

## REVIEW

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13, 4895Photocatalytic conversion of carbon dioxide,  
methane, and air for green fuels synthesis†Amira Chebbi,<sup>a</sup> Alessandro Sinopoli,<sup>b</sup> Ahmed Abotaleb<sup>b</sup> and Yusuf Bicer \*<sup>a</sup>

Green fuels are derived from renewable resources that can replace or reduce the use of fossil fuels, and they can help reduce carbon emissions and dependence on finite resources including oil and natural gas. This review reports the latest investigations and studies on methane and carbon dioxide photocatalysis as well as nitrogen fixation for the production of green fuels. Specifically, methanol, formic acid, and ammonia synthesis were thoroughly reviewed to understand the corresponding chemical processes, experimental setups, and production strategies involved. The photocatalytic production of fuels from carbon dioxide and methane is generally affected by low yield and low selectivity, representing the main challenges of these processes. Whereas, a key issue in nitrogen photofixation is the fast oxidation of ammonia to nitrate during simultaneous redox reactions. Indeed, significant yield values were reported for methanol from the partial oxidation of methane ( $4500 \mu\text{mol g}^{-1} \text{h}^{-1}$ , Pd/H-TiO<sub>2</sub>), methanol from carbon dioxide photoreduction ( $2910 \mu\text{mol g}^{-1} \text{h}^{-1}$ , 3% Cu-C/TiO<sub>2</sub>), formic acid from carbon dioxide photoreduction ( $3500 \mu\text{mol g}^{-1} \text{h}^{-1}$ , g-C<sub>3</sub>N<sub>4</sub>/(Cu/TiO<sub>2</sub>)), and ammonia from nitrogen fixation ( $3.81 \text{ mM g}^{-1} \text{h}^{-1}$ , In(OH)<sub>3</sub>/CN). To address the existing challenges and enhance efficiency, various solutions were introduced. For instance, developing photocatalysts with high surface area, fast separation of charges, large charge lifetime, photocatalyst performance, reaction conditions, efficient light absorption, appropriate band gap, changing reactor design, and the use of electron donors to consume the photogenerated electrons were proposed and adopted as potential solutions. Overall, this review provides insights into the opportunities and challenges associated with photocatalytic green fuel production from methane, carbon dioxide, and nitrogen and suggests potential avenues for future research and development.

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## 1. Introduction

Greenhouse gases, including carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>), contribute to global warming and climate change. Human daily activities, such as burning fossil fuels and deforestation, have led to the release of high carbon dioxide levels into the atmosphere. These increasing levels result in more frequent and longer-lasting natural disasters, including droughts, heat waves, flooding, forest wildfires, and acid rain. Statistics indicate that the global land and ocean surface temperature increased by 0.85 °C from 1880 to 2012, and the average global sea level rose by 0.19 meter.<sup>1</sup> Despite the fact that the amount of CO<sub>2</sub> released from burning fossil fuels, which is 29 Gt, is relatively minor compared to the 750

Gt released during the natural carbon cycle, it still contributes to the rising temperature and sea level because some of the CO<sub>2</sub> cannot be absorbed by the land and ocean.<sup>2</sup> Approximately 40% of excess CO<sub>2</sub> is absorbed, and the rest remains in the atmosphere. CO<sub>2</sub> emissions are mainly released from vehicles, heavy industries, chemical plants, and burning fossil fuels.<sup>3</sup> As shown in Table 1, the industrial sector is the third largest emitting greenhouse gases in the US, with 24% greenhouse gas emissions. Table 2 illustrates that in 2020, all economic sectors collectively contributed 79% of CO<sub>2</sub> emissions and 11% of CH<sub>4</sub> emissions.

Fig. 1 presents the emissions in metric tons of carbon dioxide equivalent from various industrial sectors in the United States. The data reveals that the leading sources of CO<sub>2</sub> emissions are fossil fuel combustion and those associated with natural gas and petroleum systems, accounting for 51% and 19.5% of the total emissions, respectively. Several studies have focused on finding alternative ways to reduce or eliminate the emissions of CO<sub>2</sub>, and one of the most promising approaches is the photocatalytic process. It involves using light (potentially solar light) to activate and generate charges on the surface of

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**Table 1** The US economic sectors and their associated greenhouse gas emissions in 2020

| Economic sectors       | Total US greenhouse gas emissions by economic sector in 2020 |
|------------------------|--------------------------------------------------------------|
| Transportation         | 27%                                                          |
| Electricity generation | 25%                                                          |
| Industry               | 24%                                                          |
| Agriculture            | 11%                                                          |
| Commercial             | 7%                                                           |
| Residential            | 6%                                                           |

Data retrieved from ref. 4.

**Table 2** The greenhouse gases and their corresponding emissions

| Greenhouse gases                  | US greenhouse gas emissions in 2020 |
|-----------------------------------|-------------------------------------|
| Carbon dioxide (CO <sub>2</sub> ) | 79%                                 |
| Methane (CH <sub>4</sub> )        | 11%                                 |
| Nitrous oxide (N <sub>2</sub> O)  | 7%                                  |
| Fluorinated gases                 | 3%                                  |

Data retrieved from ref. 4.

a semiconductor to perform oxidation or reduction reactions at mild conditions. This technology can be used to produce valuable chemicals, such as green fuels (low-carbon fuels), methanol (CH<sub>3</sub>OH), formic acid (HCOOH), and ammonia (NH<sub>3</sub>).

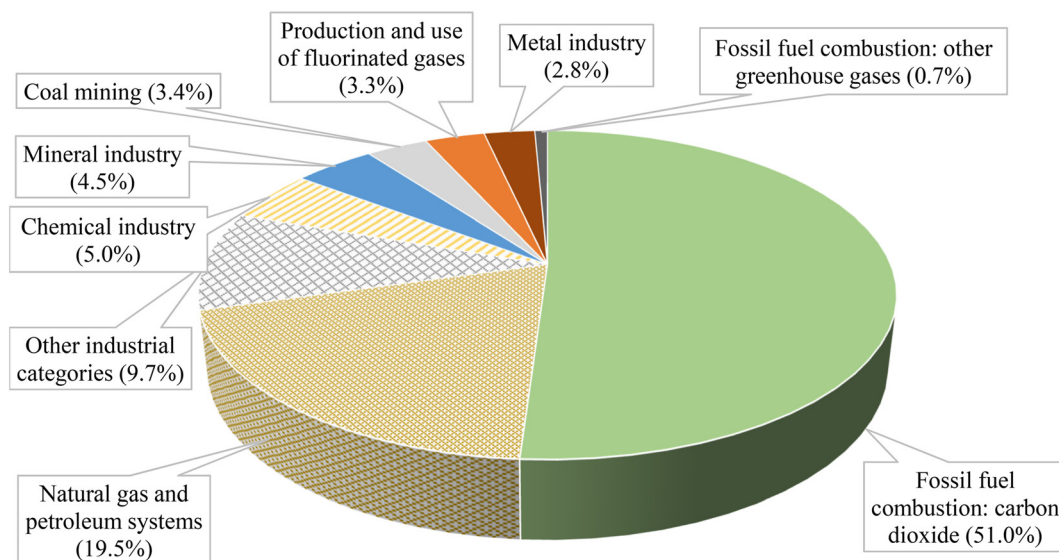
The aforementioned green fuels are highly advantageous due to their ease of handling, storage, and transportation, making them excellent energy carriers. NH<sub>3</sub>, in particular, is widely used as a fertilizer and a significant source of hydrogen (H<sub>2</sub>) due to its high H<sub>2</sub> density. CH<sub>3</sub>OH serves as an alternative fuel, while HCOOH is used as a medium for storing H<sub>2</sub> and syngas. CH<sub>3</sub>OH and HCOOH production offer

a means of transforming excess CO<sub>2</sub> into valuable fuels, thus reducing CO<sub>2</sub> emissions.

The photocatalysis process induces chemical reactions by exposing a semiconductor photocatalyst to visible or UV light. Photocatalytic reactions comprise three steps: light absorption, charge separation, and product formation. During light absorption, photons are absorbed, and the subsequent charge separation results in the excitation of electrons from the valence band to the conduction band, creating positively charged holes. In the final step, product formation occurs through a redox reaction.<sup>5</sup> Among all photocatalysts, TiO<sub>2</sub> is considered a highly attractive option due to its strong reducing and oxidizing properties, low toxicity, and photostability.<sup>3</sup> However, its large band gap (3.2 eV) limits its ability to absorb visible light. Thus, modifications through doping with metals and metal-oxides are required. Over the last two decades, CO<sub>2</sub> obtained from carbon capture from other industrial processes, CH<sub>4</sub> and nitrogen gas, have been utilized as reactants in the photocatalytic production of valuable fuels, such as CH<sub>3</sub>OH, NH<sub>3</sub>, and HCOOH.

CH<sub>4</sub> represents the predominant constituent of natural gas, and has gained considerable traction as a fuel source due to its superior mass heat relative to other hydrocarbons. CH<sub>4</sub> is also a potent greenhouse gas, with a global warming potential (GWP) that is about 28–36 times higher than CO<sub>2</sub> over a 100-year timeframe, making it a significant contributor to climate change. This means that although CH<sub>4</sub> is present in lower concentrations compared to CO<sub>2</sub>, it has a much stronger warming effect per unit of mass.

Together with being naturally produced through various biological and geological processes, CH<sub>4</sub> is also released during the production, processing, and transportation of fossil fuels, including coal mining, oil drilling, and natural gas extraction. CH<sub>4</sub> emissions from human activities, such as energy

**Fig. 1** Breakdown of the GHG emissions in million metric tons of carbon dioxide equivalent.<sup>4</sup>

production, agriculture, and waste management, contribute to the overall  $\text{CH}_4$  concentration in the atmosphere. One significant source of  $\text{CH}_4$  emissions is  $\text{CH}_4$  flaring, which is the controlled burning of  $\text{CH}_4$  during the extraction and processing of natural gas, petroleum, and coal.

$\text{CH}_4$  emissions, including those from  $\text{CH}_4$  flaring, have significant environmental impacts and contribute to climate change. Strategies to reduce  $\text{CH}_4$  emissions include improving  $\text{CH}_4$  capture and utilization technologies, promoting more efficient energy production and consumption practices, implementing better waste management practices, and advancing agricultural and livestock management techniques.

According to scientific measurements and estimates, the global abundance of  $\text{CH}_4$  in the atmosphere has increased over the past few decades. In 2021, the global average atmospheric  $\text{CH}_4$  concentration was estimated to be around 1875 parts per billion (ppb), more than two and a half times higher than pre-industrial levels.<sup>6</sup> The increase in  $\text{CH}_4$  abundance is attributed to various sources, including fossil fuel production and use, livestock and agricultural practices, natural wetland emissions, biomass burning, and waste management. Some of the major human-driven sources of  $\text{CH}_4$  emissions include livestock production, rice cultivation, coal mining, oil and gas production and distribution, and landfill waste decomposition.<sup>7–9</sup> Moreover,  $\text{CH}_4$  serves as a vital feedstock in numerous industrial chemical processes.<sup>10</sup> Nevertheless, the conversion of  $\text{CH}_4$  in these procedures necessitates extreme conditions such as (temperature and pressure) conditions to facilitate the cracking of the C–H bond, which may impede  $\text{CH}_4$  transformation mechanisms, causing carbon to further oxidize into unwanted byproducts.<sup>11</sup>

The main reserves of  $\text{CH}_4$  are found in a variety of geological formations around the world. Some of the largest and most significant  $\text{CH}_4$  reserves are located in the following regions:<sup>12,13</sup> Russia has some of the world's largest natural gas reserves, which are mainly associated with large oil fields, and are concentrated in regions such as the Yama Peninsula, the Barents Sea, and the Russian Arctic. Several countries in the Middle East, including Iran, Qatar, and Saudi Arabia, are known to have significant  $\text{CH}_4$  reserves, which are often associated with large oil fields. The United States and Canada are also major producers of natural gas, with significant  $\text{CH}_4$  reserves located in various regions. China has significant  $\text{CH}_4$  reserves located in various regions, including the Sichuan Basin, the Trim Basin, and the Ordos Basin, among others. Thus, there are ongoing global efforts to monitor and reduce  $\text{CH}_4$  emissions, including regulations, policies, and technological innovations to mitigate  $\text{CH}_4$  emissions from various sectors and activities.

$\text{CH}_4$  conversion processes can be classified as steam  $\text{CH}_4$  reforming (SMR), dry reforming of  $\text{CH}_4$  (DRM), pyrolysis, and partial oxidation of  $\text{CH}_4$  (POM). The steam  $\text{CH}_4$  reforming (SMR) process involves using a catalyst to react  $\text{CH}_4$  gas with steam, forming carbon monoxide (CO),  $\text{H}_2$ , and  $\text{CO}_2$  as by-products. This is currently the most commonly used method for commercial  $\text{H}_2$  production.<sup>14</sup> As an energy carrier,  $\text{H}_2$  is

highly regarded as one of the most promising options due to its reputation as the cleanest fuel, as its combustion solely generates water.<sup>15</sup> Furthermore, the combustion of  $\text{H}_2$  produces more energy per unit of mass compared to traditional fossil fuels.<sup>16,17</sup> SMR releases large amounts of greenhouse gas (GHG) emissions associated with its production, making it less sustainable. The reaction takes place between 700 and 800 °C, consuming a high amount of energy, and a water gas shift (WGS) and  $\text{CO}_2$  removal stage are added to obtain pure  $\text{H}_2$  product.

DRM is used for the conversion of greenhouse gases into valuable chemicals and fuels. Under high operating pressure and temperature with a catalyst, the process involves the reaction of  $\text{CH}_4$  and carbon to produce synthesis gas (syngas), which can be utilized in the Fischer-Tropsch process.<sup>18–21</sup> Over the past few decades, there has been significant research into the DRM as a means of generating syngas.<sup>22</sup>

While DRM can potentially be a promising route for converting two greenhouse gases into valuable products,<sup>22</sup> several limitations need to be addressed for its successful implementation at an industrial scale, including high process temperatures, carbon deposition, catalyst stability, and environmental considerations. DRM typically requires high temperatures (700–1000 °C) to achieve reasonable conversion rates. This can result in higher energy consumption and operational costs, as well as increased equipment and material requirements. Furthermore, during DRM, carbon deposition can occur on the catalyst surface. This leads to catalyst deactivation and reduced activity, increasing maintenance costs and limiting the overall process efficiency. DRM also requires catalysts that are capable of withstanding high temperatures and harsh reaction conditions. Finally, while DRM has the potential to reduce  $\text{CO}_2$  emissions by converting it into valuable products, the overall environmental impact and sustainability of the process, including the capture, transport, and utilization of  $\text{CO}_2$ , need to be carefully evaluated.<sup>23–25</sup>

The pyrolysis of  $\text{CH}_4$  is being recognized as a potentially viable method in shifting towards a sustainable  $\text{H}_2$  economy.<sup>26</sup>  $\text{CH}_4$  pyrolysis involves thermally decomposing  $\text{CH}_4$  at high temperatures with the absence of oxygen to obtain  $\text{H}_2$  and carbon as separate products. The most significant benefit of this approach is the production of carbon-free  $\text{H}_2$ , with only solid carbon left as a residue. This attribute provides  $\text{CH}_4$  pyrolysis with a unique advantage over conventional methods such as steam  $\text{CH}_4$  reforming and coal gasification.<sup>27</sup>

Currently, the ocean removes approximately a quarter of the current  $\text{CO}_2$  emissions from human-centric activities.<sup>28</sup> Higher  $\text{CO}_2$  levels absorbed in the seawater will alter the chemical buffering capacity of seawater, which affects and reduces the fraction of  $\text{CO}_2$  emission taken up by the ocean.<sup>29</sup>  $\text{CO}_2$  capture and conversion is a growing field of research and innovation, with various technologies being developed and tested worldwide.<sup>30</sup> One example of  $\text{CO}_2$  capture and conversion technology is direct air capture

(DAC), which uses specialized chemical processes to capture CO<sub>2</sub> directly from ambient air.<sup>31,32</sup> Another example is carbon mineralization, which involves converting CO<sub>2</sub> into stable mineral forms through chemical reactions with naturally occurring minerals.<sup>33</sup>

There are also efforts to develop novel catalysts and electrochemical methods for converting CO<sub>2</sub> into valuable products, such as fuels, chemicals, and building materials. These technologies can potentially contribute to reducing greenhouse gas emissions and developing a circular economy by turning CO<sub>2</sub> into a valuable resource.<sup>34,35</sup>

To utilize CO<sub>2</sub> in eco-friendly processes, it is necessary to capture it from various industrial processes. CO<sub>2</sub> capture technologies can be classified as pre-combustion, combustion, and post-combustion. As a result of the gasification process, the fuel undergoes pre-combustion, which leads to the production of syngas primarily composed of H<sub>2</sub> and carbon monoxide. The subsequent step involves the conversion of H<sub>2</sub> and CO into CO<sub>2</sub>; after that, it undergoes a separation of gas. This is generally recognized as pre-combustion technology.<sup>36</sup>

The second technology is the process of capturing gases during combustion, commonly referred to as “oxygen combustion”. This process involves burning fuel in an environment enriched with oxygen to achieve optimal results.<sup>36</sup>

The capture of gases during the ultimate stage of releasing the combustion products is called post-combustion technology. This method is particularly effective for capturing CO<sub>2</sub> from various sources that generate energy, including thermal power plants and waste-to-energy facilities. Following the emission of flue gases, a suitable technology is utilized to separate CO<sub>2</sub> from other gases in a distinct process.<sup>36</sup>

NH<sub>3</sub> is a crucial chemical in the production of fertilizers, and it has many other applications, such as in the manufacture of chemicals, pharmaceuticals, and refrigerants. NH<sub>3</sub> has the potential to become an H<sub>2</sub> storage medium in the near future, thus enabling the development of CO<sub>2</sub>-free energy systems. NH<sub>3</sub> is advantageous for H<sub>2</sub> storage due to its high volumetric H<sub>2</sub> density, low storage pressure, and long-term stability during storage. Additionally, NH<sub>3</sub> is viewed as a safe option because of its high auto-ignition temperature, low gas density, and lower condensation pressure compared to air.<sup>37</sup> NH<sub>3</sub> is known for its low cost, making it the most economical fuel choice (compared to LPG & gasoline).<sup>38</sup> As of now, the global production of NH<sub>3</sub> stands at approximately 200 million metric tons per year.<sup>39</sup>

Several different conversion technologies can be utilized for the production of NH<sub>3</sub>, including Haber–Bosch, electrochemical, photocatalytic, and thermochemical cycle processes. The Haber–Bosch process is the most commonly used method for producing NH<sub>3</sub>, accounting for approximately 85% of NH<sub>3</sub> production worldwide.<sup>40</sup> The synthesis of NH<sub>3</sub> involves the reaction of nitrogen and H<sub>2</sub> gas. It is an exothermic reaction that occurs spontaneously at low temperatures. Although the reaction is thermodynamically favorable at room temperature, the rate of reaction is too slow to be practical on an industrial scale.<sup>37</sup> Therefore, the reaction is set to occur at relatively high pressure

(10–30 MPa) and temperature (400–500 °C). The challenge associated with this technology is the low conversion rate, even at high pressures.

The electrochemical conversion process involves the direct N<sub>2</sub> reduction, held at temperatures between 100–500 °C, on a catalyst surface able to adsorb and activate N<sub>2</sub> molecules.<sup>41</sup> Electrochemical NH<sub>3</sub> production has been gaining attention due to its potential benefits, such as higher energy efficiency compared to the conventional Haber–Bosch process. This process also offers environmental compatibility by utilizing carbon-free renewable energy resources, such as solar, tidal, and wind power. Another advantage is the elimination of fossil fuels as a source of H<sub>2</sub>. Instead, the required protons (H<sup>+</sup>) can be generated *in situ* through water oxidation.<sup>41</sup>

The thermochemical cycle process involves a sequence of chemical reactions in the absence of a catalyst at high temperatures of 1500 °C.<sup>37</sup> The process comprises two interconnected cycles: the reduction cycle for nitrogen activation and the steam-hydrolysis cycle for the formation of ammonia. The initial reaction is an endothermic process at high temperatures, which remains the main challenge associated with this technology, where aluminum nitride is produced by reducing alumina using carbon in an N<sub>2</sub> atmosphere. The subsequent reaction involves the hydrolysis of aluminum nitride to form NH<sub>3</sub> and alumina, which is then recycled back into the process.<sup>42</sup>

### 1.1. Methodology

A comprehensive search strategy was developed to identify relevant studies or articles for this review by searching for relevant literature in electronic databases, such as Elsevier, Scopus, ACS, Wiley, and Google scholar. Several publications on the photocatalytic conversion topic for the three fuels (CH<sub>3</sub>OH, HCOOH and NH<sub>3</sub>) were obtained. In this work, we mainly focused on the research and review papers published over the last 5 years.

### 1.2. Significance and contribution

This review aims to provide a comprehensive analysis of the current state of research on the photocatalytic conversion systems for green fuels. The significance of this review lies in its ability to synthesize and evaluate the vast and growing body of research on photocatalytic fuel production. By critically evaluating and summarizing research from multiple sources, this review paper includes the conversion systems for CH<sub>3</sub>OH using two different pathways: photocatalytic reduction of CO<sub>2</sub> and photocatalytic partial oxidation of CH<sub>4</sub> (Fig. 2). Additionally, it evaluates the photocatalytic production of HCOOH and ammonia. This paper discusses the fuel synthesis method, challenges and potential solutions, and experimental setup, identifies knowledge gaps, highlights inconsistencies, and suggests potential avenues for future research. Overall, this review paper contributes to the advancement of scientific knowledge in photocatalytic processes that has the potential to make a meaningful contribution to the development of sustainable energy sources and the reduction of environmental impact.



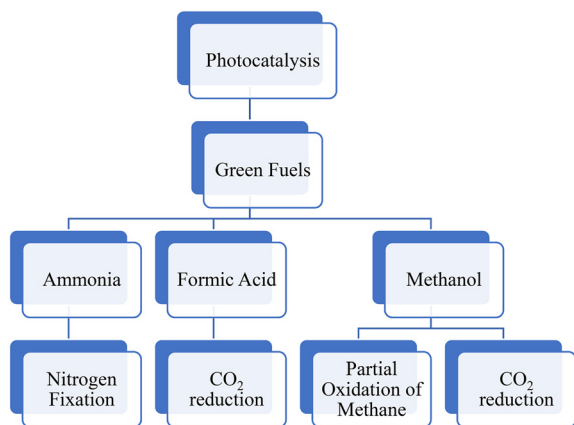


Fig. 2 The scope of the review.

## 2. Green fuels

Green fuels, also known as renewable fuels, biofuels, green hydrocarbons, and low carbon fuels, come from energy sources that are renewable and have a lower environmental impact compared to conventional fossil fuels, such as coal, oil, and natural gas.<sup>43</sup> Sharing similar chemical-physical properties to fossil fuels makes them fully infrastructure-compatible fuels. These fuels are derived from sustainable sources, including wind, solar, hydro, geothermal, and biomass, which enhance their eco-friendliness and reduce the greenhouse gas emissions associated with them.<sup>44</sup>  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ , and  $\text{HCOOH}$  are typical examples of green fuels.

GWP is a measurement that gauges the relative impact of various greenhouse gases on global warming. It quantifies the ability of a specific greenhouse gas to trap heat in the Earth's atmosphere over a defined period, typically 100 years, relative to carbon dioxide. We calculated the potential greenhouse gases produced during the complete combustion of the three fuels considered in this review:  $\text{HCOOH}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{NH}_3$ . This calculation included the presence of the GWP of water vapor, as it is considered the most abundant greenhouse gas in the Earth's atmosphere.<sup>45</sup> Total GWP of the reaction was calculated by multiplying the GWP of each greenhouse gas, produced by the complete combustion of the individual fuels, by the number of moles produced, and calculating the sum of products for each reaction. The GWP reported for  $\text{CO}_2$  in the literature is 1,<sup>46</sup> and the GWP of water vapor was extracted from a study conducted by Sherwood *et al.*<sup>45</sup> and was found to be  $5 \times 10^{-4}$ .

The equations used to calculate the GWP of complete combustion products can be summarized as follows (eqn (1)–(3)):

$$\text{GWP of } \text{CH}_3\text{OH} = (1 \text{ mole} \times \text{GWP of } \text{CO}_2) + (2 \text{ moles} \times \text{GWP of } \text{H}_2\text{O}_{(\text{g})}) \quad (1)$$

$$\text{GWP of } \text{HCOOH} = (2 \text{ moles} \times \text{GWP of } \text{CO}_2) + (2 \text{ moles} \times \text{GWP of } \text{H}_2\text{O}_{(\text{g})}) \quad (2)$$

$$\text{GWP of } \text{NH}_3 = (1 \text{ moles} \times \text{GWP of } \text{H}_2\text{O}_{(\text{g})}) \quad (3)$$

The calculated GWP values for  $\text{CH}_3\text{OH}$ ,  $\text{HCOOH}$  and  $\text{NH}_3$  combustion are 1.001, 2.001, and 0.0005  $\text{CO}_2$  eq., respectively. Here, complete  $\text{NH}_3$  combustion stands out as an exceptionally clean process, yielding solely water vapor as GHG emissions, noting that there might be  $\text{NO}_x$  emissions in the case of incomplete combustion. In contrast, the combustion of  $\text{HCOOH}$  fuel accounted for the highest impact of GHG on global warming. Consequently,  $\text{NH}_3$  is widely acknowledged as the cleanest fuel option when subjected to combustion characteristics.

The growing awareness of the need to reduce the carbon footprint and mitigate climate change has led to a significant surge in the use of green fuels in recent years. The adoption of green fuels can facilitate the creation of a cleaner and more sustainable future. The following sections introduce the most recent technologies for green fuel production ( $\text{CH}_3\text{OH}$ ,  $\text{HCOOH}$ , and  $\text{NH}_3$ ) using photocatalytic processes.

### 2.1. Methanol production

$\text{CH}_3\text{OH}$  is a widely used chemical in several industrial applications and processes. It is a valuable alternative fuel to LPG, gasoline, and gas oil.<sup>47</sup> Its ease of handling, storage, and transportation makes it a more advantageous energy carrier compared to  $\text{H}_2$ . Additionally,  $\text{CH}_3\text{OH}$  has several chemical derivatives, as shown in (Fig. 3). This section will be centered on the methods of producing  $\text{CH}_3\text{OH}$ , with a primary focus on the photocatalytic reduction of  $\text{CO}_2$  and photocatalytic partial oxidation of  $\text{CH}_4$ .

Photocatalytic reduction of  $\text{CO}_2$  uses carbon dioxide as a carbon source and raw material in the synthesis of  $\text{CH}_3\text{OH}$ . From an environmental perspective, transforming  $\text{CO}_2$  into

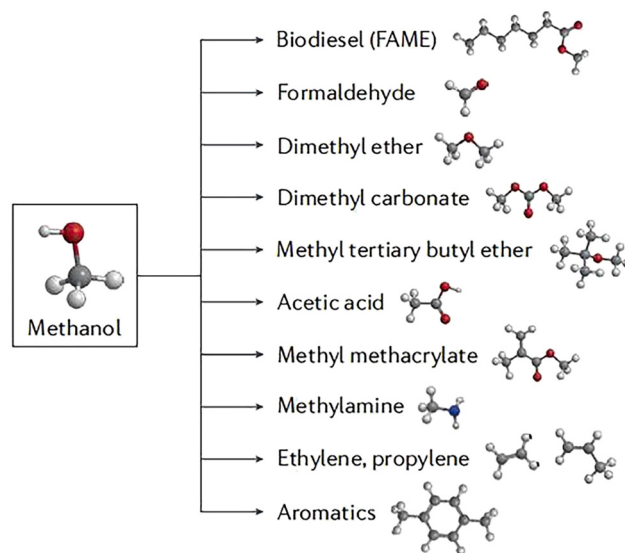


Fig. 3 Methanol chemical derivatives. Reproduced with permission from ref. 49.

other value-added products and fuels will help to reduce/limit global CO<sub>2</sub> emissions.

Photocatalytic partial oxidation of CH<sub>4</sub> is a process that uses CH<sub>4</sub> as a raw material, converting it to CH<sub>3</sub>OH through a series of steps using light. CH<sub>4</sub> is one of the prospective substitutes for non-renewable petroleum resources since it can be converted to other added value-chemicals, such as syngas for NH<sub>3</sub> production and CH<sub>3</sub>OH.<sup>48</sup> Currently, CH<sub>3</sub>OH is produced using a thermal catalytic process in which syngas is produced (H<sub>2</sub> and CO) from steam reforming of CH<sub>4</sub> at high process conditions (very high temperature and pressure), and then hydrogenated to produce CH<sub>3</sub>OH. Photocatalytic partial oxidation of CH<sub>4</sub> is an alternative way of producing CH<sub>3</sub>OH at ambient temperatures and potentially using solar light; reducing the energy requirements means reducing the greenhouse gas emissions released to the atmosphere.

**2.1.1 Photocatalytic reduction of CO<sub>2</sub> to methanol.** The CO<sub>2</sub> photoreduction mechanism can lead to different products, primarily CO, CH<sub>4</sub>, CH<sub>3</sub>OH, and HCOOH, plus C<sub>2</sub> products, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>OH,<sup>50</sup> depending on the catalyst used in the photocatalytic reaction and reaction conditions, as reported in (Fig. 4). Several types of photocatalysts, such as metals, metal oxides, and metal-organic frameworks (MOFs), have been used.<sup>51</sup>

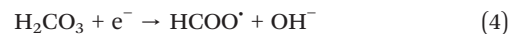
One of the earliest studies published on the photocatalytic reduction of CO<sub>2</sub> to CH<sub>3</sub>OH was introduced by Solymosi and Tombácz.<sup>53</sup> Their work provided valuable insights into this emerging field, as they thoroughly investigated and explored the effect of catalysts and doping in photocatalytic CO<sub>2</sub> reduction products. 1% Rh/TiO<sub>2</sub>/2% WO<sub>3</sub> exhibited a shift towards high CH<sub>3</sub>OH selectivity compared to TiO<sub>2</sub> and TiO<sub>2</sub>/0.1% WO<sub>3</sub>, where no CH<sub>3</sub>OH yield was observed.<sup>53</sup> Since then, extensive research has been conducted on the implementation of TiO<sub>2</sub> in photocatalytic CO<sub>2</sub> reduction under visible and UV irradiation, starting with the investigation of pristine TiO<sub>2</sub> and

its subsequent combination with diverse materials to assess the impact of metal doping.<sup>54–56</sup>

A case study was conducted on a porphyrin-based MOF, where we observed a notable enhancement in the photocatalytic conversion of CO<sub>2</sub> to CH<sub>3</sub>OH when Cu<sup>2+</sup> was introduced. The presence of Cu<sup>2+</sup> resulted in a remarkable sevenfold increase in the rate of CH<sub>3</sub>OH production compared to the sample without Cu<sup>2+</sup>.<sup>57</sup>

Other metal oxides, such as CeO<sub>2</sub>/Bi<sub>2</sub>MoO<sub>6</sub> nanocomposites, exhibit significant enhancements in specific surface area, visible light responsiveness, as well as improved efficiency in charge carrier separation and transfer compared to pure CeO<sub>2</sub> and pure Bi<sub>2</sub>MoO<sub>6</sub>.<sup>58</sup>

In 2018, Kavil *et al.*<sup>3</sup> conducted an experiment involving the production of CH<sub>3</sub>OH from CO<sub>2</sub> using two samples of polluted seawater. The system used TiO<sub>2</sub> (P25), C/TiO<sub>2</sub>, and Cu-C/TiO<sub>2</sub> doped catalysts under UV and visible light. Doping the photocatalyst with 3 wt% copper restricted the recombination of the electron-hole pair, and carbon modification reduced the TiO<sub>2</sub> band gap. Both modifications enhanced the photocatalytic reaction under UV and visible light. After 5 hours of UV light irradiation, the CH<sub>3</sub>OH yields were 2910 mol g<sup>-1</sup> and 2250 mol g<sup>-1</sup>. However, 5 hours of natural sunlight irradiation resulted in CH<sub>3</sub>OH yields of 990 mol g<sup>-1</sup> and 910 mol g<sup>-1</sup>. This difference has been attributed to the different concentrations of CH<sub>4</sub> in the samples. PSW-2 reported a quite high concentration of CH<sub>4</sub> (4.09 μM) compared to the PSW-1 (0.4 μM) system, and that is due to the presence of oxygen in the water samples. De-aeration caused a depletion of oxygen in PSW-1, producing methanogenic bacteria over CH<sub>3</sub>OH production.<sup>3</sup> The production process requires six H<sub>2</sub> radicals to reduce CO<sub>2</sub> to CH<sub>3</sub>OH (eqn (4)–(8)), and goes through the formation of formate radicals as reported below:



The final step, the conversion of HCOOH to CH<sub>3</sub>OH:



The experiment shown in (Fig. 5) was conducted using a stirred annular apparatus, including a glass reactor and CO<sub>2</sub> cylinder. The reactor was firmly connected to the CO<sub>2</sub> cylinder, and the polluted water samples were dosed at regular time intervals. The catalyst was added, and the glass reactor was purged with CO<sub>2</sub> for 60 minutes for saturation before light irradiation. The UV light was irradiated from all sides. Regarding the visible light experiment, the reactor was exposed to natural sunlight for 5 hours.

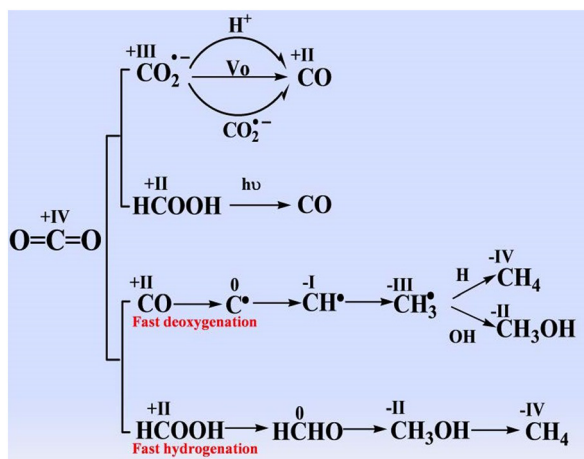


Fig. 4 Proposal of the reaction pathways for forming CO, CH<sub>4</sub>, and CH<sub>3</sub>OH in the photocatalytic CO<sub>2</sub> reduction. Reproduced with permission from ref. 52 under the terms of the CC BY 4.0 license.

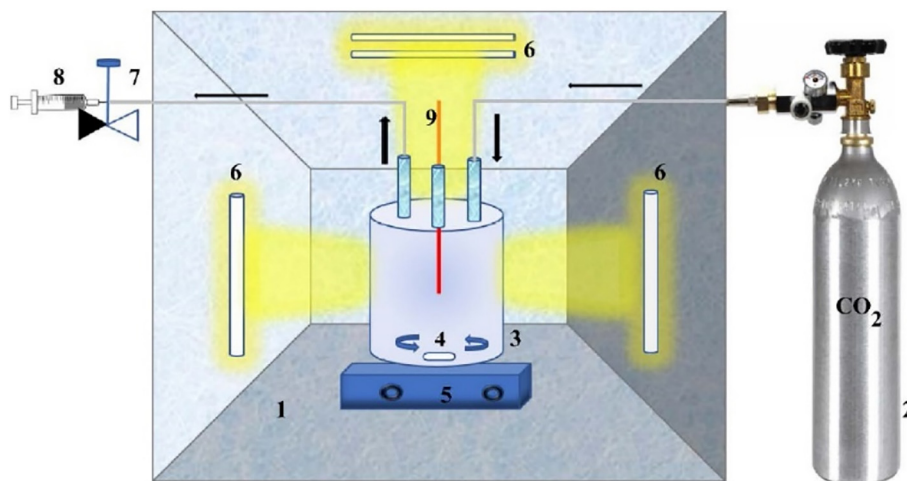


Fig. 5 Photocatalytic reduction diagram. Reproduced with permission from ref. 3 under the terms of the CC BY-NC-ND 4.0 license.

In the same year, Wang *et al.*<sup>59</sup> shed light on developing a photocatalyst capable of stably hydrogenating gaseous CO<sub>2</sub> to CH<sub>3</sub>OH at ambient pressure with high selectivity. They reported a defect-laden indium oxide, In<sub>2</sub>O<sub>3-x</sub>(OH)<sub>y</sub>, with a rod-like nanocrystal superstructure. Under simulated solar irradiation, this catalyst demonstrates a remarkable ability to hydrogenate CO<sub>2</sub> into CH<sub>3</sub>OH with an impressive selectivity of 50%, which is much higher than for the other photocatalysts at that time.

Cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) has also been employed for the photocatalytic production of CH<sub>3</sub>OH using aqueous carbon dioxide (CO<sub>2</sub> aq) under solar light of 100 mW cm<sup>-2</sup> without any sacrificial agent.<sup>60</sup> The aim of this experiment was to analyze the catalytic activity under ambient conditions of temperatures, pressures, and the quantity of CO<sub>2</sub> determined by the solubility of the gas in water at atmospheric pressure. Initially, the deionized water was saturated with CO<sub>2</sub> for one hour, followed by adding the photocatalyst to the CO<sub>2</sub> solution in a sealed reactor under stirring. The irradiation was conducted with a xenon lamp at ambient/room temperature for 6 hours. CH<sub>3</sub>OH was detected in the gas phase but not in the liquid phase, which is attributed to the fact that the solution temperature reached 35 °C and caused the CH<sub>3</sub>OH to evaporate. CH<sub>3</sub>OH was the only product detected at the end of the experiment. Two reaction pathways are associated with this experiment, shown in Fig. 6. When CO<sub>2</sub> dissolves in water, it forms two products: CO<sub>2</sub> (aq) and carbonic acid (H<sub>2</sub>CO<sub>3</sub>). As a result, CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub>, when reacting with protons (H<sup>+</sup>), form CH<sub>3</sub>OH as a final product. From different perspectives, both pathways have distinct advantages. In terms of concentration, the CO<sub>2</sub> (aq) pathway is favored because the concentration of CO<sub>2</sub> (aq) in solution is 500 times greater than that of H<sub>2</sub>CO<sub>3</sub> in solution. However, the carbonic acid pathway is preferred regarding the reduction potential because H<sub>2</sub>CO<sub>3</sub> has a more positive reduction potential.

Doping titania with metal nanoparticles represents a typical strategy to improve the performances of a photocatalyst. Shtyka

*et al.*<sup>61</sup> reported on an investigation of gas phase CO<sub>2</sub> reduction using a series of TiO<sub>2</sub> loaded with various metals (Pt, Pd, Ni, and Cu) under continuous flow mode.<sup>61</sup> The study stated that Pt and Ni (2%) emerged as the most active catalysts among all of the investigated options, exhibiting a higher CH<sub>3</sub>OH formation rate.

In the context of nanotechnologies, Kazemi Movahed *et al.*<sup>62</sup> performed a detailed study to thoroughly examine the preparation of copper oxide(i) nanoparticles on the nitrogen-doped carbon (N-C) rod-shaped core-shell nanostructure and its selective CO<sub>2</sub> reduction. CH<sub>3</sub>OH was detected as the primary product.<sup>62</sup> The photocatalytic activity of Fe<sub>3</sub>O<sub>4</sub>@N-C/Cu<sub>2</sub>O in CO<sub>2</sub> reduction was approximately four times greater than that of the Fe<sub>3</sub>O<sub>4</sub>@Cu<sub>2</sub>O photocatalyst. This could be attributed to the improved absorption of visible light and the more efficient separation of photogenerated electron-hole pairs.

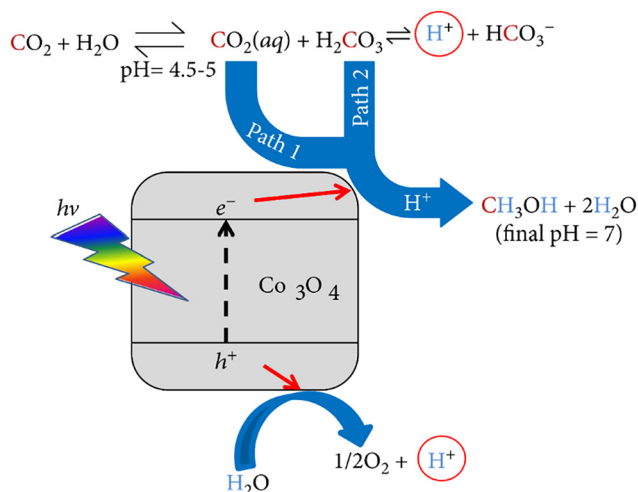


Fig. 6 Mechanism for the photocatalytic reduction of aqueous CO<sub>2</sub> in the presence of Co<sub>3</sub>O<sub>4</sub>. Reproduced with permission from ref. 60 under the terms of the CC BY 4.0 license.

In 2021, Albo & García<sup>63</sup> evaluated the performance of Mo<sub>2</sub>C/TiO<sub>2</sub> heterojunctions in the continuous photocatalytic reduction of CO<sub>2</sub> to CH<sub>3</sub>OH within a micro-optofluidic reactor, using both UV and visible LED lights (5 mW cm<sup>-2</sup>) for illumination. The doping effect of Mo<sub>2</sub>C on TiO<sub>2</sub> renders the composite material capable of exhibiting activity within the visible region compared to bare TiO<sub>2</sub>, and additionally, it affects the morphology of TiO<sub>2</sub>. When exposed to visible irradiation, these heterostructures demonstrate enhanced stability and recyclability in photocatalytic reactions. The experiment's results can be primarily attributed to the decreased bandgap energy, effective separation of electron-hole pairs, and enhanced interfacial conductivity.<sup>63</sup>

An interesting example focused on a copper-based photocatalyst is discussed by Xi *et al.*<sup>64</sup> Here, copper species with different valences are loaded onto TiO<sub>2</sub> through treatment in oxidizing and reducing atmospheres. These loaded species are referred as Cu/Ti(air) and Cu/Ti(H<sub>2</sub>). Towards CO<sub>2</sub> photoreduction, Cu/Ti(H<sub>2</sub>) demonstrated superior CH<sub>3</sub>OH yield and selectivity compared to Cu/Ti(air), and that is due to the generation of oxygen vacancies through the reducing atmosphere, resulting in the availability of surface-adsorbed hydroxyl protons and photo-electrons on Cu/Ti(H<sub>2</sub>).<sup>64</sup>

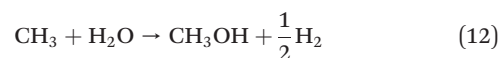
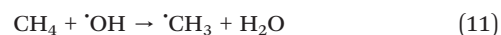
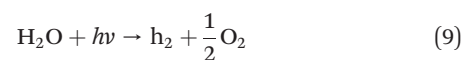
The photocatalytic reduction of CO<sub>2</sub> to CH<sub>3</sub>OH using bismuth-promoted BaTiO<sub>3</sub> was the focus of a recent study conducted by Dasireddy & Likoar.<sup>56</sup> The doping of Ba/Bi to titania increased the TiO<sub>2</sub> band gap and enhanced the photocatalytic activity, producing a yield of 5.95 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. The experiment demonstrated a high yield compared to other catalytic systems in the literature. Adding a metal ion acts as a photoelectron trap that reduces the recombination of electron-hole pairs. The experiment involved UV irradiation; the reactor was flushed with He to remove gas impurities such as trapped air. The main products associated with the experiment were carbon monoxide, H<sub>2</sub>, and CH<sub>3</sub>OH, plus trace amounts of other hydrocarbons.<sup>56</sup>

Not only metal oxide but also metal organic frameworks (MOFs) have been explored and analyzed in capturing CO<sub>2</sub> and its conversion into fuels with improved energy efficiency.<sup>65</sup> A metal-organic framework (MOF) is a crystalline material that consists of organic ligands coordinated with metal ions or clusters. MOFs possess a porous structure with high surface area, enabling them to adsorb efficiently and store gases or molecules. The study by Sonowal *et al.*<sup>66</sup> introduces the graphitic carbon nitride quantum dots-coupled Zr(IV)-based MOF composite (g-CNQDs@MOF) under visible light. The MOF composite (co-catalyst) exhibits excellent photochemical properties, which enhances the electronic conductance. As a result, the electron-hole separation was improved by extending the lifespan of photogenerated charge carriers on the surface of the composites. The presence of the excess electrons facilitated the rapid generation of catalytically active sites, resulting in the selective conversion of CO<sub>2</sub>. The yield of CH<sub>3</sub>OH was found to be 386 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> under visible light.<sup>66</sup> Significant advancements in this field (MOF-based composites) have resulted in a substantial increase in the CH<sub>3</sub>OH yield. N. Li

*et al.*<sup>67</sup> reported a method that involves encapsulating CuO quantum dots (QDs) within the pores of the metal-organic framework MIL-125(Ti) using a simple complexation-oxidation process. This composite photocatalyst is then formed by combination with g-C<sub>3</sub>N<sub>4</sub>, resulting in g-C<sub>3</sub>N<sub>4</sub>/CuO@MIL-125(Ti) with a CH<sub>3</sub>OH yield of 997.2 μmol g<sup>-1</sup>.<sup>67</sup>

Recently, a study was conducted by H. Yu *et al.*<sup>68</sup> where a novel multicomponent hetero-structure photocatalyst has been developed. It demonstrates the efficient and stable photoreduction of CO<sub>2</sub> in water, producing CH<sub>3</sub>OH as the primary product, using a triphase reaction system (gas-liquid-solid interfacial system). The catalyst developed was SrTiO<sub>3</sub> (LaCr)/Cu@Ni/SiO<sub>2</sub>/TiN. Observations point to the fact that the photocatalyst demonstrates exceptional light absorption capabilities and effectively separates charge carriers. In fact, the triphase interfacial system enhances the efficiency of photocatalytic CO<sub>2</sub> to CH<sub>3</sub>OH conversion by an impressive 50-fold compared to the diphasic interfacial system. This study successfully achieves the low-cost and highly efficient photocatalytic CO<sub>2</sub> reduction to CH<sub>3</sub>OH.<sup>68</sup> Table 3 provides a concise summary of the catalysts that have been investigated and reported concerning photocatalytic reduction.

**2.1.2 Photocatalytic partial oxidation of methane to methanol (POM).** One of the early explorations in the field of CH<sub>4</sub> photoconversion to CH<sub>3</sub>OH was conducted by Ogura & Kataoka in 1988.<sup>71</sup> The reaction introduced was water vapor and CH<sub>4</sub> at standard atmospheric pressure. The typical POM mechanism is shown in (eqn (9)–(12)) and Fig. 9. When water gets exposed to photons, it produces hydroxide radicals (·OH) (eqn (10)). The hydroxyl radical further reacts with CH<sub>4</sub> to form a methyl radical (·CH<sub>3</sub>) (eqn 11). The final step is the reaction of the methyl radical with water to form CH<sub>3</sub>OH (eqn 12). One promising catalyst for the photo-partial oxidation of CH<sub>4</sub> is TiO<sub>2</sub>, which has been extensively studied due to its high stability and photocatalytic activity.<sup>72,73</sup> Other catalysts, such as WO<sub>3</sub>, Bi<sub>2</sub>WO<sub>6</sub>, and ZnO, have also been investigated. The photocatalytic performance of these materials can be improved by doping with metal ions or modifying the surface.<sup>74–76</sup> A few review papers have been recently published on photo-partial oxidation of CH<sub>4</sub>, and we invite the reader to consult them for a deeper knowledge of the topic.<sup>48,77,78</sup>



In 2008, Y. Hu *et al.*<sup>79</sup> prepared catalysts containing V in MCM-41 (vanadium in MCM-41 mesoporous material) using



**Table 3** Performance of CO<sub>2</sub> reduction and its corresponding methanol yield

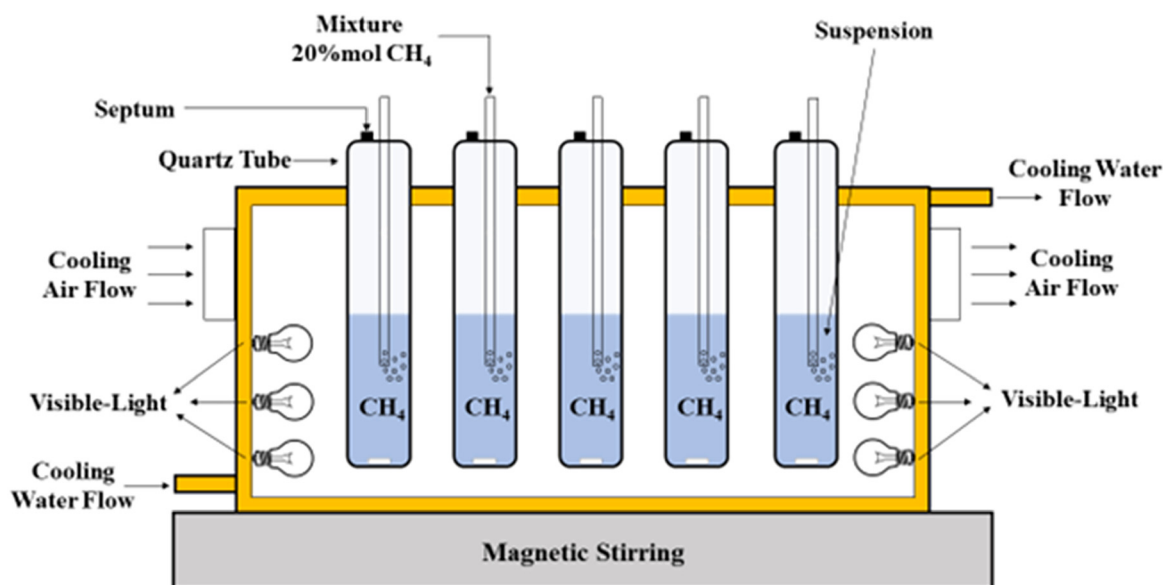
| Catalyst                                                   | Main products                                                                  | CH <sub>3</sub> OH yield ( $\mu\text{mol gcat}^{-1} \text{ h}^{-1}$ ) | Light irradiation | Ref. |
|------------------------------------------------------------|--------------------------------------------------------------------------------|-----------------------------------------------------------------------|-------------------|------|
| P25                                                        | CO                                                                             | 0.045                                                                 | Visible           | 54   |
| 20% FeTiO <sub>3</sub> /TiO <sub>2</sub>                   | CO, CH <sub>3</sub> OH, or CH <sub>4</sub>                                     | 0.43                                                                  | Visible           | 54   |
| g-C <sub>3</sub> N <sub>4</sub> /ZnO                       | CH <sub>3</sub> OH                                                             | 0.6                                                                   | Visible           | 69   |
| In <sub>2</sub> O <sub>3-x</sub> (OH) <sub>y</sub>         | —                                                                              | 60                                                                    | —                 | 70   |
| 3% Cu-C/TiO <sub>2</sub>                                   | CH <sub>3</sub> OH                                                             | 2910                                                                  | UV                | 3    |
| CeO <sub>2</sub> /Bi <sub>2</sub> MoO <sub>6</sub> (5C-BM) | CH <sub>3</sub> OH and C <sub>2</sub> H <sub>5</sub> OH                        | 32.5                                                                  | Visible           | 58   |
| CeO <sub>2</sub>                                           | CH <sub>3</sub> OH and C <sub>2</sub> H <sub>5</sub> OH                        | 5.1                                                                   | Visible           | 58   |
| Bi <sub>2</sub> MoO <sub>6</sub>                           | CH <sub>3</sub> OH and C <sub>2</sub> H <sub>5</sub> OH                        | 17.6                                                                  | Visible           | 58   |
| Fe <sub>3</sub> O <sub>4</sub> @N-C/Cu <sub>2</sub> O      | —                                                                              | 146.7                                                                 | Visible           | 62   |
| Cu <sub>2</sub> O/TiO <sub>2</sub>                         | CH <sub>3</sub> OH                                                             | 9–13                                                                  | UV                | 55   |
| Cu <sub>2</sub> O/TiO <sub>2</sub>                         | CH <sub>3</sub> OH                                                             | 12–70                                                                 | Visible           | 55   |
| Mo <sub>2</sub> C/TiO <sub>2</sub>                         | —                                                                              | 11.8                                                                  | UV-vis            | 63   |
| Cu/Ti(H <sub>2</sub> )                                     | —                                                                              | —                                                                     | Visible           | 64   |
| (g-CNQDs@MOF)                                              | —                                                                              | 386                                                                   | Visible           | 66   |
| BiO/TiO <sub>2</sub>                                       | CO, CH <sub>4</sub> , H <sub>2</sub>                                           | 0.52                                                                  | UV                | 56   |
| BaO/TiO <sub>2</sub>                                       | CO, CH <sub>4</sub> , H <sub>2</sub>                                           | 0.65                                                                  | UV                | 56   |
| BiTiO <sub>3</sub>                                         | CO, CH <sub>4</sub> , H <sub>2</sub> , CH <sub>3</sub> OH                      | 3.83                                                                  | UV                | 56   |
| BaTiO <sub>3</sub>                                         | CO, CH <sub>4</sub> , H <sub>2</sub> , CH <sub>3</sub> OH                      | 4.37                                                                  | UV                | 56   |
| BiO/BaTiO <sub>3</sub>                                     | CO, H <sub>2</sub> , CH <sub>3</sub> OH and CH <sub>4</sub>                    | 5.95                                                                  | UV                | 56   |
| Cu <sub>2</sub> O/TiO <sub>2</sub>                         | CO, CH <sub>4</sub> and CH <sub>3</sub> OH                                     | 53.75                                                                 | Full spectrum     | 64   |
| SrTiO <sub>3</sub> (LaCr)/Cu@Ni/SiO <sub>2</sub> /TiN      | CH <sub>3</sub> OH, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>4</sub> , and CO | 25.8                                                                  | Visible           | 68   |

a direct synthesis technique in both acidic and basic conditions, and through impregnation. The catalysts were subjected to UV irradiation at 295 K for the selective oxidation of methane with nitric oxide (NO) to evaluate their photocatalytic performance. Notably, the V-MCM-41 catalyst prepared in an acidic solution and impregnated V/MCM-41 exhibited the formation of CH<sub>3</sub>OH with high selectivity.<sup>79</sup>

The group of Murcia-López *et al.*<sup>80</sup> successfully synthesized and characterized photocatalysts based on bismuth for the first time, including Bi<sub>2</sub>WO<sub>6</sub>, BiVO<sub>4</sub>, and a coupled Bi<sub>2</sub>WO<sub>6</sub>/TiO<sub>2</sub>-P25. The photocatalysts were investigated with UV-visible radiation for their ability to

selectively oxidize methane to CH<sub>3</sub>OH. Among the photocatalysts obtained, BiVO<sub>4</sub> stands out as the most promising catalyst for this specific reaction, exhibiting superior selectivity towards CH<sub>3</sub>OH production and greater stability compared to the other catalysts.<sup>80</sup>

The Bi<sub>2</sub>O<sub>3</sub> photocatalyst was investigated by de Oliveira *et al.*,<sup>81</sup> for CH<sub>4</sub> reforming to CH<sub>3</sub>OH under visible light at ambient temperature and pressure. The production rate of CH<sub>3</sub>OH was approximately 3771  $\mu\text{mol g}^{-1} \text{ h}^{-1}$  and a selectivity of 65%. The photooxidation was conducted in a 150 mL homemade-quartz reactor (Fig. 7) at ambient conditions (25 °C and atmospheric pressure). A mass of 100 mg Bi<sub>2</sub>O<sub>3</sub> was

**Fig. 7** Experimental setup for the photocatalytic partial oxidation of CH<sub>4</sub> to CH<sub>3</sub>OH. Reproduced with permission from ref. 81.

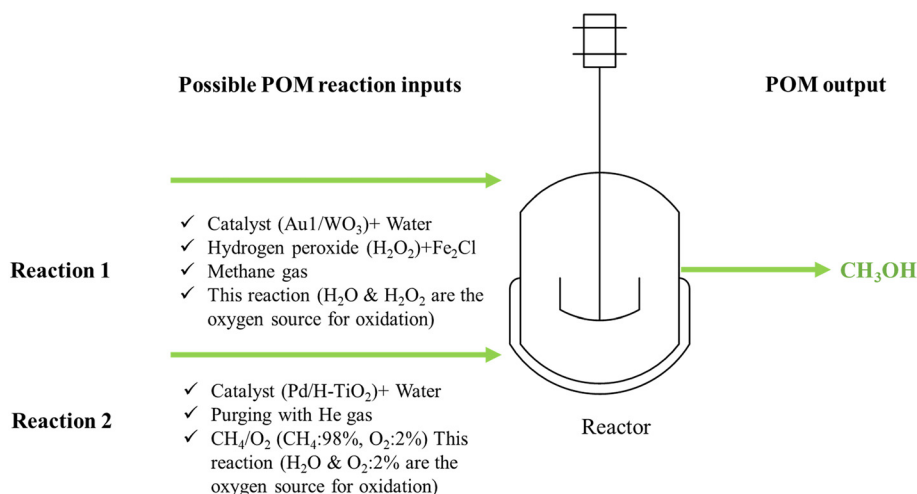


Fig. 8 Possible POM inputs with different reaction conditions.

added to 100 mL deionized water, along with purging the suspension with a  $\text{CH}_4$  mixture containing 20% mol  $\text{CH}_4$  in argon. The flow was interrupted and sealed with Teflon-lined caps after 30 minutes. The reaction was operated for 4 hours under six 18 W lamps.<sup>81</sup>

As discussed in the previous section, doping metal oxide with metal nanoparticles is a common strategy in photocatalysis. In this regard, a study was conducted on the photocatalytic conversion of  $\text{CH}_4$  to  $\text{CH}_3\text{OH}$  using tungsten trioxide with atomically dispersed gold.<sup>82</sup> The production rate of  $\text{CH}_3\text{OH}$  reached up to  $589 \mu\text{mol g}^{-1} \text{h}^{-1}$ . The light source was a 300 W xenon lamp providing visible light ( $\lambda \geq 420 \text{ nm}$ ). 20 mg of catalyst was dispersed in 20 mL deionized water, then 200  $\mu\text{L}$   $\text{H}_2\text{O}_2$  and  $\text{Fe}_2\text{Cl}$  (0.01 M, 2 mL) were added to the catalyst solution to obtain the precursor solution. The precursor solution was placed in the reactor. Thereafter, the reactor was purged by  $\text{CH}_4$  to remove  $\text{O}_2$  and air. Then,  $\text{CH}_4$  was introduced at a pressure of 2 MPa, and the reaction was held at 25 °C for 1 hour. After cooling down the system, the products were evaluated using an ice bath for 1 h to recondense potential  $\text{CH}_3\text{OH}$  vapors.

Similarly, X. Zhang *et al.*<sup>83</sup> developed a hollow porous Pd/H-TiO<sub>2</sub> photocatalyst to perform the successful photocatalytic oxidation of  $\text{CH}_4$  using  $\text{O}_2$  gas. The experiment was held under mild conditions and light irradiation. The resulting production rate of  $\text{CH}_3\text{OH}$  was found to be  $4500 \mu\text{mol g}^{-1} \text{h}^{-1}$ , with a selectivity of up to 70%. To perform the experiment, 10 mg catalyst was dispersed with 60 mL  $\text{H}_2\text{O}$  and placed into a stainless-steel reactor with a quartz window. After purging He gas,  $\text{CH}_4/\text{O}_2$  ( $\text{CH}_4$ : 98%,  $\text{O}_2$ : 2%) was introduced to the reactor, followed by light irradiation using a 300 W xenon lamp.<sup>83</sup>

To enhance efficiency and achieve successful  $\text{CH}_3\text{OH}$  production, modifications to the reaction conditions can be made, as indicated in Fig. 8.

Recently, J. Wang *et al.*<sup>85</sup> conducted a photocatalytic conversion of  $\text{CH}_4$  to  $\text{CH}_3\text{OH}$  under mild conditions, using BiOCl with oxygen vacancies under visible light irradiation in NaCl aqueous solution with  $\text{H}_2\text{O}_2$  to promote the oxidation. The  $\text{CH}_3\text{OH}$  production rate was  $180.75 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$  with 80.07% selectivity. Prior to the reaction, a mixture of  $\text{CH}_4$  (10%) and nitrogen (90%) was continuously purged through the reactor for 30 minutes under dark conditions to eliminate any atmospheric air. Ultimately, the reactor was sealed and exposed to a 500 W xenon lamp for one hour.<sup>85</sup>

Another recent interesting study was reported by Du *et al.*<sup>86</sup> using AuFe-ZnO as a bifunctional catalyst. The study yielded  $1365 \mu\text{mol g}^{-1} \text{h}^{-1}$  with high selectivity of  $\text{CH}_3\text{OH}$  up to 90.7%. The reaction was performed in a 100 mL autoclave reactor with a quartz window, with 40 mg of photocatalyst dispersed in 20 mL of water. The reactor was then pressurized with 2 bar  $\text{O}_2$  and 18 bar  $\text{CH}_4$  after being purge-gassed with oxygen ( $\text{O}_2$ ) multiple times to remove air. The photocatalytic reaction was irradiated using a 300 W Xe lamp at 20 °C. After the reaction, the mixture was cooled to 10 °C.<sup>86</sup> Table 4 outlines a comprehensive collection of catalysts investigated and reported in the context of POM reactions.

**2.1.3 Challenges and potential solutions.** Herein, we list the main challenges and linked solutions for  $\text{CO}_2$  reduction and partial oxidation of  $\text{CH}_4$  to  $\text{CH}_3\text{OH}$  in Table 5.

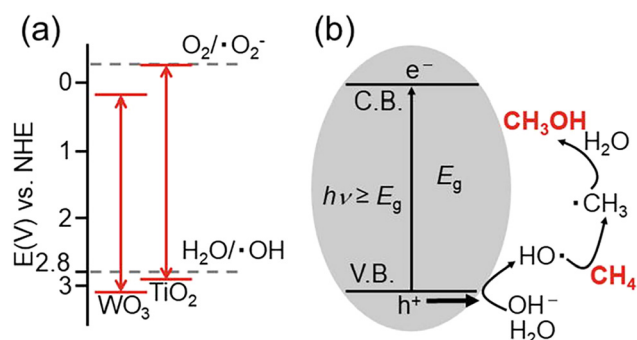


Fig. 9 Typical photocatalytic partial oxidation of methane to methanol mechanism catalyzed by metal oxide. (a) Redox potentials of  $\text{WO}_3$  and  $\text{TiO}_2$ . (b) Mechanism of the conversion of  $\text{CH}_4$  to  $\text{CH}_3\text{OH}$  by photocatalytic reaction. Adapted with permission from ref. 84 under the terms of the CC BY 3.0 license.

**Table 4** Performance of POM catalysts and its methanol yield and selectivity

| Catalyst                                       | Temperature | Product                                                                                                                       | Yield $\mu\text{mol g}^{-1} \text{h}^{-1}$ | Selectivity | Ref. |
|------------------------------------------------|-------------|-------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|-------------|------|
| WO <sub>3</sub> /F                             | 55 °C       | CH <sub>3</sub> OH, C <sub>2</sub> H <sub>6</sub> , CO <sub>2</sub>                                                           | —                                          | 17.90%      | 75   |
| WO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> | 55 °C       | CH <sub>3</sub> OH, C <sub>2</sub> H <sub>6</sub> , CO <sub>2</sub>                                                           | —                                          | 13.70%      | 75   |
| WO <sub>3</sub> /Fe <sup>3+</sup>              | 55 °C       | CH <sub>3</sub> OH, C <sub>2</sub> H <sub>6</sub> , CO <sub>2</sub>                                                           | 67.5                                       | 58.50%      | 76   |
| WO <sub>3</sub>                                | 55 °C       | CH <sub>3</sub> OH, C <sub>2</sub> H <sub>6</sub> , CO <sub>2</sub>                                                           | 27.1                                       | 46%         | 76   |
| 0.12 wt% Au/TiO <sub>2</sub>                   | 25 °C       | CH <sub>3</sub> OH                                                                                                            | 150                                        | 30%         | 72   |
| FeOOH/m-WO <sub>3</sub>                        | 25 °C       | CH <sub>3</sub> OH, C <sub>2</sub> H <sub>6</sub> , and CO <sub>2</sub>                                                       | 211.2                                      | 91%         | 74   |
| Co–SrTiO <sub>3</sub>                          | 80 °C       | —                                                                                                                             | 1840                                       | 98.7%       | 73   |
| Bi <sub>2</sub> O <sub>3</sub>                 | 25 °C       | CH <sub>3</sub> CH <sub>2</sub> OH, CH <sub>3</sub> CO <sub>2</sub> H, (CH <sub>3</sub> ) <sub>2</sub> CO, CH <sub>3</sub> OH | 3771                                       | 65%         | 81   |
| Au <sub>1</sub> /WO <sub>3</sub>               | 25 °C       | CH <sub>3</sub> OH, HCHO                                                                                                      | 589                                        | 75%         | 82   |
| BiOCl                                          | 25 °C       | CH <sub>3</sub> OH, HCOOH                                                                                                     | 180.75                                     | 80.07%      | 85   |
| Pd/H–TiO <sub>2</sub>                          | 45 °C       | CO <sub>2</sub> , HCHO, CH <sub>3</sub> OH                                                                                    | 4500                                       | 70%         | 83   |
| AuFe–ZnO                                       | 20 °C       | CH <sub>3</sub> OOH, HCHO, HCOOH, CO, and CO <sub>2</sub>                                                                     | 1365                                       | 90.7%       | 86   |

**2.1.4 Research gaps.** The following research gaps shown in Fig. 10 are identified based on the previous literature work.<sup>47,87,88</sup>

Catalyst development is a critical area requiring further research and development. Although several catalysts have been reported, they often suffer from low selectivity, stability, or activity. Additional research is required to design catalysts with properties such as high efficiency, enduring stability, fast kinetics, high selectivity, and low manufacturing cost. Moreover, understanding the mechanism of the reaction is crucial, and the specific reaction pathways lack clear understanding. Further research and evaluation are needed to identify the intermediates involved in the reaction, their stability, and their role in the overall reaction. For example, carbon-based materials are unique and can function as light absorbers, catalysts, or both, owing to their electronic properties and intrinsic high charge transport. Additional work is required to fully understand the advantages of carbon-based support and viability (cost).

The effect of light on the reaction mechanism is not adequately perceived. A deeper exploration is mandatory to understand the effect of different wavelengths of light on the reaction rate and selectivity. In terms of energy efficiency, although the process has the potential to use renewable energy sources such as solar energy, the overall energy efficiency of the process is often low. Extended research efforts are necessary to develop systems that

efficiently produce CH<sub>3</sub>OH using renewable energy sources. For this reason, future studies should focus more on the life cycle assessment. A comprehensive life cycle of CO<sub>2</sub> photoreduction and POM technologies is required. This includes assessing the environmental impact of the entire process, from the extraction of raw materials to the disposal of waste products. Such an assessment will help identify the potential environmental benefits and limitations.

Scaling up is another area of concern for photocatalytic technologies. When seeking sustainable and renewable methods alternative to conventional processes, the following should be considered: stability, durability, and economic viability related to the reaction and the process in general. Extended research efforts are necessary to address these knowledge gaps. An attractive approach could be integrating photocatalytic CO<sub>2</sub> conversion with other processes, such as CO<sub>2</sub> capture and storage, to create a complete carbon capture and utilization system.

## 2.2. Photocatalytic reduction of CO<sub>2</sub> to formic acid.

HCOOH is a commonly used chemical raw material characterized by relatively non-toxic and non-corrosive properties.<sup>89</sup> As a result, it is considered a source of H<sub>2</sub> or CO that is safe, easy to handle, and transport for a variety of reactions, especially in fuel generation.<sup>89,90</sup> Furthermore, it can be used as important

**Table 5** The challenges associated with CO<sub>2</sub> reduction and partial oxidation of methane to methanol and possible solutions

| Challenges                                                                                                                                                                                                                                                                                   | Solutions                                                                                                                                                                                                                                         |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"> <li>Insufficient catalytic stability</li> <li>Fast recombination of electron-hole pair, large band gap</li> </ul>                                                                                                                                         | <ul style="list-style-type: none"> <li>✓ Use and modify catalysts with high surface area and high porosity</li> <li>✓ Doping the catalysts with metals, metal oxides, and non-metals or using metal-organic framework (MOFs) catalysts</li> </ul> |
| <ul style="list-style-type: none"> <li>Lack of selectivity</li> </ul>                                                                                                                                                                                                                        | <ul style="list-style-type: none"> <li>✓ The use of innovative reactors and optimizing reaction conditions (temperature, pressure, and light intensity)</li> <li>✓ Introducing additional oxygen sources</li> </ul>                               |
| <ul style="list-style-type: none"> <li>In case of using polluted seawater, oxygen depletion causes the production of methanogenic bacteria over CH<sub>3</sub>OH production</li> <li>Low CH<sub>3</sub>OH yield</li> </ul>                                                                   | <ul style="list-style-type: none"> <li>✓ Use the suitable catalyst dosage while improving the light absorption properties of the material</li> </ul>                                                                                              |
| <ul style="list-style-type: none"> <li>Very high catalyst concentration can reduce CH<sub>3</sub>OH yield due to the turbidity of suspension, which stops the light source from penetrating, whereas surface agglomeration diminishes the active sites available for the reaction</li> </ul> | <ul style="list-style-type: none"> <li>✓ Observe the effect of increasing catalyst dosage on the CH<sub>3</sub>OH yield until you examine a decrease in the CH<sub>3</sub>OH yield</li> </ul>                                                     |

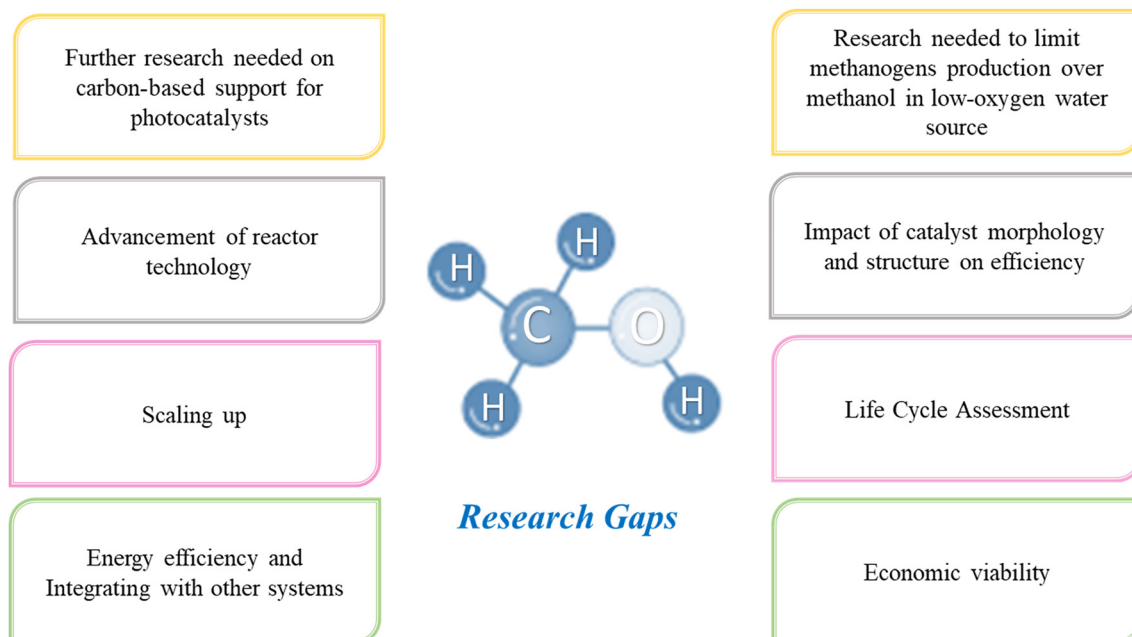


Fig. 10 Knowledge gaps related to the photocatalytic production of methanol.

feedstock to produce  $\text{CH}_3\text{OH}$  and other fine chemicals, plus it can substitute other inorganic acids as it is considered as the less corrosive among them.

$\text{HCOOH}$  is one of the valuable derivatives of  $\text{CO}_2$  reduction.<sup>89</sup> It can be produced through a photocatalytic reaction of  $\text{CO}_2$  in the presence of water and a photocatalyst (semiconductors doped with other substances), as shown in Fig. 5. Various products can be generated through  $\text{CO}_2$  photoconversion, which can occur *via* distinct mechanisms, as illustrated in Fig. 11. In general,  $\text{HCOOH}$  and  $\text{CO}$  are the most generated products from the  $\text{CO}_2$  reduction process.<sup>91</sup>

Back in 1989, an important study by Aliwi and Al-Jubori<sup>93</sup> was revealed to the scientific community as it revealed one of the earliest investigations into the world of photocatalytic  $\text{CO}_2$  reduction to  $\text{HCOOH}$ . The photoreduction uses metal

sulfide semiconductors ( $\text{n-Bi}_2\text{S}_3$  and  $\text{n-CdS}$ ) in the presence of  $\text{H}_2\text{S}$ . The presence of hydrogen sulfide was found to increase the rate of the photoreduction processes. This study holds significant interest; however, to what extent can  $\text{H}_2\text{S}$  be safely used and handled due to its toxic properties, even at relatively low concentrations? This is why the attention has been focused on developing more safe and sustainable oxide-based photocatalysts (Table 6).

A study by Maeda *et al.*<sup>94</sup> successfully showcased the capability of a polymeric carbon nitride semiconductor in the photocatalytic conversion of  $\text{CO}_2$  into  $\text{HCOOH}$  under visible light. This process exhibits exceptional performance metrics, including a selectivity of  $>80\%$  achieved by combining the semiconductor with a molecular ruthenium complex acting as a catalyst.<sup>94</sup>

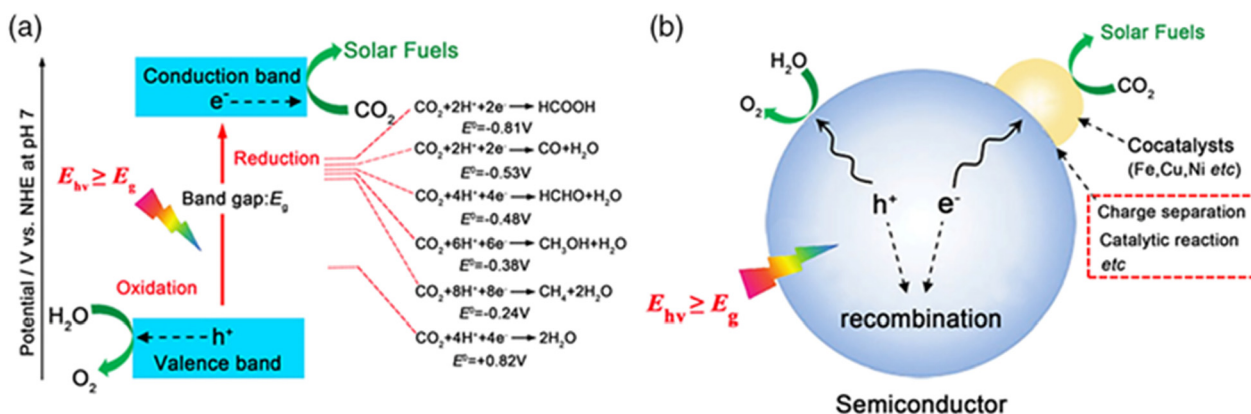


Fig. 11 Schematic diagram of the photocatalytic reduction of  $\text{CO}_2$  to solar fuels. (a) Energy diagram for  $\text{CO}_2$  reduction and water oxidation on a semiconductor. (b) Schematic of the photocatalytic reaction process and influencing factors. Reproduced with permission from ref. 92 under the terms of the CC BY-NC-ND 4.0 license.



**Table 6** Performance of catalysts for CO<sub>2</sub> reduction to formic acid

| Catalyst                                                | Temperature | Product                      | Yield (HCOOH)                                                      | Ref. |
|---------------------------------------------------------|-------------|------------------------------|--------------------------------------------------------------------|------|
| TiO <sub>2</sub> -CuPc                                  | 25 °C       | HCOOH                        | 208.5 μmol g <sup>-1</sup> h <sup>-1</sup>                         | 102  |
| PdAu@Fe <sub>2</sub> Mn-MOF                             | 25 °C       | HCOOH                        | 725 μmol g <sup>-1</sup>                                           | 98   |
| InPc                                                    | 26 °C       | Formate                      | —                                                                  | 96   |
| H-TiO <sub>2</sub>                                      | —           | HCOOH-CO                     | —                                                                  | 97   |
| α-FeOOH/Al <sub>2</sub> O <sub>3</sub>                  | 25 °C       | HCOOH, CO and H <sub>2</sub> | —                                                                  | 100  |
| Ru-N <sub>2</sub> CTF                                   | —           | Formate                      | 2090 μmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (formate) | 101  |
| N-TiO <sub>2</sub> /CuO                                 | 50 °C       | HCOOH, H <sub>2</sub>        | 33 μmol g <sup>-1</sup> min <sup>-1</sup>                          | 99   |
| TiO <sub>2</sub> /CuO                                   | 50 °C       | HCOOH, H <sub>2</sub>        | 26 μmol g <sup>-1</sup> min <sup>-1</sup>                          | 99   |
| N-TiO <sub>2</sub> /CeO <sub>2</sub> /CuO               | 50 °C       | HCOOH, H <sub>2</sub>        | 28 μmol g <sup>-1</sup> min <sup>-1</sup>                          | 99   |
| N-TiO <sub>2</sub> /CeO <sub>2</sub>                    | 50 °C       | HCOOH, H <sub>2</sub>        | 2 μmol g <sup>-1</sup> h <sup>-1</sup>                             | 99   |
| TiO <sub>2</sub> /CeO <sub>2</sub> /CuO                 | 50 °C       | HCOOH, H <sub>2</sub>        | 25 μmol g <sup>-1</sup> min <sup>-1</sup>                          | 99   |
| TiO <sub>2</sub>                                        | 50 °C       | HCOOH, H <sub>2</sub>        | 0.9 μmol g <sup>-1</sup> min <sup>-1</sup>                         | 99   |
| g-C <sub>3</sub> N <sub>4</sub> /(Cu/TiO <sub>2</sub> ) | 25 °C       | HCOOH, CH <sub>3</sub> OH    | 3500 μmol g <sup>-1</sup> h <sup>-1</sup>                          | 103  |

A comprehensive study was conducted by Nakada *et al.*<sup>95</sup> to examine the photophysical, photochemical, and photocatalytic capabilities of a binuclear complex (RuReCl) containing a Ru(II) photosensitizer and a Re(I) catalyst unit connected by a bridging ligand in aqueous solution. Remarkably, RuReCl demonstrated its ability to catalyze the reduction of CO<sub>2</sub> using ascorbate as an electron donor. Notably, HCOOH was the main product generated from the photocatalytic reaction in the aqueous solution.<sup>95</sup>

In 2020, a study by Omadoko *et al.*<sup>96</sup> provided insights into the conversion of carbon dioxide into HCOOH under acidic conditions and formate under basic or neutral conditions. The method employed photoreduction, utilizing an affordable setup comprising titanium dioxide, metal phthalocyanines (PC), and an inexpensive incandescent source. It was found that InPC exhibits a more significant generation of formate when compared to NiPC, ZnPC, and CuPC, resulting in a higher quantity of formate production. This can be attributed to the lowest degree of aggregation of InPC promoting electron transfer reactions.

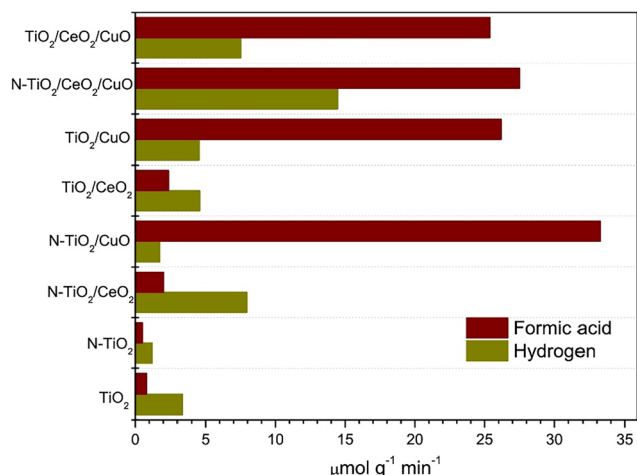
Instead, H. Zhang *et al.*<sup>97</sup> investigated HCOOH production using a different approach: the hydride transfer pathway for the photocatalytic reduction of CO<sub>2</sub> on TiO<sub>2</sub>. In this experiment, using UV light, hydrogenated TiO<sub>2</sub> functions as a hydride donor for the selective reduction of CO<sub>2</sub>. The experiment involved treating TiO<sub>2</sub> with both argon (Ar) and H<sub>2</sub>. Ar-treated TiO<sub>2</sub> produced CO and hydrogen-treated generated HCOOH as a product. Electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS) analyses illustrated that the O-vacancy was predominant on Ar-treated TiO<sub>2</sub>, while the H<sub>2</sub>-treated TiO<sub>2</sub> exhibited H on the surface. The findings prove that hydrogenation can generate hydride-like sites, allowing TiO<sub>2</sub> to function as a hydride reagent to directly participate in the CO<sub>2</sub> photocatalytic reduction process to HCOOH. The hydride transfer (H<sup>-</sup>) to CO<sub>2</sub> enhances the C-H bond formation and the HCOOH production. However, hydride transfer may not be restricted to CO<sub>2</sub> reduction; it can also be implemented in the H<sub>2</sub> evolution process in further studies.<sup>97</sup>

The advent of MOFs also played a role in the photoconversion of CO<sub>2</sub> to HCOOH. Mori *et al.*<sup>98</sup> documented

the results of the photoreduction of CO<sub>2</sub> to formic acid by Fe-based MOFs. The study examined how heteroatom doping and the confinement of Pd alloy nanoparticles (NPs) influenced an amine-functionalized Fe-based metal organic framework (Fe<sub>3</sub>-MOF). It was observed that the electron-hole separation efficiency of the photocatalysts was enhanced through the incorporation of Pd and Au NPs, which acted as electron scavengers for excited electrons. The research paper revealed that the HCOOH production of PdAu@Fe<sub>2</sub>Mn-MOF was 3.6 times higher than that of the unmodified Fe<sub>3</sub>-MOF.<sup>98</sup>

Mixed oxide composite catalysts have been investigated by Ibarra-Rodriguez *et al.*<sup>99</sup> In their work, the photocatalytic reduction of CO<sub>2</sub> to produce HCOOH and H<sub>2</sub> with visible light using activated N-TiO<sub>2</sub>/CeO<sub>2</sub>/CuO composites was assessed. Specifically, the ternary titania-based compounds were synthesized by implementing two steps, pure and nitrogen-doped titanium dioxide, followed by adding 3% wt of cerium and copper oxide particles. Due to the synergy effect of the urea precursor, the nitrogen-doped composite resulted in a higher surface area. A mixed valence state of Ti and the presence of oxygen vacancies was observed during the characterization, which is responsible for the higher adsorption of the desired molecules. N-TiO<sub>2</sub>/CuO generated the highest HCOOH yield (33 μmol g<sup>-1</sup> min<sup>-1</sup>), as indicated in Fig. 12, with better CO<sub>2</sub> adsorption capacity and following a Z-scheme where the charges are efficiently separated. On the other hand, adding the CeO<sub>2</sub> co-catalyst reduced the HCOOH yield due to its affinity towards adsorbing CO<sub>3</sub><sup>2-</sup> and OH ions that could occupy the active sites. However, N-TiO<sub>2</sub>/CeO<sub>2</sub>/CuO results in the maximum production of H<sub>2</sub> due to its highest Ti<sup>3+</sup>/Ti<sup>4+</sup> valence state ratio, resulting in more active sites for water adsorption, and therefore, the production of H<sub>2</sub>. The experiment was conducted at room temperature; the composite powder was added to the water, followed by the addition of CO<sub>2</sub> gas to the solution for 15 minutes in a batch reactor. The system's pressure was 2 psi and irradiated for three hours using two xenon lamps.<sup>99</sup>

The findings of a study reported by An *et al.*<sup>100</sup> offer fresh insights into employing a recyclable solid catalyst with an appropriate support material that constitutes a different approach for catalyst activation in achieving selective CO<sub>2</sub>



**Fig. 12** Formic acid and hydrogen yields reported for different metal oxide composites. Reproduced with permission from ref. 99 under the terms of the CC BY-NC-ND 4.0 license.

reduction. This group presented a widely available soil mineral alpha-iron(III) oxyhydroxide ( $\alpha$ -FeOOH; goethite) that was loaded onto an  $\text{Al}_2\text{O}_3$  support, and tested under visible light. The reaction was conducted in the presence of a  $\text{Ru}^{\text{II}}$  photosensitizer and 1-benzyl-1,4-dihydronicotinamide (BNAH) as an electron donor.<sup>100</sup>

Recently, building upon prior research, Wang *et al.*<sup>101</sup> embarked on an experimental work that expanded our understanding of the negative impact of uncontrolled and non-uniformly dispersed active sites on the selectivity and activity. The authors introduced a novel *in situ* covalent-bonding approach to integrate the precisely defined single-site  $\text{Ru-N}_2$  species into conjugated covalent triazine frameworks (CTFs) for achieving a remarkably selective photoreduction of  $\text{CO}_2$ . The resultant  $\text{Ru-CTF}$  structure was found to enhance the charge separation and provide stability to the molecular catalyst, thereby facilitating a solar-to-formate conversion.<sup>101</sup> Table 6 presents a concise compilation of the catalysts examined and reported in studies focusing on the photocatalytic  $\text{CO}_2$  reduction to HCOOH.

**2.2.1 Challenges and potential solutions.** Within this section, Table 7 is presented, highlighting the primary challenges involved in the reduction of  $\text{CO}_2$  to HCOOH.

**2.2.2 Research gaps.** The following research gaps are identified based on the previous literature work as shown in Fig. 13.

The effectiveness of direct HCOOH production using photons *versus* the generation of electrons through photovoltaics followed by electro-catalyst use for HCOOH depends on various factors, including efficiency, cost, and application requirements. Since both approaches are under development, several criteria should be investigated, such as the efficiency of the process, the ability of both processes to meet the industrial demand, and the technological maturity. Additionally, one of the most important factors is the environmental impact. Hence, evaluating factors such as the carbon footprint, energy consumption, and the potential environmental impacts, including the generation of pollutants or by-products, associated with each method can contribute to assessing the sustainability and desirability of the production approach.

Further development of the large-scale photoreduction of  $\text{CO}_2$  and assessing the feasibility of the photoreactors require careful consideration of various factors, the availability of the light source, the cost, energy consumption, process control and automation (reaction conditions), and maintenance. Moreover, understanding the reaction kinetics and efficient mass transfer is vital as it directly influences the process efficiency and the resulting products.

### 2.3. Ammonia production through nitrogen photofixation

$\text{NH}_3$  is a widely used chemical fertilizer that has significantly raised agricultural output worldwide.<sup>104</sup> It is a significant energy carrier that can easily be condensed, stored, and transported. Due to its high  $\text{H}_2$  density (17.6 wt%) and low liquefying pressure,  $\text{NH}_3$  is also a promising  $\text{H}_2$  source. It can potentially be a significant focal point in a future  $\text{H}_2$  economy.  $\text{H}_2$  can be easily extracted from  $\text{NH}_3$  when needed. On the other hand, the current Haber-Bosch process, which produces  $\text{NH}_3$  through the catalytic synthesis of  $\text{H}_2$  and  $\text{N}_2$  over an iron-based catalyst, is not long-term viable because it requires high temperatures (400–500 °C) and high pressures (150–250 bar), using enormous amounts of fossil fuels and generating a lot of  $\text{CO}_2$ .<sup>105</sup> Nitrogen photofixation is the reaction of nitrogen gas (or nitrate) in the presence of water, catalyzed by a semiconductor and light. It generally occurs at

**Table 7** The challenges associated with  $\text{CO}_2$  reduction to HCOOH and possible solutions

| Challenges                                                                                                                                                                                                                                                                             | Solutions                                                                                                                                                                                                                                                                                                    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"> <li>Low production efficiency</li> </ul>                                                                                                                                                                                                            | <ul style="list-style-type: none"> <li>✓ Developing photocatalysts with high surface area, fast separation of charges, long charge lifetime, efficient light absorption, and appropriate band gap</li> <li>✓ Tuning the reaction conditions and better understanding the single reaction pathways</li> </ul> |
| <ul style="list-style-type: none"> <li>Controlling the <math>\text{CO}_2</math> reduction pathway for CO and HCOOH is challenging since they are key elements in producing other hydrocarbons</li> <li>Developing an efficient photocatalyst with co-catalyst modifications</li> </ul> | <ul style="list-style-type: none"> <li>✓ CuO has shown a high affinity for <math>\text{CO}_2</math>, designing a catalyst able to activate the hydride transfer pathway (<math>\text{H}^-</math>) instead of proton transfer</li> </ul>                                                                      |

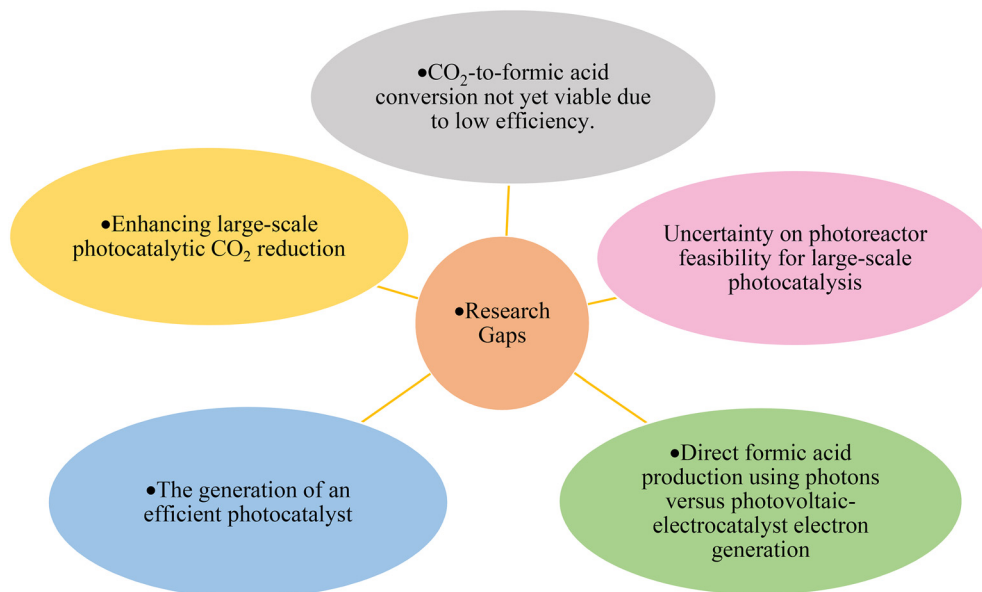
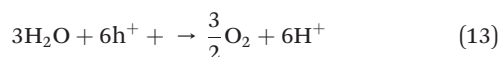
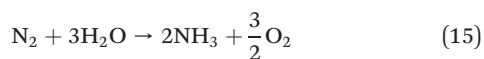


Fig. 13 Research gaps associated with CO<sub>2</sub>-to-formic acid conversion.

ambient conditions, reducing the environmental impact associated with the Haber–Bosch process. The general mechanism of nitrogen fixation involves the reaction of water with photo-generated holes ( $h^+$ ) (eqn (13)), producing oxygen and protons ( $H^+$ ), followed by the reaction of nitrogen ( $N_2$ ), protons ( $H^+$ ) and electrons to produce  $NH_3$  (eqn (14)).<sup>106</sup>



The overall reaction of ammonia production (eqn (15))



Tungsten oxides and tungsten trioxide ( $WO_3$ ) were introduced earlier in 1986 by Endoh *et al.*<sup>107</sup> in a heterogeneous photoreduction of nitrogen to produce ammonia. The reaction occurred by exposing moist  $N_2$  to  $WO_3$  or sub stoichiometric  $WO_{3-x}$ , or using sub stoichiometric tungsten oxide dispersions in  $N_2$ -saturated aqueous solutions.<sup>107</sup> Later, tungsten trioxide was modified and used in conjunction with other doping materials and different reaction conditions, for example using  $C/WO_3-H_2O$ , as reported previously.<sup>108</sup>

An interesting experimental approach was introduced in 2014 by Oshikiri *et al.*,<sup>109</sup> involving the plasmon-induced technique for  $NH_3$  synthesis using visible light irradiation, as shown in Fig. 14, at room temperature. It involved a strontium titanate ( $SrTiO_3$ ) semiconductor photoelectrode loaded with gold (Au) nanoparticles and doped with 0.05 wt.% niobium ( $Nb-SrTiO_3$ ). The photoelectrochemical

reaction cell is split into two-section chambers to provide an efficient separation between the oxidized products (on the anodic side) and reduced (on the cathodic side), enhancing the  $NH_3$  formation. The rate of formation of  $NH_3$  is  $0.231 \text{ nmol h}^{-1}$ .<sup>109</sup>

The use of graphitic carbon nitride ( $g-C_3N_4$ ) in combination with other composites has generated significant interest in nitrogen photofixation, as demonstrated in various experimental studies over the last decade.<sup>110–114</sup> Notably, the reported yield using  $g-C_3N_4$  composites surpasses that of other photocatalysts, highlighting its promising potential in this field.

$N_2$  gas is not the only feedstock for the production of ammonia. The reduction of nitrate has also been explored. Tong *et al.*<sup>115</sup> reported on the photocatalytic synthesis of  $NH_3$  by the reduction of nitrate ( $NO_3^-$ ) under UV irradiation, using a  $PdSn/NiO/NaTaO_3:La$  photocatalyst in the presence of  $HCOOH$  in an aqueous solution. Nitrate is used because it is one of the most widespread water contaminants. It is hazardous to both human health and the ecosystem. Several factors were evaluated, including the initial concentration and pH of nitrate, plus the co-catalyst loading. The photocatalyst was doped with 5% bimetallic  $PdSn$  and 0.2%  $NiO$  loadings. This was done to achieve a high efficiency of  $NH_3$  production due to the efficient electron-hole pair separation of  $PdSn$  acting as an electron trap and the strong affinity of  $NiO$  to adsorb nitrite.

Moreover, aqueous  $HCOOH$  was adopted as a hole scavenger due to its strong reducing property, the ability to supply carboxyl anion radicals for nitrate reduction, and *in situ* buffer effect on  $NH_3$  reduction. This resulted in a remarkable nitrogen conversion, reaching 100% and  $NH_3$  selectivity of 72% within 2 hours. The experiment was carried out in an immersion well reactor connected to a

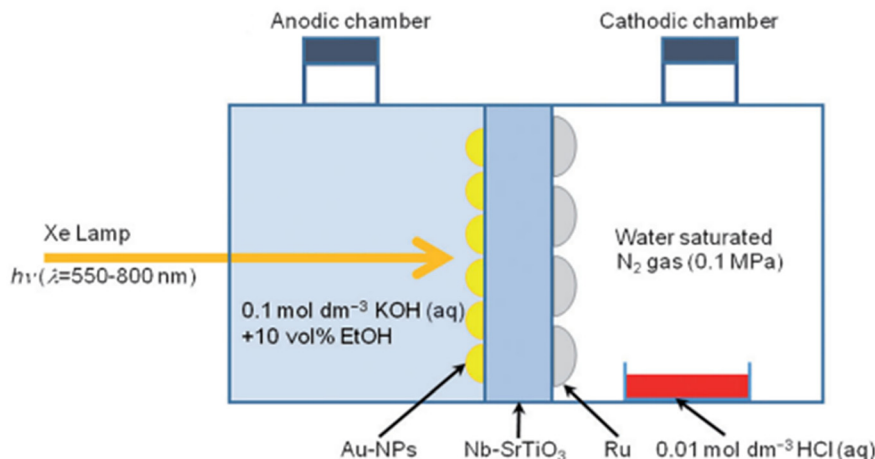


Fig. 14 Schematic of a plasmon-induced device for the photoelectrochemical synthesis of ammonia. Reproduced with permission from ref. 109. Copyright John Wiley & Sons.

closed gas circulation system, including a high-pressure mercury lamp as the light source. The temperature remained constant at 5 °C.<sup>115</sup>

Other studies have emphasized the crucial significance of oxygen vacancies in enhancing the photocatalytic reaction, as reported by ref. 116 and 117. G. Zhang *et al.*<sup>117</sup> specifically investigated the role of oxygen vacancies in TiO<sub>2</sub>. One can observe a substantial difference in the yield between TiO<sub>2</sub> and oxygen vacancies compared to another study by Walls *et al.* using a Pd-TiO<sub>2</sub> photocatalyst.<sup>118</sup>

Photocatalytic nitrogen fixation was investigated using Bi/InVO<sub>4</sub> by Dong *et al.*<sup>119</sup> They found that 5% Bi/InVO<sub>4</sub> reached the optimal photocatalytic performance with a rate that was 5.3 times higher compared to pure InVO<sub>4</sub>. The increased activity reported can be attributed to the surface plasmon resonance (SPR) induced by metallic Bi, which enhances light absorption and facilitates the efficient separation of charge carriers.<sup>119</sup>

In 2022, C. Li *et al.*<sup>120</sup> investigated a novel perspective on enhancing the performance of photocatalytic nitrogen fixation by employing catalysts that possess oxygen vacancies. N-doping TiO<sub>2</sub> hollow microspheres with oxygen vacancies were introduced. The structure improved the efficiency and stability of nitrogen photofixation.<sup>120</sup>

Several factors can affect the performance of photocatalysts in a reaction. There has been an attempt to improve photocatalysis through heterojunction catalysts such as zinc oxide/zinc sulfide (ZnO@ZnS), which was conducted by Guo *et al.*<sup>121</sup> The composite catalysts can address the issues of low carrier separation efficiency and inadequate light absorption capacity commonly found in individual catalysts.<sup>121,122</sup>

Another factor is the synthesis pathways, which are also quite important. In a study conducted by Huo *et al.*,<sup>123</sup> they used a facile solvothermal route and applied the heat treatment method for BMO@BOC heterojunctions photocatalyst synthesis, demonstrating improved photocatalytic efficiency.<sup>123</sup>

Other studies were conducted on tailoring specific catalysts with preferable activity in photocatalysis reactions.

For example, a novel approach was devised to boost the photocatalytic efficiency by testing bismuth oxyhalides having the lowest thermodynamic energy barrier for photocatalytic nitric oxide oxidation reaction.<sup>124</sup>

A recent study was performed by Morawski *et al.*<sup>125</sup> that involved the green synthesis of NH<sub>3</sub> from gaseous nitrogen and CO<sub>2</sub>-saturated water vapor. A novel gas phase photocatalytic reactor, including a bed in the form of UV transparent glass fiber cloth coated with titanium dioxide (P25 TiO<sub>2</sub>), was used (Fig. 15). The bed is located just above the water surface. The gases circulate from the top to the water surface, where NH<sub>3</sub> gas is produced and directly gets dissolved in the water phase, continuously separating the ammonia from the gas phase and immediately shifting the equilibrium to the product side. The highest ammonia production was 1.3 mmol NH<sub>4</sub><sup>+</sup> g<sub>cat</sub><sup>-1</sup> after 6 hours at 20 °C. The presence of CO<sub>2</sub> caused a gas phase reduction to carbon monoxide (100 μmol CO/g TiO<sub>2</sub>/dm<sup>3</sup>), CH<sub>4</sub> (7 μmol CH<sub>4</sub>/g TiO<sub>2</sub>/dm<sup>3</sup>), and H<sub>2</sub> (1–2 μmol H<sub>2</sub>/g TiO<sub>2</sub>/dm<sup>3</sup>). A rise in temperature from 20 °C to 50 °C did not remarkably increase

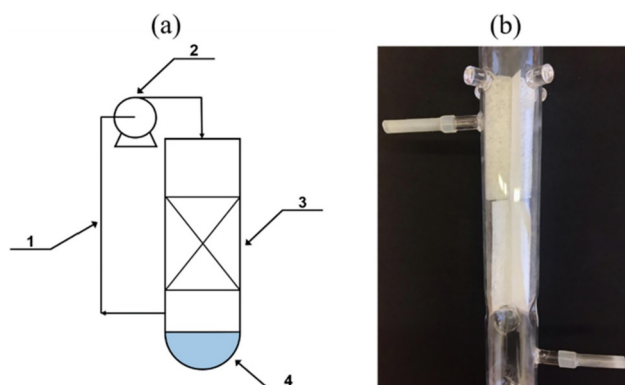


Fig. 15 The reactor diagram: (a) 1 – circulation loop; 2 – pump; 3 – photocatalyst on a glass fiber cloth; 4 – water; (b) the quartz reactor bed. Reproduced with permission from ref. 125 under the terms of the CC BY license.



**Table 8** The performance of the catalysts for nitrogen photofixation

| Catalyst                                                          | Temperature | Light irradiation | N <sub>2</sub> source        | NH <sub>3</sub> yield                       | Ref. |
|-------------------------------------------------------------------|-------------|-------------------|------------------------------|---------------------------------------------|------|
| C/WO <sub>3</sub> ·H <sub>2</sub> O                               | 25 °C       | UV-vis            | N <sub>2</sub>               | 205 μmol g <sup>-1</sup> h <sup>-1</sup>    | 108  |
| g-C <sub>3</sub> N <sub>4</sub> /rGO                              | 30 °C       | Visible           | Air                          | 515 μM g <sup>-1</sup> h <sup>-1</sup>      | 110  |
| g-C <sub>3</sub> N <sub>4</sub> /MgAlFeO                          | 30 °C       | Visible           | N <sub>2</sub>               | 417 μM g <sup>-1</sup> h <sup>-1</sup>      | 111  |
| PdSn/NiO/NaTaO <sub>3</sub> :La                                   | 5 °C        | UV                | NO <sub>3</sub> <sup>-</sup> | 3.6 mmol                                    | 115  |
| MXene-derived TiO <sub>2</sub> @C/g-C <sub>3</sub> N <sub>4</sub> | —           | Visible           | N <sub>2</sub>               | 250.6 μmol g <sup>-1</sup> h <sup>-1</sup>  | 113  |
| SiW <sub>12</sub> /K-C <sub>3</sub> N <sub>4</sub>                | 25 °C       | UV                | N <sub>2</sub>               | 353.2 μM g <sup>-1</sup> h <sup>-1</sup>    | 112  |
| Pd-TiO <sub>2</sub>                                               | 25 °C       | UV                | N <sub>2</sub>               | 21.2 mmol                                   | 118  |
| TiO <sub>2</sub> (oxygen vacancies)                               | 25 °C       | UV-vis            | N <sub>2</sub>               | 324.86 μmol g <sup>-1</sup> h <sup>-1</sup> | 117  |
| (OV-In(OH) <sub>3</sub> /CN)                                      | 25 °C       | Visible           | N <sub>2</sub>               | 3.81 mM h <sup>-1</sup> g <sup>-1</sup>     | 116  |
| Bi/InVO <sub>4</sub>                                              | 25 °C       | —                 | N <sub>2</sub>               | 626 μmol g <sup>-1</sup> h <sup>-1</sup>    | 119  |
| g-C <sub>3</sub> N <sub>4</sub> /MgZnAl-MMO                       | 25 °C       | Visible           | N <sub>2</sub>               | 47.56 μmol L <sup>-1</sup>                  | 114  |
| AN/BiOBr-Cl                                                       | —           | Visible           | N <sub>2</sub>               | 234.4 μmol g <sup>-1</sup> h <sup>-1</sup>  | 127  |
| La/MoO <sub>3</sub> -x                                            | 25 °C       | Visible           | N <sub>2</sub>               | 209.0 μmol g <sup>-1</sup> h <sup>-1</sup>  | 128  |
| Fe-WO <sub>3</sub>                                                | 55 °C       | UV-vis            | Air                          | 477 μg g <sup>-1</sup> h <sup>-1</sup>      | 126  |
| N-TiO <sub>2</sub> (oxygen vacancies)                             | —           | Visible           | N <sub>2</sub>               | 80.09 μmol g <sup>-1</sup> h <sup>-1</sup>  | 120  |

the yield of ammonia. However, it did eliminate the production of CO. No CH<sub>4</sub> was produced when the NH<sub>3</sub> yield increased, regardless of the temperature. The ammonium ions that are dissolved in water were in the form of ammonium hydrogen carbonate NH<sub>4</sub>HCO<sub>3</sub> or ammonium carbonate (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. Whereas in the case of pure nitrogen, it appears as NH<sub>4</sub>OH.<sup>125</sup>

Another experiment was conducted by Shen *et al.*<sup>126</sup> of a photocatalytic nitrogen fixation using air and visible light as the light source under mild conditions. The photocatalyst used is tungsten trioxide (WO<sub>3</sub>) doped with iron (Fe) prepared by high-temperature calcination. The Fe-doped WO<sub>3</sub> contains oxygen vacancies that are introduced to fix the nitrogen from the air at atmospheric pressure. The highest nitrogen fixation rate (nitrogen reduction) can increase to 477 μg g<sub>cat</sub><sup>-1</sup>.<sup>126</sup> Table 8 compiles a comprehensive range of catalysts investigated and reported in nitrogen photofixation.

**2.3.1 Challenges and potential solutions.** Table 9 presents the challenges associated with ammonia synthesis and associated solutions, which can overcome the bottlenecks of this process.

**2.3.2 Research gaps.** The following research gaps are identified based on the previous literature work, as presented in Fig. 16.<sup>129,130</sup>

In the field of nitrogen photofixation, introducing an electrical field (hence, photo-electrocatalysis) could

represent a winning strategy for enhancing the efficiency of NH<sub>3</sub> production. In fact, including an electrical source in the photoconversion process is a significant topic of discussion, as it is essential to determine whether it would result in a higher yield of NH<sub>3</sub> and improved process efficiency. Additionally, it is imperative to investigate how the introduction of electricity would impact the catalyst and its stability. In general, as discussed for the other processes, it is necessary to develop efficient catalysts with high stability and activity to perform the NH<sub>3</sub> reaction and increase the selectivity towards ammonia, reducing the probability of other undesired by-products. One of the major issues with nitrogen photofixation is the quick oxidation of the NH<sub>3</sub> product to nitrate due to the simultaneous redox reaction. Numerous methods have been proposed to address this issue, including removing the product during the reaction, separating the catalyst suspension from the reaction, and utilizing plasmon-induced techniques to isolate the two reaction chambers. Nevertheless, the efficacy of these approaches in resolving this challenge has not been fully validated. Further investigation is required to explore the feasibility of carrying out the reaction in a gaseous state due to the inherent lack of solubility of nitrogen gas in aqueous solutions, which has been identified as a limiting factor in achieving a satisfactory level of NH<sub>3</sub> conversion.

**Table 9** Challenges associated with the photocatalytic synthesis of ammonia and possible solutions

| Challenges                                                                          | Solutions                                                                                                                                                                                        |
|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| • Poor activity, poor selectivity towards NH <sub>3</sub> , and low reaction yields | ✓ NiO has demonstrated strong adsorption of nitrite, using electron donors to consume the photogenerated holes ( <i>e.g.</i> , formic acid), using oxides characterized by high oxygen vacancies |
| • Quick oxidation of ammonia to nitrate                                             | ✓ Quickly separating the reaction products if they are produced in the same chamber, separating the catalyst from water suspension or performing the photofixation in the gas phase              |
| • Above 50 °C, the ammonia yield decreases                                          | ✓ The temperature of the reaction should be controlled; the ammonia reaction is reversible and shifts towards the products at low temperature                                                    |

Source: compiled from ref. 129 and 130.

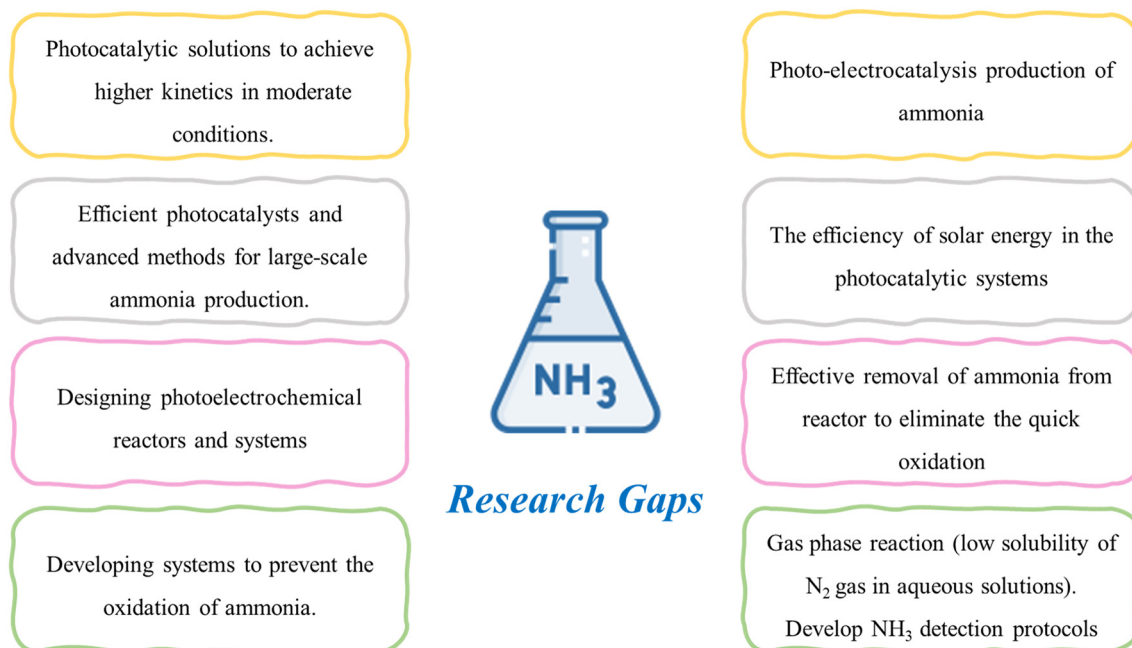


Fig. 16 Areas requiring further investigation for successful nitrogen fixation.

Despite the existence of multiple studies demonstrating the feasibility of photocatalytic nitrogen fixation technology at the laboratory level, there is a lack of research examining its practicality and viability when implemented on a larger scale. Hence, there is a pressing need for further research to bridge this gap and facilitate the commercialization of this promising technology.

### 3. Comparative evaluation

This section presents a concise assessment of the three green fuels, HCOOH,  $CH_3OH$ , and  $NH_3$  based on the reviewed literature. The four processes discussed in this review have been compared in terms of production yield and photoproduction selectivity *versus* the conventional methods' selectivity. In this comparison, the selectivity benchmark technologies used are the conversion of  $CO_2$  into HCOOH through catalytic hydrogenation of  $CO_2$ , and the production of  $NH_3$  *via* steam reforming of methane/Haber–Bosch process and  $CH_3OH$  *via* the steam reforming of methane/catalytic hydrogenation of  $CO_2$ , as illustrated in Table 10.

Table 10 provides an overview of the catalysts that have exhibited outstanding performance, and display promising

potential for the four technologies. Among the four technologies, POM exhibits the highest selectivity with a value of 98.7%, followed by HCOOH with a range between 80–90%. Photocatalytic nitrogen fixation technology reported the lowest selectivity (72%). This is attributed to the reversible nature of the reaction, which can be affected by a change in reaction conditions such as temperature and pressure.

When the photocatalytic processes of  $CH_3OH$ , HCOOH, and  $NH_3$  are compared with the benchmark technologies currently being used, a promising trend was observed that could displace the conventional processes in the future. The selectivity data obtained for HCOOH and  $CH_3OH$  production, through  $CO_2$  reduction and partial oxidation of  $CH_4$ , demonstrates a strong correlation with benchmark technologies. This alignment is highly advantageous in the context of photocatalytic  $CO_2$  reduction, as it significantly reduces energy consumption compared to conventional processes. Moreover, using renewable energy sources, coupled with reaction conditions at ambient temperatures and pressures, overcomes the requirement for additional downstream separation steps to enhance selectivity. The selectivity of Haber–Bosch technology has very low selectivity

Table 10 The highest reported yield and selectivity for the four technologies

| Criteria                             | Formic acid      | Ammonia            | Methanol ( $CO_2$ reduction) | Methanol (POM)     |
|--------------------------------------|------------------|--------------------|------------------------------|--------------------|
| Yield ( $\mu mol\ g^{-1}\ h^{-1}$ )  | 3500 (ref. 103)  | 626 (ref. 119)     | 2910 (ref. 3)                | 4500 (ref. 83)     |
| Selectivity (%)                      | 80–90 (ref. 100) | 72 (ref. 115)      | 98 (ref. 131)                | 98.7 (ref. 73)     |
| Benchmark technology selectivity (%) | 96 <sup>a</sup>  | 20–25 <sup>a</sup> | 95–98 <sup>a</sup>           | 95–98 <sup>a</sup> |

<sup>a</sup> Benchmark technology selectivity compiled from ref. 132–136.

(20–25%) compared to nitrogen photofixation (72%) due to the equilibrium and kinetic limitations of the reaction, resulting in by-product formation.

The main purpose of photocatalysis is to utilize abundant and easily accessible sunlight as an energy source to initiate and drive reactions, thereby eliminating the need for additional energy inputs. This has significant implications for reducing reliance on fossil fuels and minimizing the environmental footprint associated with traditional energy-intensive processes. The value reported of the energy consumption of the steam reforming of methane/catalytic hydrogenation of CO<sub>2</sub> technology ranges between 28–32 GJ per ton of CH<sub>3</sub>OH produced.<sup>135,136</sup>

It is important to highlight that photocatalytic technologies are still at an early stage of development, particularly in the context of NH<sub>3</sub> production, and several challenges need to be addressed. Besides the yield of the reaction, the key focal points that should be tackled are the fast oxidation of NH<sub>3</sub> to nitrate, low stability of N<sub>2</sub> in water, and poor activity. Further research is required to investigate the solution of separating the redox products during the reaction to avoid NH<sub>3</sub> oxidation and the importance of conducting photoreduction of NH<sub>3</sub> in the gas phase.

Notably, the literature and experimental data on NH<sub>3</sub> and HCOOH production were found to be relatively limited. On the other hand, there has been a notable increase in exploration and research activity regarding the partial oxidation of CH<sub>4</sub> and CO<sub>2</sub> reduction to CH<sub>3</sub>OH over the past five years, both holding promising potential for industrial implementation within the next decade.

For photocatalytic CH<sub>3</sub>OH production, an additional oxygen source should be introduced to enhance the POM reaction, such as oxygen and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Additionally, a pressurized stainless steel batch reactor for POM can significantly improve the reaction outcomes, with pressures ranging from 2 to 3 MPa.

The reduction of CO<sub>2</sub> to CH<sub>3</sub>OH and HCOOH poses significant challenges in controlling the CO<sub>2</sub> reduction pathway, as it inhibits further reaction and produces other undesired hydrocarbons. Furthermore, there is a need to develop a scalable system to make these processes economically viable in terms of reactor design and reaction conditions.

## 4. Conclusions

This review highlights the importance of the photocatalytic process in producing green fuels. Herein, we discussed the photoproduction of three different types of fuels, including the fundamentals, significance, concepts, and mechanism. In addition, the fuel synthesis methods, different catalysts used, experimental setups, reaction conditions, and reactor design were specifically identified, addressed, and evaluated. Upon thorough evaluation, this review has identified and presented the main challenges and potential solutions associated with four photocatalytic technologies. Furthermore, research

directions to address the existing research gaps, paving the way for further advancements in the field of photocatalysis of CH<sub>4</sub>, CO<sub>2</sub> and NH<sub>3</sub> have been highlighted.

Through the research conducted, synthesis method, and results obtained in order to enhance the photocatalytic activity, the following points were concluded:

- Guarantee effective separation of the electron-hole pair of the photocatalyst by providing doping or co-catalysts (such as carbon-based supports).
- Employing an appropriate bandgap energy for the photocatalyst to ensure photon absorption *via* effective light sources.
- Developing photocatalysts with high surface area, fast separation of charges, long charge lifetime, efficient light absorption, and appropriate band gap.
- Enhancing the reaction kinetics by adding sacrificial agents to utilize photo-generated electrons.
- Tuning the reaction conditions, such as operating temperature and light irradiation, to improve the effectiveness of single reaction pathways.

Further research should be done to understand and clarify ways in which secondary NH<sub>3</sub> oxidation could be prevented. For CH<sub>4</sub> conversion through partial oxidation, doping the catalysts with metals, metal oxides, and non-metals or using metal-organic framework (MOFs) catalysts are suggested. The development of photoreactors that allow the reaction to be carried out effectively on a large scale is subjected to ongoing development.

## Author contributions

Amira Chebbi: conceptualization, methodology, formal analysis, writing – original draft. Alessandro Sinopoli: conceptualization, writing – review & editing. Ahmed Abotaleb: writing – review & editing. Yusuf Bicer: conceptualization, methodology, writing – review & editing, supervision.

## Conflicts of interest

There are no conflicts to declare.

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