an overview of the research trend for future development of new ideas for CO<sub>2</sub> reduction in a large scale.

**Keywords:** CO<sub>2</sub> Utilization, Heterogeneous Catalysis, Electrocatalysis, Photocatalysis, Photoelectrocatalysis

## Introduction

Carbon dioxide, which is considered as a primary Greenhouse-Gas (GHG), is periodically exchanged within land surface, ocean and atmosphere where a variety of creatures, including animals, plants and microorganisms absorb and produce it daily. However, the process of releasing and consuming CO<sub>2</sub> trends has to be balanced by nature. Since 1750, when the industrial revolution began, so did climate change, following the activities related to industries (USEPA, 2016). Nowadays, the demand of energy is rapidly increasing because of the economic growth worldwide. In order to meet this growing demand, an abundant amount of fossil fuel (oil, coal and natural gas) is needed (Leung *et al.*, 2014). Fossil fuel combustion is often considered as one of the main threats to the environment because of the CO<sub>2</sub> release in the atmosphere. Studies have shown that around 78% of the total CO<sub>2</sub> emission was released by fossil fuel combustion and other industrial processes

within the period from 2000 to 2010. Further, in 2014, CO<sub>2</sub> emission was about 80.9% of all U.S greenhouse gases emissions and it reached around 5500 million metric tons (Fig. 1) greenhouse gas emission (Luu *et al.*, 2015). In the United States, the main purposes for the combustion of fossil fuel are electricity production, transportation and some industrial processes, which are the sources of CO<sub>2</sub> emissions as shown in Fig. 2. These sources are described below (USEPA, 2016).

### Electricity Production

The first largest source of CO<sub>2</sub> emission in the U.S. is fuel burning to generate electricity. The amounts of CO<sub>2</sub> emitted from producing electricity are based on the type of fossil fuel used; for example, burning coal will emit more CO<sub>2</sub> compared to the burning of oil or natural gas. In which the burning of coal and natural gas can produce around 228.6 and 117.0 Btu respectively as mentioned by U.S. Energy Information Administration (USEIA, 2016).

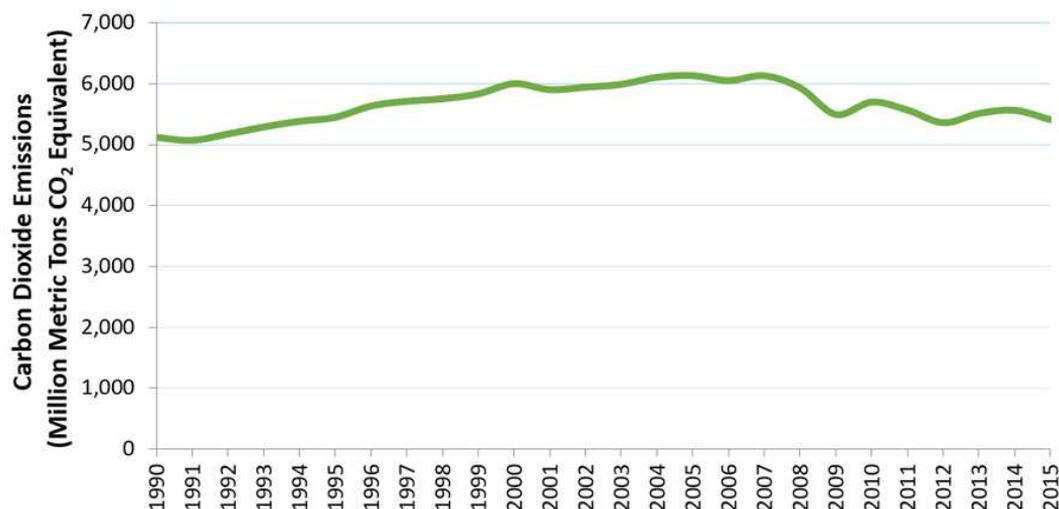


Fig. 1: The emission of CO<sub>2</sub> in the U.S. (1990-2014) (USEPA, 2016)

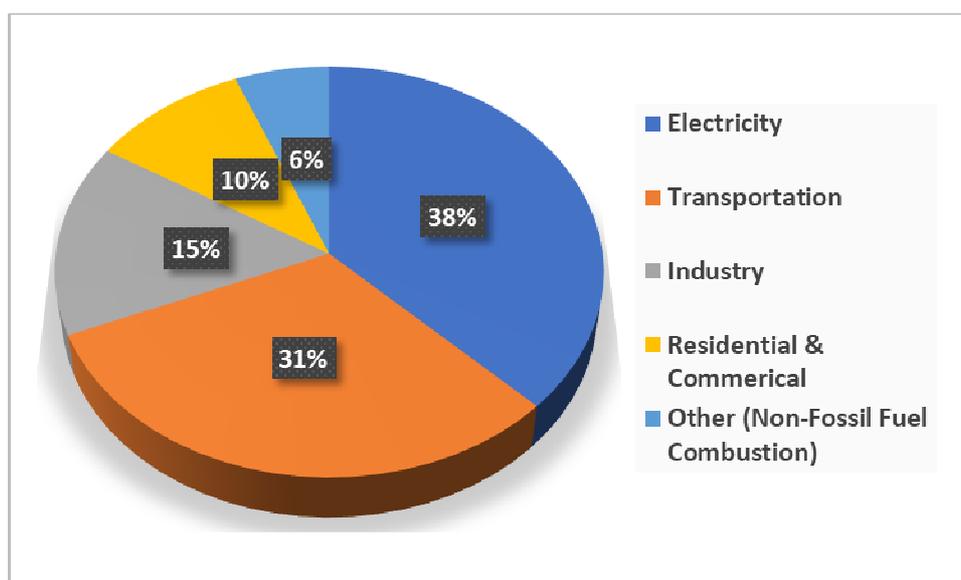


Fig. 2: Sources of CO<sub>2</sub> emission in the U.S. (1990-2014) (USEPA, 2016)

### Transportation

Transportation sources such as air travel, highway vehicles, rail and marine transportation, combust considerable amounts of fossil fuels like diesel and gasoline. The transportation sector occupies the second largest source of CO<sub>2</sub> emissions in the U.S.

### Industrial Processes

CO<sub>2</sub> can be emitted from industrial plants in two ways: Burning the fossil fuel through the industrial processes and producing CO<sub>2</sub> through the chemical reactions without involving the combustion such as producing cement, which is one of the mineral products and producing the metals such as steel and iron. Furthermore,

industries can be the indirect cause of CO<sub>2</sub> emission by generating and using electricity. The harmful effects of the presence of greenhouse gases in atmosphere are global warming, ozone depletion, climate change and sea level rise. Wherefore, the higher concentrations of greenhouse gases in the atmosphere mean more solar radiation was trapped within the atmosphere, making the temperatures rise (Guemene Dountio *et al.*, 2016).

However, considering this situation it will be difficult in the coming few decades to reduce the CO<sub>2</sub> emissions in order to reach the allowed limits and the reason is that the burning of fossil fuel will continue being the main source of energy (Huang and Tan, 2014). In order to solve this problem, two CO<sub>2</sub> emission reduction strategies can be used, namely CO<sub>2</sub> Capture and Storage

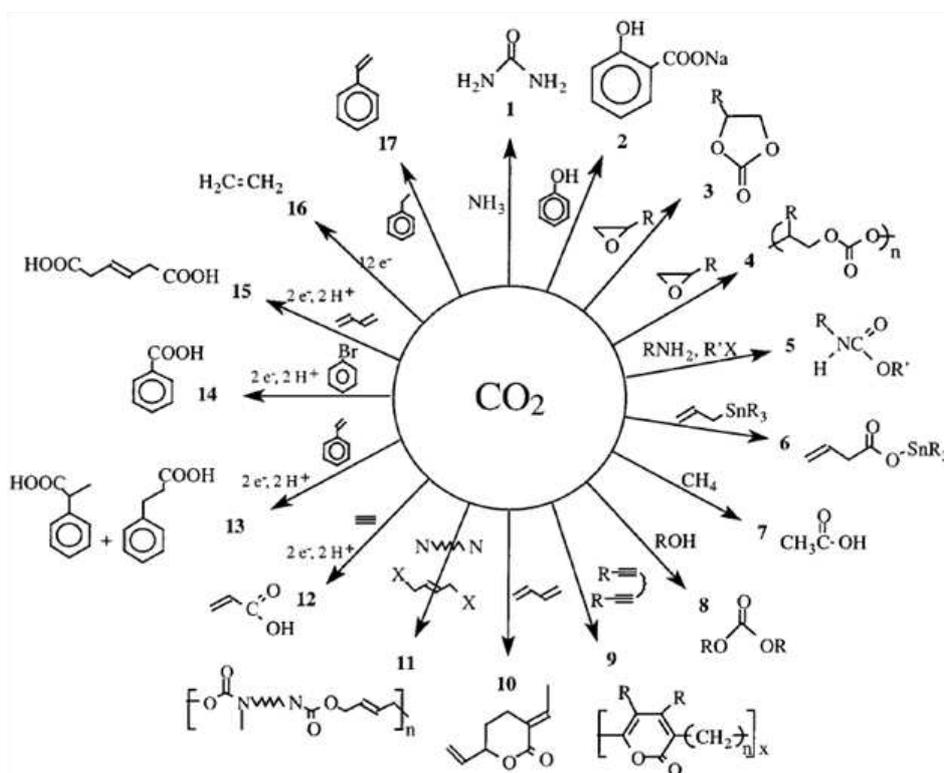
(CCS) and CO<sub>2</sub> utilization (Hurst *et al.*, 2012; Qu and Duan, 2012). However, the utilization of CO<sub>2</sub> is more preferable since it results in converting this harmful gas into valuable products. Low cost, pure CO<sub>2</sub> can be easily obtained from CCS plants (Benson *et al.*, 2009; Centi and Perathoner, 2009; Hossain, 2012). Moreover, many factors support the utilization of CO<sub>2</sub> in the production of different useful products, some of them listed below (Arakawa *et al.* 2001):

- It is considered as in expensive, nontoxic compound which can replace some toxic compounds such as isocyanates
- The conversion of CO<sub>2</sub> can produce totally new materials (i.e., Polymers)
- New way which is more efficient and economical to produce chemical products compared to conventional methods

As a result, the chemical conversion of CO<sub>2</sub> to renewable fuel and useful chemicals is considered as the most attractive way to mitigate the CO<sub>2</sub> emissions due to the high potential market and promising benefits (Centi and Perathoner, 2009). Table 1 presents the products that can be formed through CO<sub>2</sub> conversion process with their potential of CO<sub>2</sub> reduction and market scale. This paper gives an overview of CO<sub>2</sub> utilization in which the challenges and opportunities of CO<sub>2</sub> utilization are discussed, because CO<sub>2</sub> utilization and conversion is considered as an integral part of carbon management. Reviewing these different catalytic methods will be the focus of the review paper. During the last few years, numerous studies have been proved towards the utilization of CO<sub>2</sub> through different methods such as heterogeneous catalysis, electrocatalysis and photocatalysis (Jovanov *et al.*, 2016; Kumar *et al.*, 2016; Roy *et al.*, 2010).

**Table 1:** Potential of CO<sub>2</sub> reduction and market scale for products that can be formed by CO<sub>2</sub> conversion process

Product	Potential of CO <sub>2</sub> reduction (ton CO <sub>2</sub> / ton of product)	Market scale (per year)		References
		Global demand	Market value	
Dimethyl ether (DME)	1.9	6.3 MT	\$3.2 billion	(Huang and Tan, 2014)
Dimethyl carbonate (DMC)	1.47	0.24 MT	\$280 billion	(Huang and Tan, 2014)
Methanol	1.38	75 MT	\$36 billion	(2013)
Polycarbonate	0.5	3.6 MT	\$14.4 billion	(Huang and Tan, 2014)
Urea	0.735-0.75	198.4 MT	\$59.5 billion	(Heffer PaPh, 2013)



**Fig. 3:** CO<sub>2</sub> utilization for different chemicals (Arakawa *et al.*, 2001)

## CO<sub>2</sub> Utilization Methods

### Heterogeneous Catalysis

Various research studies have been conducted on the CO<sub>2</sub> conversion to useful chemicals by using heterogeneous and homogeneous catalysts. Unfortunately, under mild conditions, the heterogeneous catalysts typically show lower catalytic selectivity and activity compared to the homogeneous catalysts. However, the use of heterogeneous catalysis method has many advantages (Fujita *et al.*, 2014). This includes high efficiency in the separation and recycling stages and the significant durability and stability in handling and reactor design. Thus, this method is widely used in the industries and is preferred to be used in the CO<sub>2</sub> conversion process (Razali *et al.*, 2012). Some researchers discussed the produced chemicals that are shown in (Fig. 3) which include urea (Number 1), salicylic acid (Number 2) and cyclic carbonates (Number 3). Urea is considered to be the largest product used, which it reached around 90 million metric tons per year in 1997. In addition to these industrial processes using CO<sub>2</sub> (compounds 1-3 in Fig. 3), many processes are still under laboratory scale studies which are the remaining reactions in (Fig. 3) (Aresta and Tommasi, 1997).

Heterogeneous catalysts can convert CO<sub>2</sub> into chemicals or intermediates such as cyclic carbonates, methanol and dimethyl carbonate. Heterogeneous catalysts include electrocatalysts, photocatalysts and photo-electro-catalysts. CO<sub>2</sub> is currently used to convert CO with H<sub>2</sub> to methanol (Aresta and Dibenedetto, 2003). During the past few years, more efficient heterogeneous catalysts have been developed for CO<sub>2</sub> hydrogenation to methanol and pilot scale plants based on these catalysts have been tested (Inui *et al.*, 1998). However, the thermodynamics for the reaction of methanol synthesis from CO is more favorable compared to that of methanol synthesis from CO<sub>2</sub> (Kusama *et al.*, 1996). Cu/ZrO<sub>2</sub>/SiO<sub>2</sub> catalysts have been studied by in-situ infrared spectroscopy and suggested the pathway to produce methanol (Fig. 4) (Fisher and Bell, 1998). Further, the production of ethanol by the hydrogenation of CO<sub>2</sub> has been studied in 1996 by Kusama *et al.* (1996).

### Electrocatalytic CO<sub>2</sub> Reduction

The electrochemical reduction method is used to convert the CO<sub>2</sub> gas to valuable chemicals and fuels such as hydrocarbons, carbon monoxide, methanol and formic acid, using electricity as the main source of energy (Fig. 5A) (Jovanov *et al.*, 2016; Kuhl *et al.*, 2014). The cost-effective electrochemical reduction process of CO<sub>2</sub> requires a very good electrocatalysts that are stable, selective and efficient. Nonetheless, there is no known catalyst that can meet these criteria; that is why the development of new efficient catalysts will be essential

for the development of the CO<sub>2</sub> conversion process (Kuhl *et al.*, 2014). In order to develop the new catalyst, more studies are needed on the various chemical reactions. The electrocatalysts provide decisive solutions to make the over potential lower and increase the selectivity as well as the kinetics of CO<sub>2</sub> conversion reaction (Hossain, 2012).

During the last decades, several research studies were focused on the metal catalysts and the different products that were formed using these catalysts. There are four main classes of simple metal catalysts depending on the type of the products that are formed by the CO<sub>2</sub> electrochemical reduction process (Hori, 2003; Jhong *et al.*, 2013). This include Cu, Au, Pb and Ni to be used as electrodes in order to convert CO<sub>2</sub> by electrochemical process to hydrocarbons, CO, HCOO- and H<sub>2</sub>, receptively as shown in Fig. 6.

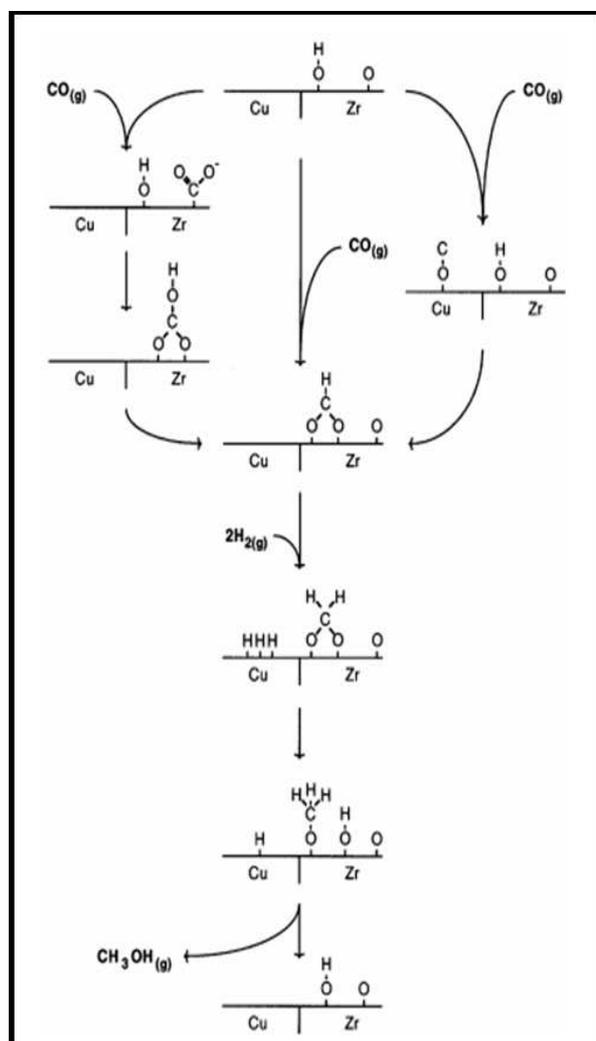
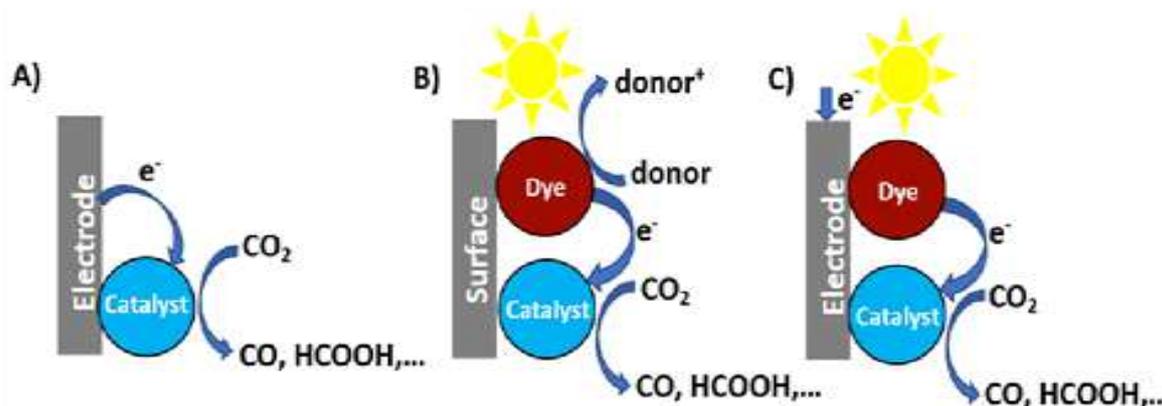
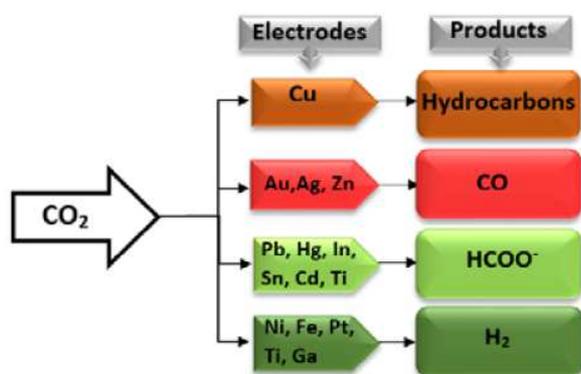


Fig. 4: The Mechanism of the Heterogeneous Catalytic Hydrogenation reduction of CO to Methanol on Cu- and ZrO<sub>2</sub>-containing catalysts (Fisher and Bell, 1998)



**Fig. 5:** Heterogeneous molecule systems: (A) Electrocatalysis, (B) Photocatalysis and (C) Photoelectrocatalysis (Windle and Reisner, 2015)



**Fig. 6:** Different electrode material and the reaction products of CO<sub>2</sub> electrochemical reduction (Hori, 2003)

There are other products that can be formed by the metal catalysts such as oxalic acid and alcohol (Hori, 2003). Organometallic catalysts (Tornow *et al.*, 2012), metal organic frameworks (Hinogami *et al.*, 2012) and metal oxides (i.e., Cu<sub>2</sub>O) (Chen *et al.*, 2012; Li and Kanan, 2012) have been studied by some researchers within the last few years.

### Hydrocarbons

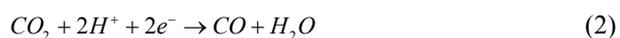
A copper catalyst is considered to be the most suitable metal catalyst to convert CO<sub>2</sub> to hydrocarbons at ambient temperature and pressure (Kuhl *et al.*, 2012). Many different hydrocarbon products with their production mechanisms, through the use of Cu as a cathode in flow cell have been studied by Tang *et al.*, (2012). Further, the copper surfaces show increase in the selectivity and make the over potential lower for hydrocarbon production processes (Kondratenko *et al.*, 2013). Due to the abundance of the under-coordinated sites, the Cu electrode, which is covered by Cu nanoparticles, gives higher selectivity toward the CO<sub>2</sub> conversion to hydrocarbons. Some researchers studied the modified Cu electrodes by annealing Cu foil in air,

which resulted in a stable electrode that can make the overpotential lower for CO<sub>2</sub> reduction by 0.5 V compared to polycrystalline Cu (Tang *et al.*, 2012). Using two single crystal copper electrodes through two different mechanisms to produce ethylene, has been studied by Schouten *et al.* (2012):



### Carbon Monoxide

Gold, silver and zinc are the most metal catalysts used to adsorb CO; it has been reported that the adsorbed CO is preventing more reduction of CO<sub>2</sub>, hence contributing in H<sub>2</sub> production (Kondratenko *et al.*, 2013). Diaminotriazole-based organometallic silver catalysts have been studied by Tornow *et al.* (2012), in which the gold loading has been decreased by a factor of around 20 by keeping the same performance. Interestingly, at this point, it is not clear if these organometallic silver species are considered as catalytically active species on the surface of electrode or not. The effect of the silver particle size on CO<sub>2</sub> reduction has been investigated by Salehi-Khojin *et al.* (2013); they observed the maximum level of activity for the silver particle size of 5 nm. Further, by reducing the gold oxide films, the gold nanoparticles are synthesized which are considered to have highly selectivity to reduce CO<sub>2</sub> to CO (Chen *et al.*, 2012):



### Formic Acid

Palladium and mercury are considered as the high efficiency metals to produce the formic acid. Further, other metals were found to be active for formic acid production process, such as MOF catalysts (Hinogami *et al.*, 2012), alloys (Agarwal *et al.*, 2011) and metal oxides (Chen and

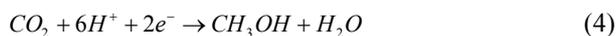
Kanan, 2012). The Sn/SnOx metal/metal oxides catalyst is participating in the CO<sub>2</sub> reduction methods, which the Sn/SnOx catalyst shows higher efficiency for formic acid production while Sn0 is producing only hydrogen (Chen and Kanan, 2012). The pure Sn gives lower efficiency than the Sn-alloy at lower polarization (Agarwal *et al.*, 2011). Furthermore, some results have been reported regarding the behavior of Copper Rubenate Metal Organic Framework (CR MOF) catalyst (Inui *et al.*, 1998). The results indicate that the (CR MOF) catalyst can make the onset for CO<sub>2</sub> reduction lower by approximately 0.2 V, compared to the plain copper electrode:



The Gas Diffusion Electrodes (GDE) has been developed in order to improve the electrocatalytic cell (Agarwal *et al.*, 2011). GDE consists of a Teflon-bonded carbon matrix where the metal particles are scattered. The applications of GDE for the CO<sub>2</sub> electrocatalytic reduction process was studied by Mahmood *et al.* (1987) to convert CO<sub>2</sub> to HCOOH at a current efficiency of 100% and a current density of 150 mA cm<sup>-2</sup> with a potential of -1.8 V versus the standard calomel electrode. An experiment was conducted on the platinum GDE, where the methane has been produced from CO<sub>2</sub> at 30 bars and a Faradaic efficiency was around 34.8% at a current density of 900 mA cm<sup>-2</sup> (Hara *et al.*, 1995).

### Methanol

Methanol is considered as a valuable product while it has many different applications, it is manufactured as an intermediate to produce various chemicals (i.e., acetic acid and formaldehyde) (Olah *et al.*, 2008). Recently, the formation of methanol from CO<sub>2</sub> and H<sub>2</sub> by electrochemical methods has been studied by several researchers (Le *et al.*, 2011). Hence, the results obtained were as follows, the reduction of CO<sub>2</sub> to methanol process accomplish low efficacy and/or low current densities, while both have to be high for the commercial process. The direct electrochemical reduction of CO<sub>2</sub> to methanol reaction is kinetically a little bit complex and requires an effective electrocatalysts (Olah *et al.*, 2008; Wang *et al.*, 2015):



Some experiments have been conducted on the single crystal Cu electrodes, where the various surface faces show different selectivity and activity in CO<sub>2</sub> electrocatalytic reduction process. Single crystal of copper electrodes have been controlled by Cu(100) faces favour C<sub>2</sub>H<sub>4</sub> formation, while the other types which is

controlled by Cu(111) faces show better selectivity towards CH<sub>4</sub> (Hori *et al.*, 2003).

Other researchers conducted an experiment with low-density energy cell, which is used to convert CO<sub>2</sub> and H<sub>2</sub> to methanol at ambient pressure with current efficiency up to 97% and a potential of -0.1 V versus the standard hydrogen electrode (Kobayashi and Takahashi, 2004).

### Ethanol

Ren *et al.* (2016) conducted an experiment, using a prepared series of oxide-derived CuxZn catalysts (i.e., Cu<sub>10</sub>Zn, Cu<sub>4</sub>Zn and Cu<sub>2</sub>Zn) in order to improve the conversion of CO<sub>2</sub> to ethanol by electroreduction process. Further, it was proved that CO<sub>2</sub> will be reduced more preferentially on metallic compared to the oxide surfaces. However, the selectivity of ethanol production versus ethylene has been discovered by defining the ratio of their Faradaic efficiencies (FEethanol/FEethylene); the ratio can be tuned by the factor of 12.5 by changing the amount of Zn in the CuxZn catalysts. The maximum ethanol production has been achieved by using Cu<sub>4</sub>Zn at -1.05 V at a Faradaic efficiency of 29.1% with a partial current density of -8.2 mA cm<sup>-2</sup>. Ren *et al.* (2016) studied the conversion of CO<sub>2</sub> to n-propanol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH) through the electrocatalytic process by using mass of around 15 nm sized copper nanocrystals in an aqueous 0.1 M KHCO<sub>3</sub>. In which the onset potential was within the range between 200 to 300 mV for the n-propanol formation, which is more positively than for CuO nanoparticles or electropolished Cu surface. The production of this cell is n-propanol at a potential of -0.95 V versus the reversible hydrogen electrode where the total current density was -1.74 mA cm<sup>-2</sup>, which is much larger, compared to the one that found on CuO nanoparticles at the same conditions (Ren *et al.*, 2016).

### Synthesis Gas

The conversion of CO<sub>2</sub> into synthesis gas in a cell that employs Ni/active carbon fibre and Cu/metal oxide GDEs was studied by Kohno *et al.* (2001b). Many cells for the production of synthesis gas from CO<sub>2</sub> by electrocatalytic process have been studied during the last few years. For example, different cell designs have been tested by Delacourt *et al.* (2008) which are based on Proton Exchange Membrane Fuel Cells (PEMFCs) for the conversion of CO<sub>2</sub> and H<sub>2</sub>O to synthesis gas. The best results were found when the enhanced PEMFC is used, which can be modified by adding a glass fibre supported layer of the aqueous KHCO<sub>3</sub> between the proton-exchange membrane (Nafion). The production of this cell is a synthesis gas at a potential of -2 V versus the standard calomel electrode where the total current density was 80 mA cm<sup>-2</sup> at 25°C.

Table 2 summarizes the different electrocatalyst systems (i.e., Au<sub>25</sub>, Au-oxide NPs, Ag, SnO<sub>2</sub>, etc.) which are used to convert one tonne CO<sub>2</sub> into various products such as carbon monoxide, formic acid, ethylene, methane and methanol with the energy requirements in MWh/tonne CO<sub>2</sub> by assuming 500 mV overpotential for anodic OER and all voltages are in the RHE scale (Kauffman *et al.*, 2015).

### Photocatalytic CO<sub>2</sub> Reduction

The photocatalytic CO<sub>2</sub> reduction method converts the CO<sub>2</sub> to valuable products, such as methane and methanol, by using solar energy (i.e., light or laser) (Fig. 5B) (Fan *et al.*, 2013; Hossain, 2012). During the past few years, this method has been considered as the most attractive method for CO<sub>2</sub> reduction. The photocatalytic conversion process is a complex combination of photochemical and photophysical processes (Fan *et al.*, 2013). The artificial photoconversion for CO<sub>2</sub> utilization (Fig. 7) presents a challenge to the hydrogenation process which requires H<sub>2</sub> (Arakawa *et al.*, 2001).

In general, the photocatalysis process to reduce CO<sub>2</sub> with H<sub>2</sub>O involve three main steps (Xie *et al.*, 2016) (Fig. 8). Generating electron-hole pairs is done in the first step when the semiconductor is supported by an appropriate light/laser source, which has energy greater than, or equal to the band-gap Energy (E<sub>g</sub>) of the semiconductor. Then, the generated electrons-holes transfer to the surface of the semiconductor in the second step as shown in Fig. 8. After that, large fraction of electron-hole pairs will recombined together with the energy being released in the form of heat or photons. CO<sub>2</sub> will be reduced by the generated electrons into HCOOH, CH<sub>4</sub>, CH<sub>3</sub>OH, or CO and H<sub>2</sub>O will be oxidized by the holes to O<sub>2</sub> in the third step.

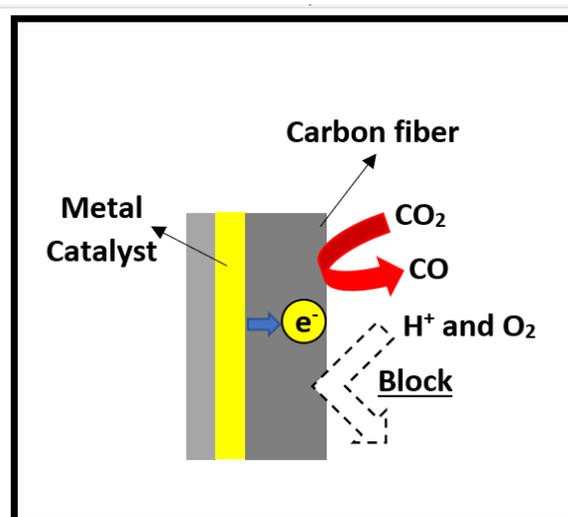


Fig. 7: CO<sub>2</sub> utilization by artificial photoconversion (Sato *et al.*, 2016)

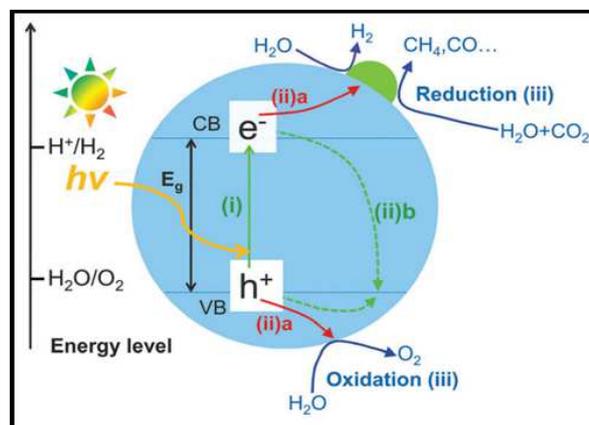


Fig. 8: The basic mechanism of CO<sub>2</sub> photocatalytic

**Table 2:** Energy needed and Faradaic efficiency for selected catalyst systems to convert 1 tonne CO<sub>2</sub> in to different products

Electrocatalyst	Product	Faradaic efficiency	Energy needed (MWh/tonne CO <sub>2</sub> )	References
Au <sub>25</sub>	Carbon monoxide	99%	3.36	(Kauffman <i>et al.</i> , 2014; 2012)
Au-oxide NPs		99%	2.74	(Chen <i>et al.</i> , 2012)
Cu-oxide NPs		61%	5.45	(Kauffman <i>et al.</i> , 2011)
Ag		99%	3.08	(Rosen <i>et al.</i> , 2011)
Cu-oxide	Carbon monoxide +	69%	3.94	(Li and Kanan, 2012)
SnO <sub>2</sub>	Formic acid	99%	2.99	(Chen and Kanan, 2012)
SnO <sub>2</sub> NPs	Formic acid	86%	4.72	(Zhang <i>et al.</i> , 2014)
PbO <sub>2</sub>		100%	3.02	(Lee and Kanan, 2014)
Cu	Ethylene	48%	42.28	(Qiao <i>et al.</i> , 2014)
Cu		50%	38.84	(Gattrell <i>et al.</i> , 2006)
Cu NPs	Methane	77%	19.50	(Manthiram <i>et al.</i> , 2014)
Cu		72%	18.74	(Peterson and Nørskov, 2012)
Mo	Methanol	50%	15.40	(Qiao <i>et al.</i> , 2014)
Cu-oxide		40%	21.50	(Qiao <i>et al.</i> , 2014)
RuO <sub>2</sub>		60%	14.20	(Herron <i>et al.</i> , 2015)
RuO <sub>2</sub> -TiO <sub>2</sub>		50%	17.00	(Qiao <i>et al.</i> , 2014)

The chemical reductant is required for the photocatalytic reactions, where these reactions do not include any electrical wiring to reduce the oxidized semiconductor or photocatalyst (Windle and Reiser, 2015). Some researchers studied the use of transition-metals oxide as both solar energy converters and photocatalysts and the reasons are that their absorption properties of the solar spectrum and they can be excited for long time (Arakawa *et al.*, 2001). There are many different semiconductor systems for the CO<sub>2</sub> photoreduction, but the most commonly used systems are the semiconducting material systems which consist mainly of TiO<sub>2</sub> (Wang *et al.*, 2014). It has been reported that the advantages of TiO<sub>2</sub> semiconductor, such as, its high availability with comparatively low cost, low toxicity and it has good resistance to the photo-oxidation corrosion (Indrakanti *et al.*, 2009).

### TiO<sub>2</sub>-Related Photocatalysts

#### TiO<sub>2</sub> Nanomaterials

Semiconductors Nanoparticles (NPs) were the result of some improvements that have been made on the semiconductor powders systems (e.g., TiO<sub>2</sub> suspended in a beaker of water). Using the TiO<sub>2</sub> NPs systems increases the surface area of the used catalysts, which leads to an increase in the frequency between TiO<sub>2</sub> and CO<sub>2</sub> (Wang *et al.*, 2014). P<sub>25</sub> is considered as a widely available source for the anatase-rutile mixed phase TiO<sub>2</sub> NPs which can be used in photocatalytic research; due to its valuable properties, such as high catalytic activity (Hurum *et al.*, 2003). It has been proved that the TiO<sub>2</sub> crystal structure and morphology studies are one of the methods that can contribute in increasing the TiO<sub>2</sub> photocatalytic activity (Xu *et al.*, 2013). A good example to explain the crystal structure effect has been studied by Xu *et al.* (2013) which is the TiO<sub>2</sub> nanosheets with 95% exposed (100) facet where the maximum photocatalytic activity was achieved. The electron which is transferring through the TiO<sub>2</sub> can be controlled by changing the morphology of the TiO<sub>2</sub>. The porous microspheres of MgO-coated TiO<sub>2</sub> is the most studied morphology as mentioned by Liu *et al.* (2013). The anatase phase nanorods which is modified with rutile phase NPs (TiO<sub>2</sub>-RMR) has been studied by Wang *et al.* (2012a) in which TiO<sub>2</sub>-RMR showed higher conversion rate compared to the just anatase phase nanorods.

#### TiO<sub>2</sub> Crystal Structure

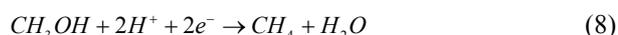
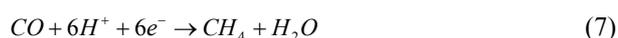
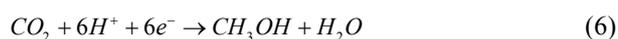
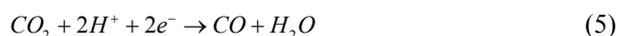
Many researches have been conducted in order to see the effect of the TiO<sub>2</sub> crystal structure on the activity of photocatalysts (Pan *et al.*, 2011). Anatase, brookite and rutile are the crystal forms of TiO<sub>2</sub>. The best studied and understood crystal phases are anatase and rutile, where the brookite is the least studied (Liu *et al.*, 2012). The optimum

composition for an anatase-brookite photocatalyst for the reduction of CO<sub>2</sub> has been reported by Zhao *et al.* (2013), where the obtained results show that the anatase-brookite system, which consists of 75% anatase and 25% brookite showed the maximum photocatalytic activity.

#### TiO<sub>2</sub> in Mesoporous Support

It has been proved that the photocatalytic activity can be increased by incorporating a mesoporous support (i.e., SiO<sub>2</sub>) into TiO<sub>2</sub> lattices (Anpo *et al.*, 1998). Furthermore, the SiO<sub>2</sub> mesoporous network contributes in increasing the surface area of the system for CO<sub>2</sub> to be reduced. A rapid and low-cost synthesis method has been studied using the Furnace Aerosol Reactor (FuAR) in order to synthesize the Cu-TiO<sub>2</sub>-SiO<sub>2</sub> photocatalyst composite particles that can be formed by evaporation driven self-assembly (Wang *et al.*, 2011).

Table 3 and Fig. 9 summarize the different semiconductors used in the CO<sub>2</sub> photoreduction process; Table 3 shows the products that can be formed by using these semiconductors and the CO<sub>2</sub> conversion in (μmol/g). The most common products in the CO<sub>2</sub> photoreduction system are CO and HCOOH, where the reactions need only 2 electrons and 2 protons. It is generally difficult to form the other products, such as ethanol, formaldehyde, methanol and methane, in the gas-solid systems. The reason is that these formation reactions need more electrons and protons; however, the reactions are thermodynamically favorable. Some other products can be formed by a series of different reactions, such as CH<sub>4</sub> (Roy *et al.*, 2010; Varghese *et al.*, 2009; Wang *et al.*, 2014):



Other photocatalysts can be used to form methanol such as noble metals (i.e., Pt, Pd, Ru and Rh) and copper based catalysts (i.e., Cu/ZnO catalyst with modifiers); the advantages and disadvantages of these processes are shown in (Table 4) (Li *et al.*, 2014; Wang *et al.*, 2015).

#### Photoelectrocatalytic CO<sub>2</sub> Reduction

The photoelectrocatalytic CO<sub>2</sub> reduction method is combining the electrocatalytic and photocatalytic methods together (Fig. 5C). Thus, it means that the electrochemical CO<sub>2</sub> conversion process is using the light as the source of energy and the semiconductor (e.g., GaP, SiC) as the cathode, where the electrons are

receiving from the anode (Chang *et al.*, 2009; Windle and Reisner, 2015). Fig. 10 presents the different two-compartment photoelectrocatalytic cells which are separated by proton exchange membranes for the reduction of CO<sub>2</sub> (Xie *et al.*, 2016). Semiconductor can be used as photocathode (Fig. 10A) or photoanode (Fig. 10B). Semiconductor can be used as both

photocathode and photoanode (Fig. 10C) where the light will be absorbed by both electrodes in order to generate electrons and holes pairs. The photoelectrochemical approach has many benefits in term of space and cost saving, where the electrochemical system in combining with the solar collection process without reducing the performance of both systems (Hossain, 2012).

**Table 3:** CO<sub>2</sub> photoreduction by different semiconductors

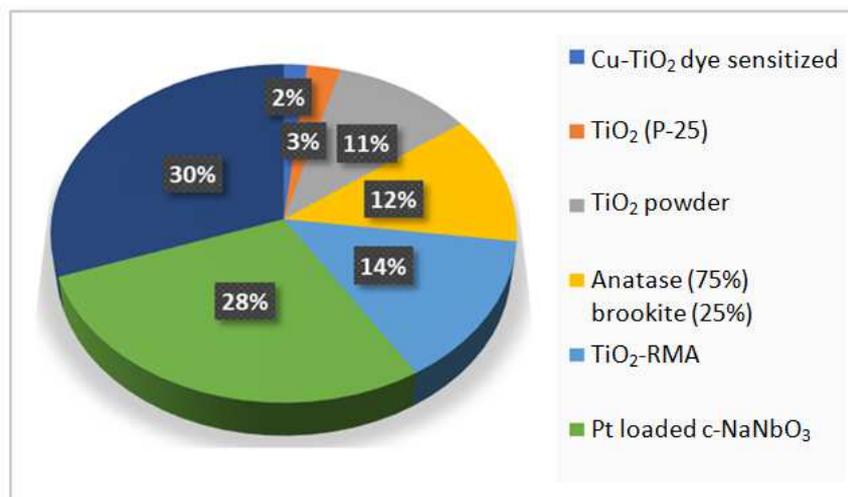
Semiconductor systems	Product	CO <sub>2</sub> Conversion (μmol/g)	References
Pt NP/TiO <sub>2</sub> film	Methane	1361.00	(Wang <i>et al.</i> , 2012b)
TiO <sub>2</sub> -RMA		2.40	(Wang <i>et al.</i> , 2012a)
Cu-TiO <sub>2</sub> dye sensitized		0.30	(Yuan <i>et al.</i> , 2012)
Pt loaded c-NaNbO <sub>3</sub>		4.86	(Li <i>et al.</i> , 2012)
TiO <sub>2</sub> (P-25)		0.43	(Kaneco <i>et al.</i> , 1998)
Cu/TiO <sub>2</sub> /SiO <sub>2</sub> (wet method)	Carbon monoxide	45.00	(Li <i>et al.</i> , 2010)
Cu/TiO <sub>2</sub> /SiO <sub>2</sub> (aerosol method)		20.00	(Wang <i>et al.</i> , 2011)
MgO		4.00	(Kohno <i>et al.</i> , 2001a)
ZrO <sub>2</sub>		5.00	(Kohno <i>et al.</i> , 2000)
Anatase(75%) brookite(25%)		2.10	(Zhao <i>et al.</i> , 2013)
TiO <sub>2</sub> /GO layered sheets	Methane/Carbon monoxide	10.00	(Tu <i>et al.</i> , 2012)
Rh-TiO <sub>2</sub>		5.20	(Kohno <i>et al.</i> , 1999)
Cu-TiO <sub>2</sub>	Methanol	20.00	(Tseng <i>et al.</i> , 2004)
TiO <sub>2</sub> /zeolite		13.00	(Yamashita <i>et al.</i> , 1998)
Cu/Fe-TiO <sub>2</sub> -SiO <sub>2</sub>		4.12	(Wu, 2009)
TiO <sub>2</sub> powder	Formic acid	1.80	(Kaneco <i>et al.</i> , 1999)
CoPc-TiO <sub>2</sub>	Formic acid/Methane	33.50	(Liu <i>et al.</i> , 2007)
Nafion layer on Pd-TiO <sub>2</sub>	Methane/Ethane	3.30	(Kim <i>et al.</i> , 2012)

**Table 4:** Advantages and disadvantages of different photocatalysts

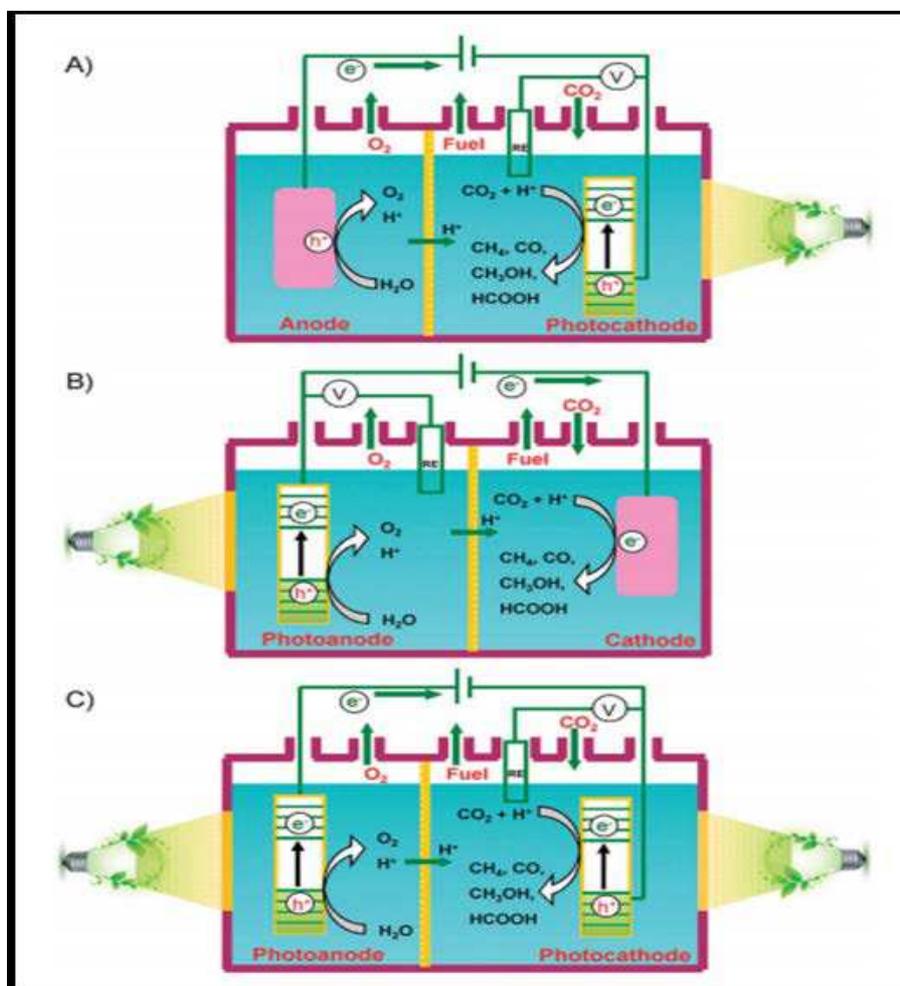
Catalyst	Advantages	Disadvantages	References
Noble metals (i.e., Pt, Pd, Ru and Rh)	Resisted to coking High activity	High cost	(Li <i>et al.</i> , 2014)
Copper based catalysts (i.e., Cu/ZnO catalyst with modifiers, such as Si, Ga, etc.)	Low cost Good thermal stability	Low activity	(Gawande <i>et al.</i> , 2016)

**Table 5:** Photoelectrocatalytic systems reported for the reduction of CO<sub>2</sub>

Electrode	Product amounts, concentrations or rates	References
(1) No co-catalyst	Photocathode: p-GaP Anode: carbon rod	HCOOH: 50 mM HCHO: 0.28 mM CH <sub>3</sub> OH: 0.81 mM (Halmann, 1978)
(2) Metal complex co-catalyst	Photocathode: Ru complex modified Zn-doped p-InP Anode: Glassy carbon	HCOOH: 0.17 mM (Arai <i>et al.</i> , 2010)
	Photocathode: Ru complex polymer modified Cu <sub>2</sub> ZnSnS <sub>4</sub> Anode: glassy carbon	HCOOH: 0.49 mM (Arai <i>et al.</i> , 2011)
(3) One-or two-dimensional nanostructure photoelectrode	Photocathode: polypyrrole-coated p-ZnTe Anode: Carbon rod	HCOOH: 131, CO: 50, H <sub>2</sub> : 108 nmol h <sup>-1</sup> cm <sup>-2</sup> (Chung <i>et al.</i> , 2016)
	Photocathode: ZnTe/ZnO nanowire/Zn substrate Anode: Pt electrode	CO: 68 mmol cm <sup>-2</sup> (Jang <i>et al.</i> , 2016)
	Photocathode: Cu/Cu <sub>2</sub> O electrode Anode: Pt electrode	CH <sub>3</sub> OH: 178 ppm, HCHO: 10 ppm (de Brito <i>et al.</i> , 2015)
	Photocathode: Cu nanoparticles-doped Co <sub>3</sub> O <sub>4</sub> nanotube arrays Anode: Pt electrode	HCOOH: 6.8 mmol L <sup>-1</sup> cm <sup>-2</sup> (Shen <i>et al.</i> , 2015)



**Fig. 9:** CO<sub>2</sub> Conversion (μmol/g) by different semiconductors (Kaneco *et al.*, 1999, 1998; Kohno *et al.*, 1999; Li *et al.*, 2012; Wang *et al.*, 2012a; Yuan *et al.*, 2012; Zhao *et al.*, 2013)



**Fig. 10:** The different two-compartment photoelectrocatalytic cells for the reduction of CO<sub>2</sub>; (A) Semiconductors as photocathodes; (B) Semiconductors as photoanodes; (C) Semiconductors as both photoanodes and photocathodes (Xie *et al.*, 2016)

The layer-by-layer structure has been studied by Windle and Reisner (2015) where the process of photo-electro-catalytic CO<sub>2</sub> reduction can be achieved. The first layer consists of dye which can be either molecular or a semiconducting material, this layer absorbs the visible light and the electrons are transferred directly to the catalyst and the oxidized dye is regenerated by hole transfer to the semiconductor. It has been mentioned that the calcium copper titanium oxide CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (CCTO), is considered as a best example of photo-electro-catalyst in which it shows excellent Photoelectrochemical (PEC) ability (Kushwaha *et al.*, 2016). Table 5 summarizes some recently reported systems with the three different types of photoelectrocatalytic cells for the CO<sub>2</sub> reduction.

### Barriers and Challenges for Future Prospective

The poor product selectivity and the high/low reaction temperatures are considered to be the main barriers in the heterogeneous CO<sub>2</sub> reduction process. For example, the suitable catalysts are needed for the conversion of CO<sub>2</sub> to methanol at lower reaction temperatures.

Further, many barriers exist in the CO<sub>2</sub> electrocatalysis reduction, in which the electrocatalysts are needed to be used at lower over potentials with higher selectivity. Many different heterogeneous electrocatalysts which are selective, fast and energy-efficient are known, but they are unstable. Photochemical processes can offer an attractive approach for CO<sub>2</sub> reduction using solar energy. However, this method is not widely used because it needs a critical condition to absorb the required amount of solar energy. In general, some of barriers still exist and make the improvements of CO<sub>2</sub> utilization technologies slower, such as:

- Compared to the other energy-related technologies
- CO<sub>2</sub> utilization technology is much less supported.
- Fossil fuel plants still get benefits currently by energy regulations
- CO<sub>2</sub> utilization processes that contribute to CO<sub>2</sub> reduction at commercial scale are yet to be demonstrated

Therefore, more researches are necessary in order to improve the effective CO<sub>2</sub> utilization technologies, to make more advances in heterogeneous catalysts for CO<sub>2</sub> reduction process and to apply various approaches in the effective catalytic CO<sub>2</sub> conversion.

### Summary and Future Outlook

CO<sub>2</sub> reduction is presenting both an opportunity and a challenge worldwide for sustainability of environment and energy. The main strategies of CO<sub>2</sub> reduction should

focus on the utilization of CO<sub>2</sub>, such as the use of CO<sub>2</sub> for the environmental processes, the CO<sub>2</sub> recycling combined with the renewable energy to save carbon sources and the production of useful chemicals from CO<sub>2</sub>. The conversion of CO<sub>2</sub> into useful chemicals such as cyclic carbonates and urea is promising and will reduce CO<sub>2</sub> emissions into the atmosphere. In order to achieve a high performance in the CO<sub>2</sub> conversion process, the development of reduction reactions and using an effective catalyst are required. However, it should be noted that the amount of generated useful chemicals is not that enough to consume all the captured CO<sub>2</sub> which means that other solutions should be taken into consideration in order to get rid of all captured CO<sub>2</sub>. On the hand, the conversion of CO<sub>2</sub> into energy product such as DMC, methanol and DME, will consume larger amount of captured CO<sub>2</sub> where the reason is that the market scale is potentially extensive. Furthermore, the generated energy products can be used instead of the fossil fuel, thus reducing the dependence on fossil fuel and contribute in the market growth of CO<sub>2</sub> utilization. There are many challenges in the catalytic CO<sub>2</sub> utilization where it requires a huge amount of used catalysts and specific conditions, such as high pressure, high temperature and long time for the reaction because of chemically stable CO<sub>2</sub>. Therefore, restrains the process in a laboratory scale with low conversion. Furthermore, the design of catalytic materials, which are featuring high product stability, selectivity and a composition of earth-abundant elements is one of the major challenges that face CO<sub>2</sub> utilization.

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### Author's Contributions

**Sajeda A. Al-Saydeh:** She made considerable contributions to carrying out the literature review. Furthermore, she prepared the initial draft of the manuscript.

**Syed J. Zaidi:** He made considerable contributions to designing the research plan. In addition, he supervised the research work and revised the draft of the manuscript.

**Muftah H. El-Naas:** He made considerable contributions to designing the research plan. In addition, he revised the draft of the manuscript.

### Ethics

This paper is original and includes unpublished materials. The corresponding author authorizes that the

other authors have read and approved the manuscript and there is no ethical issues involved.

## References

- Agarwal, A.S., Y. Zhai, D. Hill and N. Sridhar, 2011. The electrochemical reduction of carbon dioxide to formate/formic acid: Engineering and economic feasibility. *ChemSusChem*, 4: 1301-1310. DOI: 10.1002/cssc.201100220
- USEIA, 2016. United States Energy Information Administration
- Anpo, M., H. Yamashita, K. Ikeue, Y. Fujii and S.G. Zhang *et al.*, 1998. Photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O on Ti-MCM-41 and Ti-MCM-48 mesoporous zeolite catalysts. *Catalysis Today*, 44: 327-332. DOI: 10.1016/S0920-5861(98)00206-5
- Arai, T., S. Sato, K. Uemura, T. Morikawa and T. Kajino *et al.*, 2010. Photoelectrochemical reduction of CO<sub>2</sub> in water under visible-light irradiation by a p-type InP photocathode modified with an electropolymerized ruthenium complex. *Chem. Commun.*, 46: 6944-6946. DOI: 10.1039/C0CC02061C
- Arai, T., S. Tajima, S. Sato, K. Uemura and T. Morikawa *et al.*, 2011. Selective CO<sub>2</sub> conversion to formate in water using a CZTS photocathode modified with a ruthenium complex polymer. *Chem. Commun.*, 47: 12664-12666. DOI: 10.1039/C1CC16160A
- Arakawa, H., M. Aresta, J.N. Armor, M.A. Barteau and E.J. Beckman *et al.*, 2001. Catalysis research of relevance to carbon management: Progress, challenges and opportunities. *Chem. Rev.*, 101: 953-996. DOI: 10.1021/cr000018s
- Aresta, M. and A. Dibenedetto, 2003. Carbon dioxide fixation into organic compounds, *Carbon Dioxide Recovery and Utilization*. Springer.
- Aresta, M. and I. Tommasi, 1997. Carbon dioxide utilisation in the chemical industry. *Energy Convers. Manage.*, 38: S373-S378. DOI: 10.1016/S0196-8904(96)00297-X
- Benson, E.E., C.P. Kubiak, A.J. Sathrum and J.M. Smieja, 2009. Electrocatalytic and homogeneous approaches to conversion of CO<sub>2</sub> to liquid fuels. *Chem. Society Rev.*, 38: 89-99. DOI: 10.1039/B804323J
- Centi, G. and S. Perathoner, 2009. Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. *Catalysis Today*, 148: 191-205. DOI: 10.1016/j.cattod.2009.07.075
- Chang, T.Y., R.M. Liang, P.W. Wu, J.Y. Chen and Y.C. Hsieh, 2009. Electrochemical reduction of CO<sub>2</sub> by Cu<sub>2</sub>O-catalyzed carbon clothes. *Mater. Lett.*, 63: 1001-1003. DOI: 10.1016/j.matlet.2009.01.067
- Chen, Y. and M.W. Kanan, 2012. Tin oxide dependence of the CO<sub>2</sub> reduction efficiency on tin electrodes and enhanced activity for tin/tin oxide thin-film catalysts. *J. Am. Chem. Society*, 134: 1986-1989. DOI: 10.1021/ja2108799
- Chen, Y., C.W. Li and M.W. Kanan, 2012. Aqueous CO<sub>2</sub> reduction at very low overpotential on oxide-derived Au nanoparticles. *J. Am. Chem. Society*, 134: 19969-19972. DOI: 10.1021/ja309317u
- Chung, J., J. Koh, E.H. Kim and S.I. Woo, 2016. Hierarchical Cu pillar electrodes for electrochemical CO<sub>2</sub> reduction to formic acid with low overpotential. *Phys. Chem. Chemical Phys.*, 18: 6252-6258. DOI: 10.1039/C5CP07964K
- de Brito, J.F., A.R. Araujo, K. Rajeshwar and M.V.B. Zanoni, 2015. Photoelectrochemical reduction of CO<sub>2</sub> on Cu/Cu<sub>2</sub>O films: Product distribution and pH effects. *Chem. Eng. J.*, 264: 302-309. DOI: 10.1016/j.cej.2014.11.081
- Delacourt, C., P.L. Ridgway, J.B. Kerr and J. Newman, 2008. Design of an electrochemical cell making syngas (CO + H<sub>2</sub>) from CO<sub>2</sub> and H<sub>2</sub>O reduction at room temperature. *J. Electrochem. Society*, 155: B42-B49. DOI: 10.1149/1.2801871
- Fan, W., Q. Zhang and Y. Wang, 2013. Semiconductor-based nanocomposites for photocatalytic H<sub>2</sub> production and CO<sub>2</sub> conversion. *Phys. Chem. Chemical Phys.*, 15: 2632-2649. DOI: 10.1039/C2CP43524A
- Fisher, I.A., A.T. Bell, 1998. In situ infrared study of methanol synthesis from H<sub>2</sub>/CO over Cu/SiO<sub>2</sub> and Cu/ZrO<sub>2</sub>/SiO<sub>2</sub>. *J. Catalysis*, 178: 153-173. DOI: 10.1006/jcat.1998.2134
- Fujita, S.I., M. Arai and B.M. Bhalch, 2014. Direct Transformation of Carbon Dioxide to Value-Added Product over Heterogeneous Catalysts. In: *Transformation and Utilization of Carbon Dioxide, Green Chemistry and Sustainable Technology*, Bhanage, B.M. and M. Arai (Eds.), Springer-Verlag Berlin Heidelberg, pp: 39-53.
- Gattrell, M., N. Gupta and A. Co, 2006. A review of the aqueous electrochemical reduction of CO<sub>2</sub> to hydrocarbons at copper. *J. Electroanalytical Chem.*, 594: 1-19. DOI: 10.1016/j.jelechem.2006.05.013
- Gawande, M.B., A. Goswami, F.X. Felpin, T. Asefa and X. Huang *et al.*, 2016. Cu and Cu-based nanoparticles: Synthesis and applications in catalysis. *Chem. Rev.*, 116: 3722-3811. DOI: 10.1021/acs.chemrev.5b00482
- Guemene Dountio, E., P. Meukam, D.L. Pahane Tchaptchet, L.E. Okono Ango and A. Simo, 2016. Electricity generation technology options under the greenhouse gases mitigation scenario: Case study of Cameroon. *Energy Strategy Rev.*, 13-14: 191-211. DOI: 10.1016/j.esr.2016.10.003

- Halmann, M., 1978. Photoelectrochemical reduction of aqueous carbon dioxide on p-type gallium phosphide in liquid junction solar cells. *Nature*, 275: 115-116. DOI: 10.1038/275115a0
- Hara, K., A. Kudo, T. Sakata and M. Watanabe, 1995. High efficiency electrochemical reduction of carbon dioxide under high pressure on a gas diffusion electrode containing Pt catalysts. *J. Electrochem. Society*, 142: L57-L59. DOI: 10.1149/1.2044182
- Heffer PaPh, M., 2013. Fertilizer outlook 2013- 2017. Proceedings of the 81th IFA Annual Conference, (AC' 13).
- Herron, J.A., J. Kim, A.A. Upadhye, G.W. Huber and C.T. Maravelias, 2015. A general framework for the assessment of solar fuel technologies. *Energy Environ. Sci.*, 8: 126-157. DOI: 10.1039/C4EE01958J
- Hinogami, R., S. Yotsuhashi, M. Deguchi, Y. Zenitani and H. Hashiba *et al.*, 2012. Electrochemical reduction of carbon dioxide using a copper rubeanate metal organic framework. *ECS Electrochem. Lett.*, 1: H17-H19. DOI: 10.1149/2.001204eel
- Hori, Y., 2003. CO<sub>2</sub>-reduction, catalyzed by metal electrodes. *Handbook of fuel cells*.
- Hori, Y., I. Takahashi, O. Koga and N. Hoshi, 2003. Electrochemical reduction of carbon dioxide at various series of copper single crystal electrodes. *J. Molecular Catalysis A*, 199: 39-47. DOI: 10.1016/S1381-1169(03)00016-5
- Hossain, S.K., 2012. Electrochemical reduction of carbon dioxide to hydrocarbons. King Fahd University of Petroleum and Minerals (Saudi Arabia).
- Huang, C.H. and C.S. Tan, 2014. A review: CO<sub>2</sub> utilization. *Aerosol Air Qual. Res.*, 14: 480-499. DOI: 10.4209/aaqr.2013.10.0326
- Hurst, T.F., T.T. Cockerill and N.H. Florin, 2012. Life cycle greenhouse gas assessment of a coal-fired power station with calcium looping CO<sub>2</sub> capture and offshore geological storage. *Energy Environ. Sci.*, 5: 7132-7150. DOI: 10.1039/C2EE21204H
- Hurum, D.C., A.G. Agrios, K.A. Gray, T. Rajh and M.C. Thurnauer, 2003. Explaining the enhanced photocatalytic activity of degussa P25 mixed-phase TiO<sub>2</sub> using EPR. *J. Phys. Chem. B*, 107: 4545-4549. DOI: 10.1021/jp0273934
- Indrakanti, V.P., J.D. Kubicki and H.H. Schobert, 2009. Photoinduced activation of CO<sub>2</sub> on Ti-based heterogeneous catalysts: Current state, chemical physics-based insights and outlook. *Energy Environ. Sci.*, 2: 745-758. DOI: 10.1039/B822176F
- Inui, T., M. Anpo, K. Izui, S. Yanagida and T. Yamaguchi, 1998. *Advances in Chemical Conversions for Mitigating Carbon Dioxide*. 1st Edn., Elsevier, Paises Bajos, ISBN-10: 0080526578, pp: 698.
- Jang, Y.J., J. Lee, J. Lee and J.S. Lee, 2016. Solar hydrogen production from zinc telluride photocathode modified with carbon and molybdenum sulfide. *ACS Applied Mater. Interfaces*, 8: 7748-7755. DOI: 10.1021/acsami.5b07575
- Jhong, H.R.M., S. Ma and P.J.A. Kenis, 2013. Electrochemical conversion of CO<sub>2</sub> to useful chemicals: current status, remaining challenges and future opportunities. *Curr. Opin. Chem. Eng.*, 2: 191-199. DOI: 10.1016/j.coche.2013.03.005
- Jovanov, Z.P., H.A. Hansen, A.S. Varela, P. Malacrida and A.A. Peterson *et al.*, 2016. Opportunities and challenges in the electrocatalysis of CO<sub>2</sub> and CO reduction using bifunctional surfaces: A theoretical and experimental study of Au-Cd alloys. *J. Catalysis*, 343: 215-231. DOI: 10.1016/j.jcat.2016.04.008
- Kaneco, S., H. Kurimoto, Y. Shimizu, K. Ohta and T. Mizuno, 1999. Photocatalytic reduction of CO<sub>2</sub> using TiO<sub>2</sub> powders in supercritical fluid CO<sub>2</sub>. *Energy*, 24: 21-30. DOI: 10.1016/S0360-5442(98)00070-X
- Kaneco, S., Y. Shimizu, K. Ohta and T. Mizuno, 1998. Photocatalytic reduction of high pressure carbon dioxide using TiO<sub>2</sub> powders with a positive hole scavenger. *J. Photochem. Photobiol. A*, 115: 223-226. DOI: 10.1016/S1010-6030(98)00274-3
- Kauffman, D.R., D. Alfonso, C. Matranga, H. Qian and R. Jin, 2012. Experimental and computational investigation of Au<sub>25</sub> clusters and CO<sub>2</sub>: A unique interaction and enhanced electrocatalytic activity. *J. Am. Chem. Society*, 134: 10237-10243. DOI: 10.1021/ja303259q
- Kauffman, D.R., D. Alfonso, C. Matranga, P. Ohodnicki and X. Deng *et al.*, 2014. Probing active site chemistry with differently charged Au<sub>25</sub><sup>q</sup> nanoclusters (q=- 1, 0,+ 1). *Chem. Sci.*, 5: 3151-3157. DOI: 10.1039/C4SC00997E
- Kauffman, D.R., J. Thakkar, R. Siva, C. Matranga and P.R. Ohodnicki *et al.*, 2015. Efficient electrochemical CO<sub>2</sub> conversion powered by renewable energy. *ACS Applied Mater. Interfaces*, 7: 15626-15632. DOI: 10.1021/acsami.5b04393
- Kauffman, D.R., P.R. Ohodnicki, B.W. Kail and C. Matranga, 2011. Selective electrocatalytic activity of ligand stabilized copper oxide nanoparticles. *J. Phys. Chem. Lett.*, 2: 2038-2043. DOI: 10.1021/jz200850y
- Kim, W., T. Seoka and W. Choi, 2012. Nafion layer-enhanced photosynthetic conversion of CO<sub>2</sub> into hydrocarbons on TiO<sub>2</sub> nanoparticles. *Energy Environ. Sci.*, 5: 6066-6070. DOI: 10.1039/C2EE03338K
- Kobayashi, T. and H. Takahashi, 2004. Novel CO<sub>2</sub> Electrochemical reduction to methanol for H<sub>2</sub> storage. *Energy Fuels*, 18: 285-286. DOI: 10.1021/ef030121v

- Kohno, Y., H. Hayashi, S. Takenaka, T. Tanaka and T. Funabiki *et al.*, 1999. Photo-enhanced reduction of carbon dioxide with hydrogen over Rh/TiO<sub>2</sub>. *J. Photochem. Photobiol. A*, 126: 117-123. DOI: 10.1016/S1010-6030(99)00113-6
- Kohno, Y., H. Ishikawa, T. Tanaka, T. Funabiki and S. Yoshida, 2001a. Photoreduction of carbon dioxide by hydrogen over magnesium oxide. *Phys. Chem. Chemical Phys.*, 3: 1108-1113. DOI: 10.1039/B008887K
- Kohno, Y., T. Yamamoto, T. Tanaka and T. Funabiki, 2001b. Photoenhanced reduction of CO<sub>2</sub> by H<sub>2</sub> over Rh/TiO<sub>2</sub>: Characterization of supported Rh species by means of infrared and X-ray absorption spectroscopy. *J. Molecular Catalysis A*, 175: 173-178. DOI: 10.1016/S1381-1169(01)00204-7
- Kohno, Y., T. Tanaka, T. Funabiki and S. Yoshida, 2000. Photoreduction of CO<sub>2</sub> with H<sub>2</sub> over ZrO<sub>2</sub>. A study on interaction of hydrogen with photoexcited CO<sub>2</sub>. *Phys. Chem. Chemical Phys.*, 2: 2635-2639. DOI: 10.1039/B001642J
- Kondratenko, E.V., G. Mul, J. Baltrusaitis, G.O. Larrazábal and J. Pérez-Ramírez, 2013. Status and perspectives of CO<sub>2</sub> conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes. *Energy Environ. Sci.*, 6: 3112-3135. DOI: 10.1039/C3EE41272E
- Kuhl, K.P., E.R. Cave, D.N. Abram and T.F. Jaramillo, 2012. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy Environ. Sci.*, 5: 7050-7059. DOI: 10.1039/C2EE21234J
- Kuhl, K.P., T. Hatsukade, E.R. Cave, D.N. Abram and J. Kibsgaard *et al.*, 2014. Electrocatalytic conversion of carbon dioxide to methane and methanol on transition metal surfaces. *J. Am. Chem. Society*, 136: 14107-14113. DOI: 10.1021/ja505791r
- Kumar, B., J.P. Brian, V. Atla, S. Kumari and K.A. Bertram *et al.*, 2016. New trends in the development of heterogeneous catalysts for electrochemical CO<sub>2</sub> reduction. *Catalysis Today*, 270: 19-30. DOI: 10.1016/j.cattod.2016.02.006
- Kusama, H., K. Okabe, K. Sayama and H. Arakawa, 1996. CO<sub>2</sub> hydrogenation to ethanol over promoted Rh/SiO<sub>2</sub> catalysts. *Catalysis Today*, 28: 261-266. DOI: 10.1016/0920-5861(95)00246-4
- Kushwaha, H.S., N.A. Madhar, B. Ilahi, P. Thomas and A. Halder *et al.*, 2016. Efficient solar energy conversion using CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> photoanode for photocatalysis and photoelectrocatalysis. *Scientific Rep.* DOI: 10.1038/srep18557
- Le, M., M. Ren, Z. Zhang, P.T. Sprunger and R.L. Kurtz *et al.*, 2011. Electrochemical reduction of CO<sub>2</sub> to CH<sub>3</sub>OH at copper oxide surfaces. *J. Electrochem. Society*, 158: E45-E49. DOI: 10.1149/1.3561636
- Lee, C.H. and M.W. Kanan, 2014. Controlling H<sup>+</sup> Vs CO<sub>2</sub> reduction selectivity on Pb electrodes. *ACS Catalysis*, 5: 465-469. DOI: 10.1021/cs5017672
- Leung, D.Y.C., G. Caramanna and M.M. Maroto-Valer, 2014. An overview of current status of carbon dioxide capture and storage technologies. *Renewable Sustainable Energy Rev.*, 39: 426-443. DOI: 10.1016/j.rser.2014.07.093
- Li, C.W. and M.W. Kanan, 2012. 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. Society*, 134: 7231-7234. DOI: 10.1021/ja3010978
- Li, K., X. An, K.H. Park, M. Khraisheh and J. Tang, 2014. A critical review of CO<sub>2</sub> photoconversion: Catalysts and reactors. *Catalysis Today*, 224: 3-12. DOI: 10.1016/j.cattod.2013.12.006
- Li, P., S. Ouyang, G. Xi, T. Kako and J. Ye, 2012. 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>. *J. Phys. Chem. C*, 116: 7621-7628. DOI: 10.1021/jp210106b
- Li, Y., W.N. Wang, Z. Zhan, M.H. Woo and C.Y. Wu *et al.*, 2010. Photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O on mesoporous silica supported Cu/TiO<sub>2</sub> catalysts. *Applied Catalysis B*, 100: 386-392. DOI: 10.1016/j.apcatb.2010.08.015
- Liu, L., C. Zhao, H. Zhao, D. Pitts and Y. Li, 2013. Porous microspheres of MgO-patched TiO<sub>2</sub> for CO<sub>2</sub> photoreduction with H<sub>2</sub>O vapor: Temperature-dependent activity and stability. *Chem. Commun.*, 49: 3664-3666. DOI: 10.1039/C3CC39054C
- Liu, L., H. Zhao, J.M. Andino, Y. Li, 2012. 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: 1817-1828. DOI: 10.1021/cs300273q
- Liu, S., Z. Zhao and Z. Wang, 2007. Photocatalytic reduction of carbon dioxide using sol-gel derived titania-supported CoPc catalysts. *Photochem. Photobiol. Sci.*, 6: 695-700. DOI: 10.1039/B613098D
- Luu, M.T., D. Milani, A. Bahadori and A. Abbas, 2015. A comparative study of CO<sub>2</sub> utilization in methanol synthesis with various syngas production technologies. *J. CO<sub>2</sub> Utilizat.*, 12: 62-76. DOI: 10.1016/j.jcou.2015.07.001
- Mahmood, M.N., D. Mashed and C.J. Harty, 1987. Use of gas-diffusion electrodes for high-rate electrochemical reduction of carbon dioxide. I. Reduction at lead, indium-and tin-impregnated electrodes. *J. Applied Electrochem.*, 17: 1159-1170. DOI: 10.1007/BF01023599

- Manthiram, K., B.J. Beberwyck and A.P. Alivisatos, 2014. Enhanced electrochemical methanation of carbon dioxide with a dispersible nanoscale copper catalyst. *J. Am. Chem. Society*, 136: 13319-13325. DOI: 10.1021/ja5065284
- Olah, G.A., A. Goepfert and G.K.S. Prakash, 2008. Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons. *J. Organic Chem.*, 74: 487-498. DOI: 10.1021/jo801260f
- Pan, J., X. Wu, L. Wang, G. Liu and G.Q.M. Lu *et al.* 2011. Synthesis of anatase TiO<sub>2</sub> rods with dominant reactive {010} facets for the photoreduction of CO<sub>2</sub> to CH<sub>4</sub> and use in dye-sensitized solar cells. *Chem. Commun.*, 47: 8361-8363. DOI: 10.1039/C1CC13034J
- Peterson, A.A., J.K. Nørskov, 2012. Activity descriptors for CO<sub>2</sub> electroreduction to methane on transition-metal catalysts. *J. Phys. Chem. Lett.*, 3: 251-258. DOI: 10.1021/jz201461p
- Qiao, J., Y. Liu, F. Hong and J. Zhang, 2014. A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. *Chem. Society Rev.*, 43: 631-675. DOI: 10.1039/C3CS60323G
- Qu, Y. and X. Duan, 2012. One-dimensional homogeneous and heterogeneous nanowires for solar energy conversion. *J. Mater. Chem.*, 22: 16171-16181. DOI: 10.1039/C2JM32267F
- Razali, N.A.M., K.T. Lee, S. Bhatia, A.R. Mohamed, 2012. Heterogeneous catalysts for production of chemicals using carbon dioxide as raw material: A review. *Renewable Sustainable Energy Rev.*, 16: 4951-4964. DOI: 10.1016/j.rser.2012.04.012
- Ren, D., B.S.H. Ang and B.S. Yeo, 2016. Tuning the selectivity of carbon dioxide electroreduction toward ethanol on oxide-derived Cu<sub>x</sub>Zn catalysts. *ACS Catalysis*, 6: 8239-8247. DOI: 10.1021/acscatal.6b02162
- Rosen, B.A., A. Salehi-Khojin, M.R. Thorson, W. Zhu and D.T. Whipple *et al.*, 2011. Ionic liquid-mediated selective conversion of CO<sub>2</sub> to CO at low overpotentials. *Science*, 334: 643-644. DOI: 10.1126/science.1209786
- Roy, S.C., O.K. Varghese, M. Paulose and C.A. Grimes, 2010. Toward solar fuels: Photocatalytic conversion of carbon dioxide to hydrocarbons. *ACS Nano*, 4: 1259-1278. DOI: 10.1021/nn9015423
- Salehi-Khojin, A., H.R.M. Jhong, B.A. Rosen, W. Zhu and S. Ma *et al.*, 2013. Nanoparticle silver catalysts that show enhanced activity for carbon dioxide electrolysis. *J. Phys. Chem. C*, 117: 1627-1632. DOI: 10.1021/jp310509z
- Sato, S., T. Arai and T. Morikawa, 2016. Carbon microfiber layer as noble metal-catalyst support for selective CO<sub>2</sub> photoconversion in phosphate solution: Toward artificial photosynthesis in a single-compartment reactor. *J. Photochem. Photobiol. A*, 327: 1-5. DOI: 10.1016/j.jphotochem.2016.04.017
- Schouten, K.J.P., Z. Qin, E.P. Gallent and M.T.M. Koper, 2012. Two pathways for the formation of ethylene in CO reduction on single-crystal copper electrodes. *J. Am. Chem. Society*, 134: 9864-9867. DOI: 10.1021/ja302668n
- Shen, Q., Z. Chen, X. Huang, M. Liu and G. Zhao, 2015. High-yield and selective photoelectrocatalytic reduction of CO<sub>2</sub> to formate by metallic copper decorated Co<sub>3</sub>O<sub>4</sub> nanotube arrays. *Environ. Sci. Technol.*, 49: 5828-5835. DOI: 10.1021/acs.est.5b00066
- Tang, W., A. Peterson, A. Varela, Z. Jovanov and L. Bech *et al.*, 2012. Electrocatalytic process of CO selectivity in electrochemical reduction of CO<sub>2</sub> at metal-electrodes in aqueous-media.
- Tornow, C.E., M.R. Thorson, S. Ma, A.A. Gewirth and P.J.A. Kenis, 2012. Nitrogen-based catalysts for the electrochemical reduction of CO<sub>2</sub> to CO. *J. Am. Chem. Society*, 134: 19520-19523. DOI: 10.1021/ja308217w
- Tseng, I.H., J.C.S. Wu and H.Y. Chou, 2004. Effects of sol-gel procedures on the photocatalysis of Cu/TiO<sub>2</sub> in CO<sub>2</sub> photoreduction. *J. Catalysis*, 221: 432-440. DOI: 10.1016/j.jcat.2003.09.002
- Tu, W., Y. Zhou, Q. Liu, Z. Tian and J. Gao *et al.*, 2012. Robust hollow spheres consisting of alternating titania nanosheets and graphene nanosheets with high photocatalytic activity for CO<sub>2</sub> conversion into renewable fuels. *Adv. Funct. Mater.*, 22: 1215-1221. DOI: 10.1002/adfm.201102566
- USEPA, 2016. United State environmental protection agency: Overview of greenhouse gases.
- Varghese, O.K., M. Paulose, T.J. LaTempa and C.A. Grimes, 2009. High-rate solar photocatalytic conversion of CO<sub>2</sub> and water vapor to hydrocarbon fuels. *Nano Lett.*, 9: 731-737. DOI: 10.1021/nl803258p
- Wang, P.Q., Y. Bai, J.Y. Liu, Z. Fan and Y.Q. Hu, 2012a. One-pot synthesis of rutile TiO<sub>2</sub> nanoparticle modified anatase TiO<sub>2</sub> nanorods toward enhanced photocatalytic reduction of CO<sub>2</sub> into hydrocarbon fuels. *Catalysis Commun.*, 29: 185-188. DOI: 10.1016/j.catcom.2012.10.010
- Wang, W.N., W.J. An, B. Ramalingam, S. Mukherjee and D.M. Niedzwiedzki *et al.*, 2012b. Size and structure matter: enhanced CO<sub>2</sub> photoreduction efficiency by size-resolved ultrafine Pt nanoparticles on TiO<sub>2</sub> single crystals. *J. Am. Chem. Society*, 134: 11276-11281. DOI: 10.1021/ja304075b

- Wang, W.H., Y. Himeda, J.T. Muckerman, G.F. Manbeck and E. Fujita, 2015. CO<sub>2</sub> hydrogenation to formate and methanol as an alternative to photo-and electrochemical CO<sub>2</sub> reduction. *Chem. Rev.*, 115: 12936-12973.  
DOI: 10.1021/acs.chemrev.5b00197
- Wang, W.N., J. Park and P. Biswas, 2011. Rapid synthesis of nanostructured Cu-TiO<sub>2</sub>-SiO<sub>2</sub> composites for CO<sub>2</sub> photoreduction by evaporation driven self-assembly. *Catalysis Sci. Technol.* 1: 593-600.  
DOI: 10.1039/C0CY00091D
- Wang, W.N., J. Soulis, Y.J. Yang and P. Biswas, 2014. Comparison of CO<sub>2</sub> photoreduction systems: A review. *Aerosol Air Quality Res.*, 14: 533-549.  
DOI: 10.4209/aaqr.2013.09.0283
- Windle, C.D. and E. Reisner, 2015. Heterogenised molecular catalysts for the reduction of CO<sub>2</sub> to fuels. *CHIMIA Int. J. Chem.*, 69: 435-441.  
DOI: 10.2533/chimia.2015.435
- Wu, J.C.S., 2009. Photocatalytic reduction of greenhouse gas CO<sub>2</sub> to fuel. *Catalysis Surveys Asia*, 13: 30-40.  
DOI: 10.1007/s10563-009-9065-9
- Xie, S., Q. Zhang, G. Liu and Y. Wang, 2016. Photocatalytic and photoelectrocatalytic reduction of CO<sub>2</sub> using heterogeneous catalysts with controlled nanostructures. *Chem. Commun.*, 52: 35-59.  
DOI: 10.1039/C5CC07613G
- Xu, H., S. Ouyang, P. Li, T. Kato and J. Ye, 2013. High-active anatase TiO<sub>2</sub> nanosheets exposed with 95% {100} facets toward efficient H<sub>2</sub> evolution and CO<sub>2</sub> photoreduction. *ACS Applied Mater. Interfaces*, 5: 1348-1354. DOI: 10.1021/am302631b
- Yamashita, H., Y. Fujii, Y. Ichihashi, S.G. Zhang and K. Ikeue *et al.*, 1998. Selective formation of CH<sub>3</sub>OH in the photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O on titanium oxides highly dispersed within zeolites and mesoporous molecular sieves. *Catalysis Today*, 45: 221-227.  
DOI: 10.1016/S0920-5861(98)00219-3
- Yuan, Y.J., Z.T. Yu, J.Y. Zhang and Z.G. Zou, 2012. A copper (I) dye-sensitised TiO<sub>2</sub>-based system for efficient light harvesting and photoconversion of CO<sub>2</sub> into hydrocarbon fuel. *Dalton Trans.*, 41: 9594-9597.  
DOI: 10.1039/C2DT30865G
- Zhang, S., P. Kang and T.J. Meyer, 2014. Nanostructured tin catalysts for selective electrochemical reduction of carbon dioxide to formate. *J. Am. Chem. Society*, 136: 1734-1737.  
DOI: 10.1021/ja4113885
- Zhao, H., L. Liu, J.M. Andino and Y. Li, 2013. Bicrystalline TiO<sub>2</sub> with controllable anatase–brookite phase content for enhanced CO<sub>2</sub> photoreduction to fuels. *J. Mater. Chem. A*, 1: 8209-8216.  
DOI: 10.1039/C3TA11226H