

Photocatalytic and Photoelectrochemical Reduction of CO₂ to Methanol in Aqueous Medium

Abstract

In this article, we summarized the recent progress made on photocatalytic and photoelectrochemical reduction of carbon dioxide (CO₂) to methanol (CH₃OH) in aqueous medium on various photocatalytic materials, photoactive and electrocatalytic electrodes. We have provided a critical analysis as to how the final products were found to depend on the type of photocatalyst and photo electrocatalyst used. We have delineated the synthesis of some novel photocatalysts that preferentially convert CO₂ to methanol as a major or a sole product. We also discussed the reactions and parameters that are critical in enhancing the reduction yield of carbon dioxide to methanol which remains to be the major challenge. Most importantly, we explained as to why the photocatalytic reduction rates of CO₂ to methanol on nanomaterials are lower compared to those on photoelectrodes and explained the ways these rates can be enhanced in future studies. Furthermore, we highlighted the intriguing challenges involved in efficient conversion of CO₂ directly to methanol in aqueous medium and provided possible ways to address them.

Introduction

Warming of planet earth and its consequence devastating climate change prompted researchers towards developing energy sources that are carbon footprint free using photosynthesis [1-6]. It is well known that carbon dioxide accounts for the upmost share of greenhouse gas emissions by its startling increase in the atmosphere [4,7-13]. Nearly 1.0x10⁹ tons of CO₂ gas is added to the atmosphere every year, and as a result, there will be a 50% increase to ≥ 600 ppm from its level in the year 2000 in next 50 years [14]. Such huge CO₂ emissions are believed to be largely responsible for current changes in the global climate orderliness. To resolve the CO₂ problem forever would be to convert it to a valuable product, namely, methanol (CH₃OH). The energy source for such a conversion needs must be CO₂ emission free energy. For the emission of 5x10¹⁴ moles of CO₂ in next fifty years, it will be possible to convert most of CO₂ to methanol in aqueous medium using sunlight as an energy source in presence of suitable photocatalyst or photoelectrocatalyst by mimicking the natural photosynthesis process [14]. Hence, the process of CO₂ capture and its conversion to methanol will provide an ideal carbon neutral energy source to diminish the global warming and the reliance on the earth's fast exhausting fossil fuels.

Carbon dioxide is an inert molecule thereby making its reduction to methanol relatively challenging due to the high thermodynamic barrier. The drawbacks of CO₂ reduction that result from the restricted selection of semiconductors and the competitive H₂ generation in aqueous medium instead of CO₂ reduction were discussed in a review article [15]. Electrochemical studies on the reduction of CO₂ [16-25], described the conversion of CO₂ mainly



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to CO and formic acid by a 2e-(two electrons) reduction process. Importantly, Hori et al. [16, 18] observed the formation of CO, CH₄, C₂H₄ and alcohols, EtOH and PrOH during the electrochemical reduction of CO₂ in aqueous electrolyte solution at Cu electrodes. Formation of CO was found to occur at a higher negative potential than - 1.2 V vs NHE; hydrocarbons and alcohols were found to be favorably produced at a more negative potential than - 1.3 V vs NHE. However, the hydrocarbons and alcohols generated were of negligible amounts by electrochemical methods due to a competitive H₂ evolution reaction at more negative potentials than - 1.3 V vs NHE. Kuhl et al. [22] carried out the electrochemical study at copper metal at high negative potentials and reported a total of 16 different CO₂ reduction products including aldehydes, ketones, alcohols, and carboxylic acids. Electrocatalytic conversion of carbon dioxide to methanol with low selectivity at high negative voltage on transition metal surfaces were also reported [20]. Importantly, the reduction of CO₂ at silver cathode produced CO and H₂ as major and the methanol as one of the minor products [21]. These important results indicate that at a high negative applied potential on transition metal cathodes, the selectivity of formation of specific product is highly compromised producing multiple reduction products. This is because, at high negative potential, the cathodes become extremely electron rich and generate strong reducing atmosphere and thereby produced various CO₂ reduction products having virtually no selectivity.

Azuma et al. [17] reported the formation of trace amounts of methane and ethylene by the reduction of CO₂ at various metal electrodes, except some reasonable amounts of these products were observed at Cu electrodes. The high selectivity of the copper electrode in forming hydrocarbons during CO₂ reduction triggered many studies in finding the reaction mechanism on the Cu electrode surface [26-29]. Ohta et al. [19] found the main products as methanol and formic acid at copper tube electrode, under atmospheric pressure, between -1.4 V and -2.0 V vs NHE. Under the optimum experimental conditions, the Faradaic efficiencies for converting CO₂

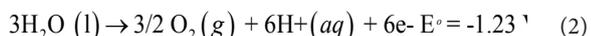
electrochemically to methanol and methane were found to be 18% and 20% at -1.7 V and -1.8 V respectively. Hence, the over potential need for these reactions on copper cathode are quite excessive and dwarfs the over potential required for the oxygen evolution reaction at the counter electrode. The electrochemical reduction of CO₂ to methanol at such negative voltage is energy intensive and therefore becomes impractical for cost-effective production of methanol from CO₂ and water. Hence, the studies on photocatalytic and photoelectrocatalytic reduction of CO₂ specifically to methanol should be focused.

Various products of CO₂ can be obtained when it is reduced in an aqueous medium either electrochemically, photocatalytically or photoelectrocatalytically. Two of these products can be directly used as fuels, one is methanol (CH₃OH), a liquid and other is methane (CH₄), a gas. The third product is carbon monoxide gas (CO), which must be used with H₂ as syngas to produce methanol in a two-step process. The two-step method of fuel production from CO may not be desirable at this time in the absence of efficient carbon neutral hydrogen generation from water. Hence, the challenge at this time is to develop a single step process that can selectively produce methanol from carbon dioxide and water with high yields.

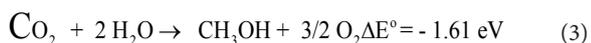
The reactions and thermodynamic potential (at pH 7) for methanol formation during CO₂ reduction in aqueous medium by simultaneous electron (e⁻) and proton (H⁺) transfer reactions can be given as [14],



Though the thermodynamic potential of this reduction reaction in water is low, the thermodynamic potential for its accompanying water oxidation reaction is quite high,



Hence, the overall reaction of CH₃OH formation by CO₂ reduction in aqueous medium is obtained by addition of Eqs. (1) and (2) as,



The limitations of the photocatalytic CO₂ reduction arise from the high voltage needs (Equation 3) and the competitive hydrogen evolution reaction in the aqueous medium [15]. In addition to the high potential needs, there is also the catalyst poisoning effect of CO₂ reduction products or intermediates which ultimately may diminish the catalyst active sites [30, 31]. Most importantly, CO₂ may preferentially adsorb in its molecular form on some catalyst surfaces that facilitates its reduction by simultaneous electron and proton transfer processes [30, 32]. The preferential adsorption of CO₂ could be advantageous to limit the competitive H₂ evolution reaction on these surfaces.

In this article, we concentrated on the photocatalytic and photoelectrochemical reduction of CO₂ to solar fuel methanol in aqueous media. We have also discussed the present challenges faced by this process, how some of these were partially addressed and how to overcome them in future studies.

Photocatalytic reduction of CO₂ to methanol

Several studies [1, 33-48] were reported on CO₂ reduction to

methanol using photocatalysts in aqueous medium. Among various semiconducting photocatalyst materials, TiO₂ was found the most feasible by various authors to use for the reduction of carbon dioxide in aqueous medium [1, 35, 38, 39, 41, 42, 44, 47, 49-52]. This is for the reason that high band gap semiconductors were needed to overcome the high thermodynamic barrier involving CO₂ reduction coupled with water oxidation in an aqueous medium.

Photocatalytic reduction of carbon dioxide using Ru-doped Titanium oxide anatase mounted on silica was reported by Sasirekha et al. [38]. In this study, Ru-TiO₂/SiO₂ showed practically four-fold enhanced activity for the methanol production compared to that on Ru-TiO₂. Methane formation was favored instead of methanol when TiO₂ photocatalyst was used in a suspension in aqueous media (0.1%, w/v) in presence of a depolarizer or hole scavenger. This indicates that Ru-decoration of TiO₂ was essential for the selective reduction of CO₂ to methanol.

Tseng et al. [53] studied the photoreduction of CO₂ using sol-gel derived TiO₂ and Cu loaded TiO₂ catalysts and observed the formation of methanol. Figure 1 shows the process of O₂ separation from water by photogenerated holes in TiO₂ and reduction of CO₂ to CH₃OH on Cu surface by electrons photogenerated on TiO₂.

However, the copper loaded titanium oxide-based photocatalyst was found active only under UV light though the Sunlight at Earth's surface is about 3 to 5 percent ultraviolet.

Ohno et al. [54] photocatalytically reduced CO₂ on exposed brookite phase TiO₂. The methanol generation enhanced considerably by Photo-deposited Au or Ag nanoparticles on brookite (TiO₂) nanorods. These metal nanoparticles may have acted as highly active sites for the reduction of CO₂ which involves multi-electron and proton transfer processes. Using the results of an isotope labeling experiment using ¹³CO₂, the generation of CH₃OH was identified to be from the ¹³CO₂ reduction.

Li et al. [55] reported photocatalytic activities of CdS (or Bi₂S₃)/TiO₂ nano tube for the reduction of CO₂ to CH₃OH under visible light illumination. The photocatalytic activity for the reduction of CO₂ to methanol on Bi₂S₃/TiO₂ under visible light illumination was

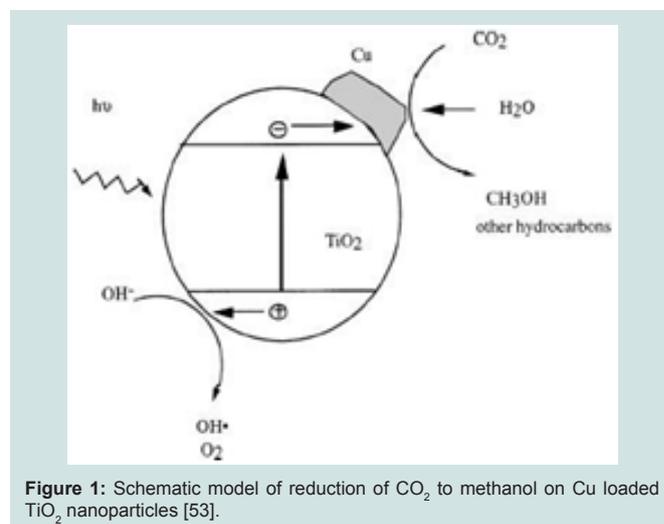


Figure 1: Schematic model of reduction of CO₂ to methanol on Cu loaded TiO₂ nanoparticles [53].

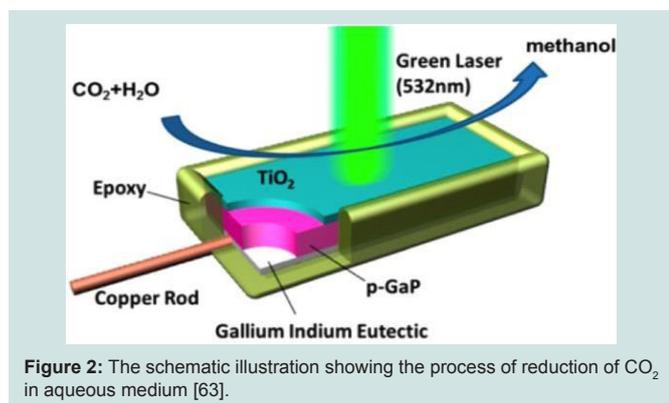


Figure 2: The schematic illustration showing the process of reduction of CO₂ in aqueous medium [63].

found to be much higher than that on CdS/TiO₂ nanotubes (TNTs). Furthermore, the yield of methanol on Bi₂S₃/TNTs photocatalyst under visible light irradiation was found to be ~ 45.0 micromoles per gram of catalyst per hour (μmol.g⁻¹.cat.h⁻¹), which was ~ 2-fold higher than that on undecorated TNTs.

The reduction of carbon dioxide was investigated on photocatalyst, AgBr/TiO₂ under exposure of visible light of wavelength, λ > 420 nm [56]. The AgBr/TiO₂ exhibited a high activity for the reduction of CO₂ to methanol in aqueous media. This was ascribed to its strong visible-light activity. Furthermore, this photocatalyst was found stable on multiple uses. This may be due to transfer of photogenerated electrons from the conduction band of AgBr to that of TiO₂.

The role of copper species (e.g. Cu⁰, Cu^I, or Cu^{II}) on photoinduced reduction of CO₂ to methanol was reported [57]. Among the Cu loaded TiO₂ species the Cu^{II}O/TiO₂ enhanced methanol generation compared to other Cu species. The activation energy (E_a) of CO₂ reduction on TiO₂ Degussa-P25 was found 26 kJ. mol⁻¹ and on 3% Cu^{II}O/TiO₂ it was found 12 kJ. mol⁻¹. The diminished activation energy on 3% Cu^{II}O/TiO₂ implies a catalytic role of copper in boosting the methanol production rate. Enhanced yield indicated that the copper (II)-oxide species acted as an electron trap and thereby reduced electron-hole recombination. The visible light absorption by p-type Cu^{II}O and generation of p/n junction between p-Cu^{II}O/n-TiO₂ also contributed in diminishing the recombination of photogenerated electrons and holes and consequently improved the yield.

Fe₂O₃-TiO₂ nanoparticles synthesized by a sol-gel method were utilized for CO₂ reduction to methanol [58]. In addition to UV light absorption, the presence of Fe₂O₃ helped to broaden the absorbance of Fe₂O₃-TiO₂ composite material to visible region. The yield of methanol formation was found to be as high as 45.6 μ mol. g⁻¹.cat.h⁻¹. The mechanism of the photocatalytic reduction of CO₂ on Fe₂O₃-TiO₂ was also explored in terms of electron-hole generation, transition and separation. Nitrogen doped n-TiO₂ was synthesized using amorphous TiO₂ anatase and ammonium hydroxide at 100°C [59]. The reduction of CO₂ to methanol in aqueous solution on this catalyst yielded methanol of 23.0 μmol. g⁻¹ cat. h⁻¹.

The photocatalytic activity of Ag-loaded TiO₂ was found to be about 9 times higher than that of bare TiO₂ [60]. The optimum amount of Ag loading on TiO₂ was found to be 2.5 % which produced an energy efficiency of 0.5 % and methanol yield of 30.0 μmol. g⁻¹.cat.h⁻¹. Furthermore, a synergetic mechanism between UV light excitation

and surface plasmon resonance enhancement was proposed to elucidate CO₂ reduction under various reaction conditions.

Cu₂O/TiO₂ nanotube (TNTs) arrays showed an enhancement in the photocatalytic activity during the reduction of CO₂ to methanol [61]. The surface morphology showed that the Cu₂O nanoparticles decorated the TNTs. The increased absorption in the visible region by Cu₂O/TiO₂ compared to the plain TNTs was determined by UV-Vis spectral analysis. This could be due to lower band gap energy of Cu₂O of ~ 2.2 eV compared to 3.2 eV for TiO₂. The Cu₂O/TiO₂ composite material facilitated the reaction process where the CO₂ photoreduction occurred on p-Cu₂O sites and water photooxidation on n-TiO₂ sites. The p/n junction between p-Cu₂O and n-TiO₂ was also responsible for high rate of CO₂ photoreduction due to voltage drop across the junction that helped to minimize the rate of recombination of photogenerated carriers.

Pure TiO₂ and silver-enriched TiO₂ powders were tested for the photocatalytic reduction of CO₂ to methanol [62]. Ag particles improved the photocatalytic activity of Ag/n-TiO₂ compared to pure n-TiO₂. When the Ag loading in TiO₂ was ≤ 5%, the impurity band due to presence of Ag was produced in the TiO₂ band gap that helped to lower the absorption edge and thereby enhanced the photogeneration of electron-hole pairs. However, metallic clusters of Ag were formed on TiO₂ crystals when the Ag loading was > 5%. This produced Schottky junction at the metal-semiconductor interface that helped to enhance electron-hole separation and thereby minimized their recombination rate.

TiO₂-passivated p-GaP was utilized to reduce CO₂ to methanol [63]. The TiO₂ layer was used to prevent the photocorrosion of the GaP. In addition to increased stability by TiO₂ the photoconversion efficiency did enhance due to formation of a p/n junction which causes to better separation of photogenerated carriers and hence minimized their recombination. This also affected a shift in the energy need by about 0.5 eV. For the TiO₂ thicknesses above 10 nm no enhancement in the photoactivity was observed due to insulating nature of the TiO₂, thus, outweighing the benefits of passivation. The process of reduction of CO₂ in aqueous media is shown in Figure 2.

Copper or Cobalt loaded TiO₂/ZSM-5 catalysts were used for the reduction of CO₂ to methanol [64]. The conversion efficiency of CO₂ to methanol was found to enhance under low energy irradiation compared to bare TiO₂. The highest rates of CH₃OH formation were found to be 50.05 and 35.12 μ mol. g⁻¹ cat. h⁻¹ for Cu and Co loaded TiO₂/ZSM-5, respectively. This indicates a better selectivity of Cu compared to Co in reducing CO₂ specifically to methanol in aqueous medium. Plasmonic Au decorated TiO₂ photocatalyst produced CH₄, CH₃OH and HCHO as main products by CO₂ reduction.

Graphene-TiO₂ (Gn-TiO₂) photocatalyst synthesized by reducing graphite oxide using hydrothermal method, reduced CO₂ to methanol and formic acid [47]. With 8.5% graphene loading the yield of methanol and formic acid, under light illumination of 365 nm wavelength, reached 160 and 150 μmol g⁻¹ cat. h⁻¹ respectively. However, it was found that an increase in graphene loading beyond the optimum 8.5% decreased the efficiency of CO₂ reduction by shielding the light from reaching the surface of the photocatalyst.

Copper nanoparticle (Cu-NP) -covered graphene oxide (GO)

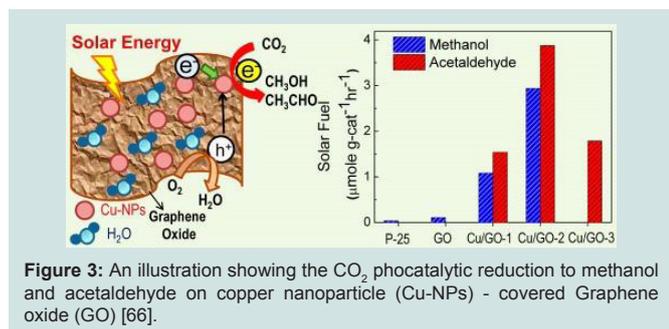


Figure 3: An illustration showing the CO₂ photocatalytic reduction to methanol and acetaldehyde on copper nanoparticle (Cu-NPs) - covered Graphene oxide (GO) [66].

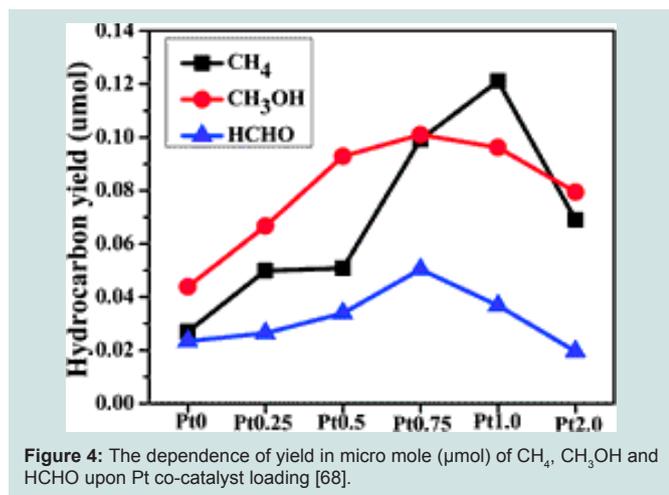


Figure 4: The dependence of yield in micro mole (μmol) of CH₄, CH₃OH and HCHO upon Pt co-catalyst loading [68].

was used to reduce CO₂ under visible light illumination [66]. Photocatalytic reduction of CO₂ was found to enhance by 60-fold or more on Cu-NP/GO (10 wt. % Cu load) compared to that on pristine GO. A schematic illustration showing the CO₂ reduction process to methanol and acetaldehyde on these nanoparticles is shown in Figure 3.

Ruthenium trinuclear polyazine complex grafted on graphene oxide support containing phenanthroline ligands (GO-phen) was used for the production of methanol from CO₂ by its photocatalytic reduction [67]. After 48 h illumination the yield of methanol was found to be 82.0 μmol. g⁻¹cat.h⁻¹. Ruthenium trinuclear polyazine complex grafted on graphene oxide support exhibited a higher photocatalytic activity compared to those on bare graphene oxide itself.

Carbon dioxide reduction products such as CH₄, CH₃OH and HCHO were observed when Pt deposited nanocomposite, g-C₃N₄-Pt photocatalyst was used for photocatalytic reduction of CO₂ under simulated solar irradiation [68]. Platinum deposited co-catalyst helped to enhance both selectivity of the products and as well as its reaction rates. The Pt nanoparticle (NP) co-catalyst facilitated the electron transfer from g-C₃N₄ to its surface for CO₂ reduction. This study shows the effect of tiny amounts of Pt to increase the photoactivity and selectivity of g-C₃N₄ for the generation of CH₃OH, CH₄ and HCHO as the reduction products of carbon dioxide (Figure 4). However, the yield was quite low.

Li et al.[69] investigated the photocatalytic performance of visible

light active Cu₂O modified SiC nanoparticles (Cu₂O/SiC NPs) for the CO₂ reduction mainly to methanol. Under visible light irradiation, the yields of methanol generated using SiC (band gap of 2.23 eV), Cu₂O (band gap of 1.95 eV) and Cu₂O/SiC photocatalysts were 153, 104 and 191 μmol. g⁻¹ cat. respectively in 5-hour reaction time. It should be noted that the p/n junction between p-Cu₂O and n-SiC in Cu₂O/SiC NPs helped to enhance the CO₂ reduction rate by enhancing the separation of photogenerated carriers and thereby minimizing their recombination.

Li et al. [70] also explored the photocatalytic activities of Bi₂S₃, CdS and Bi₂S₃/CdS for carbon dioxide reduction to methanol under the exposure to visible light. Bi₂S₃/CdS hetero-junction photocatalyst exhibited a superior photocatalytic activity during the CO₂ reduction compared to individual Bi₂S₃ and CdS photocatalysts. The highest yield of methanol was 122.6 μmol. g⁻¹cat. h⁻¹ when the optimum weight ratio of Bi₂S₃ to CdS was 15%.

Aluminum or gallium decorated ordered layered double hydroxides (LDHs) of zinc and/or copper was found to efficiently reduce CO₂ to methanol under illumination of light [71]. Producing a yield of 170 nano mol. g⁻¹ cat. h⁻¹. Additionally, the methanol selectivity was found to improve by inclusion of Cu from 5.9 to 26 mol% in Zn-Al LDH photocatalyst. Also, methanol selectivity was found to enhance by addition of Cu from 5.9 to 26.0 mol% in Zn-Ga LDH photocatalysts.

Lamellar BiVO₄ reduced CO₂ selectively to methanol under exposure to visible light [72]. This lamellar BiVO₄ was prepared using the surfactant-assisted hydrothermal process. Addition of NaOH solution to the reaction mixture with BiVO₄ suspension was found to significantly enhance methanol yield. A mechanism for the methanol generation using BiVO₄ photocatalyst by CO₂ reduction was also discussed. The possible photocatalytic mechanism was illustrated in Figure 5. The dependences of CH₃OH production by photocatalytic CO₂ reduction on photocatalyst, BiVO₄ on NaOH concentration are shown in Figure 6. This figure shows enhanced amounts of methanol formation with increase in NaOH concentration. At a higher concentration of 1.0 M NaOH the yield of methanol was found to be 27.5 μmol. g⁻¹cat. h⁻¹.

The absence of H₂ gas in the product gases confirmed that the competitive hydrogen evolution reaction (HER) did not occur. This result is consistent with the previous report that BiVO₄ cannot

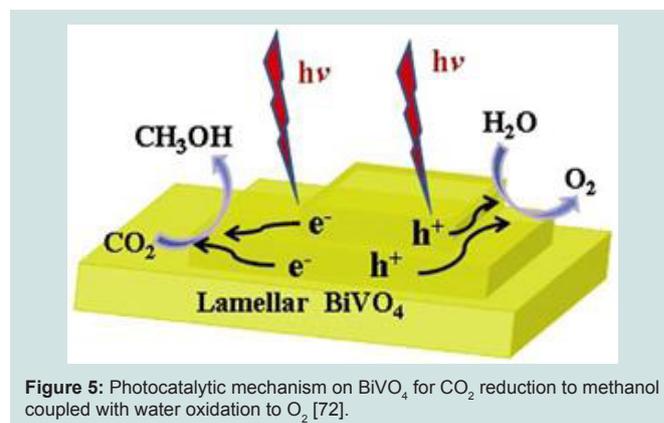


Figure 5: Photocatalytic mechanism on BiVO₄ for CO₂ reduction to methanol coupled with water oxidation to O₂ [72].

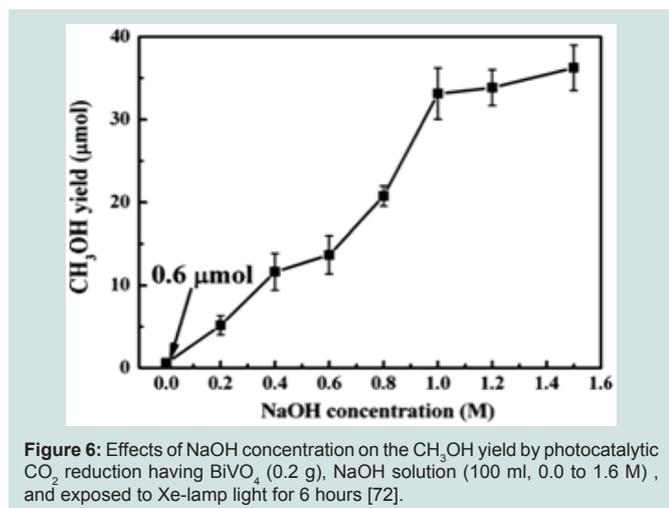


Figure 6: Effects of NaOH concentration on the CH₃OH yield by photocatalytic CO₂ reduction having BiVO₄ (0.2 g), NaOH solution (100 ml, 0.0 to 1.6 M), and exposed to Xe-lamp light for 6 hours [72].

produce H₂ due to its unmatched energy band structure with the water reduction potential [73]. Importantly, Figure 6 shows the enhanced CH₃OH production with the increase of NaOH concentration. This observation was attributed to increased dissolution of CO₂ in higher concentration of NaOH, higher reduction rate of CO₂ by minimizing the proton reduction rate and as well as enhanced coupled O₂ evolution reaction in the alkaline medium.

The influence of loading of various metal oxides such as Fe₂O₃, CuO and NiO on the photocatalytic activity of InVO₄ was reported [74]. The Fe₂O₃-loaded InVO₄ (Fe₂O₃/InVO₄) markedly enhanced the methanol yield by minimizing the recombination of the photogenerated carriers due to their effective separation on it. The yield of methanol was found to be 35.6 μ mol. g⁻¹ cat. h⁻¹.

Martin et al. [75] investigated the effect of the reaction media such as NaOH, NaOH + Na₂SO₃ (1:1), NH₄OH, NH₄OH+Na₂SO₃ (1:1), on photocatalytic reduction of CO₂ on ZnS deposited montmorillonite (ZnS-MMT). The NaOH solution was found to be most favorable reaction medium among these for the reduction of CO₂ to methanol. It should be noted that the addition of Na₂SO₃ which acted as a reducing agent resulted in improving methanol yields by minimizing its back oxidation reaction.

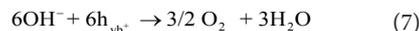
The photocatalytic reduction of CO₂ to methanol was carried out on the reduced graphene (rG) modified Ta₂O₅ photocatalyst (Ta₂O₅-rG) loaded with Ni/NiOx in aqueous solution [76]. The composite photocatalyst was prepared using a one-step hydrothermal method. Ni/NiOx was used as a co-catalyst and its load was limited to 3% per weight of the Ta₂O₅-rG. Different weight percent ratios of rG to Ta₂O₅ were investigated. In this study, methanol generation was found to depend on the amount of reduced graphene in the Ta₂O₅-rG photocatalyst. The highest activity of the composite photocatalyst was observed when 1% of rG was used. However, if the percentage of rG was increased beyond 1% then the yield of methanol decreased due to negative effect of rG on absorption of light.

Detailed studies were performed by Kavil et al. [77, 78] for the reduction of CO₂ dissolved in sea water to methanol using their hydrothermally synthesized copper loaded carbon modified n-TiO₂ (Cu/CM-n-TiO₂) under both UV-light and actual natural sunlight

illumination. Generation of methanol of maximum 582 μ mol. g⁻¹ cat. h⁻¹ under UV light illumination and 182 μ mol g⁻¹ cat. h⁻¹ under actual natural sunlight were observed. These are the highest yield of methanol reported so far under UV and natural sunlight illumination on copper loaded carbon modified n-TiO₂ (Cu/CM-n-TiO₂). It is important to note that such a high yield on this photocatalyst nanoparticles can be attributed to mainly three factors such as: (1) greater visible light absorption by carbon modified n-TiO₂ [79, 80] (2) enhanced catalytic effect of Cu for the conversion of CO₂ specifically to methanol in aqueous medium [81] and (3) increased separation of photogenerated carriers by Schottky junction at the Cu/CM-n-TiO₂ interface that minimized their recombination.

Mechanism of reduction of CO₂ to methanol on photocatalyst (e.g., n-TiO₂) surface

The mechanism of reduction of CO₂ in aqueous medium on the widely used TiO₂ photocatalyst surface can be depicted in terms of the following equations which involve six electrons and six protons transfer processes. equation (4) below shows the photogeneration of electrons e_{cb}⁻ (cb conduction band) and holes h_{vb}⁺ (vb valence band). The photogenerated electrons in the conduction band (e_{cb}⁻) react with H⁺ ions to generate hydrogen radical (H[•]) according to equation (5). The highly reactive H[•] reacts with CO₂ molecule as in equation (6) to produce methanol and water. As a counter reaction, the photogenerated holes (h_{vb}⁺) react with hydroxide ions OH⁻ to generate O₂ and H₂O as given in equation (7).



The overall reaction is given by addition of (Equations 4-7) as,



Photoelectrochemical reduction of CO₂ to methanol

The semiconductor photocatalysts [8, 35, 38, 39, 41, 49], have been used for photoreduction of carbon dioxide in an aqueous electrolyte to produce various products such as methane, methanol, ethylene, ethanol, carbon monoxide and formic acid etc. However, the limitations of the photocatalytic method are the low yield and hence the low photoconversion efficiency. This is because under sunlight illumination the photocatalysts are unable to generate high enough photovoltage to enhance the yields of this energetically challenging reaction of CO₂ reduction to methanol in aqueous medium. On the other hand, in photoelectrochemical method, in addition to the solar energy, a minimal amount of energy would be possible to be supplied from an external power source or from solar panels to enhance the rate of the reduction of CO₂ to methanol. In this section, we will discuss various studies conducted on the photoelectrochemical reduction of CO₂ to methanol.

In a study by De Brito et al. [88], the photoelectrochemical reduction of CO₂ was carried out using a Cu/Cu₂O electrode under UV-visible radiation in which the reaction products were monitored overtime. The formation of methanol, ethanol, formaldehyde,

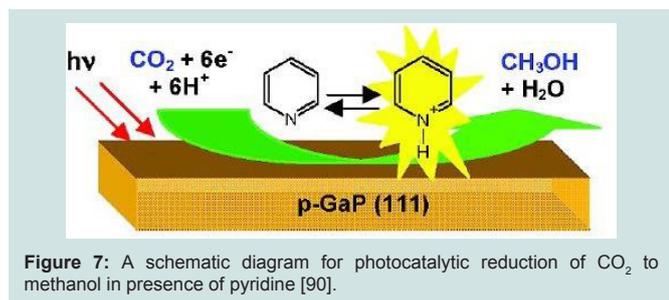


Figure 7: A schematic diagram for photocatalytic reduction of CO₂ to methanol in presence of pyridine [90].

acetaldehyde, and acetone was reported. The photoelectrons in the p-Cu₂O reduced CO₂ to methanol for period of < 30 min, but produced acetaldehyde, and acetone after a longer period > 120 min. The pH of the electrolyte was found to act as a key factor for the selective generation of the methanol. It was an interesting observation that the types of products were found time dependent. However, no explanations were provided for such a finding. This result indicates that the initially formed methanol was converted to other products after 2 hours. Hence, to collect methanol as the main product, it must be removed within 30 min from the reaction mixture. Also, the use of the Cu-oxide as photocathode may not be realistic since it may be ultimately reduced to metallic Cu under cathodic polarization and thereby will lose its photoactivity.

Morikawa et al. [89] used reverse photo-fuel cells for the photoelectrochemical oxidation of water and reduction of CO₂ using and WO₃ and a layered double hydroxide (LDH), separated by a polymer electrolyte (PE) film. WO₃ was used for the photooxidation of water, whereas LDH, comprised of Zn, Cu, and Ga, was utilized for the reduction of CO₂. The 68% - 100% of observed photocurrents were found to be due to reduction of CO₂ to methanol.

In an important communication, Barton et al. [90] investigated the reduction of CO₂ to methanol on pyridine-catalyzed p-GaP photoelectrode in a photoelectrochemical cell (PEC). The band gap energy of this p-GaP photoelectrode is 1.6 eV which allowed it to absorb most of the visible light in solar spectrum. In the presence of pyridinium, methanol formation was observed at - 0.4 V vs SCE with faradaic efficiencies extending from 88 to 100%. However, no methanol production was observed in the absence of pyridinium. The mechanism is depicted in Figure 7.

The quantum efficiency for the photoelectrochemical conversion of CO₂ to methanol was found to be as high as 10.9 % at - 0.50 V/SCE under UV light illumination of wavelength 365 nm (3.39 eV). However, at the same voltage condition of - 0.5 V/SCE, the quantum efficiency was found to be 1.05 % under visible light illumination of wavelength 465 nm (2.66 eV) at which the intensity of solar light of AM 1.5 (1 sun) is maximum. These results indicate that the photo-generated carriers under lower energy photons recombined faster than those generated under high-energy photons and thereby ten-fold lower quantum efficiency was observed. Reduction of CO₂ selectively to methanol is challenging due to closeness of reduction potentials for methanol, formic acid, and formaldehyde. However, reduction of CO₂ in presence of pyridine may have overcome this limitation. A probable mechanism of reduction of CO₂ in presence of homogeneous catalyst pyridine was put forward by Barton et al. [91].

A cluster model was used for the theoretical prediction of structures and binding energies for charged and neutral adsorbates on the GaP(110) surface [92]. The model calculations were made both with the use and without the use of van der Waals interactions and solvation. The binding energy contributions for various adsorbates were found relevant in the CO₂ reduction process.

The composition, the crystal size, pyridine coverage, and the applied bias on p-CuInS₂ photocathode were found to influence the methanol yield during the CO₂ reduction [93]. The mass transfer across the adsorbed pyridine layer was proposed to be the rate-determining step.

Deposition of the transition metal islets (i.e. Ag, Au, Cd, Cu, Pb, and Sn) on CuO/Cu₂O films increased CO₂ reduction to fuel as was identified from faradaic efficiency [94]. For example, Pb on CuO/Cu₂O showed outstanding results among the transition metals. For instance, formation of 0.524 μmol. cm⁻². h⁻¹ formic acid and 0.102 μmol. cm⁻². h⁻¹ MeOH were observed with 40.45% faradaic efficiency at -0.16 V/SHE. However, the CuO layer was found from XPS results to be readily reduced to Cu under cathodic polarization that degraded the performance of the photoelectrode. This indicates that even the metal islets deposition on CuO/Cu₂O could not protect the copper oxide layer from reduction when used as a photocathode even under the low cathodic polarization of - 0.16 V/SHE.

Carbon-modified titanium oxide (CM-n-TiO₂) was used as a photoanode and Cu metal gauze as a dark cathode to reduce CO₂ to methanol in a two-compartment PEC in an aqueous electrolyte of 5.0 M NaOH [81, 95]. The main product was found to be methanol. The highest amount of methanol formation was observed at low negative voltage when the pressurized carbonated water mixed with 5.0 M NaOH solution was used as the electrolyte. The rate of methanol formation decreased after 5 min which may be due to back reaction at the photoanode and/or consumption of all the dissolved carbon dioxide (aqueous CO₂) in the electrolyte. A two-fold increase in methanol formation was observed when 0.5 mM methanol was initially added. This enhancement may be due to added methanol acting as a depolarizer or a sacrificing agent at the photoanode and due to higher solubility of CO₂ in initially added methanol.

It should be noted that no methanol formation was observed when CO₂ was dissolved directly in 5.0 M NaOH solution [81, 95]. This observation may be attributed to formation of carbonate ion in solution when CO₂ is dissolved directly in 5.0 M NaOH, instead of having molecular form of CO₂ present in pressurized carbonated water. It was possible to reduce the linear molecular form of CO₂ to methanol at low negative voltage but not the non-linear CO₃²⁻ anion at the same low voltage.

Using platinum-deposited reduced graphene oxide (Pt-r-GO) as a cathode and Pt-decorated TiO₂ nanotubes (Pt-TNT) as a photoanode in a PEC, CO₂ was converted to methanol, ethanol etc. [96]. Total combined rate of production of CH₃OH, C₂H₅OH, HCOOH, and CH₃COOH was found to be 0.6 μmol. cm⁻². h⁻¹. It should be noted that when Pt-modified carbon nanotubes or platinized carbon was used as a cathode instead of Pt-r-GO the conversion rate of CO₂ was much lower. This observation indicates that the reduced graphene has unique property in reducing CO₂ in a PEC though it is not specific

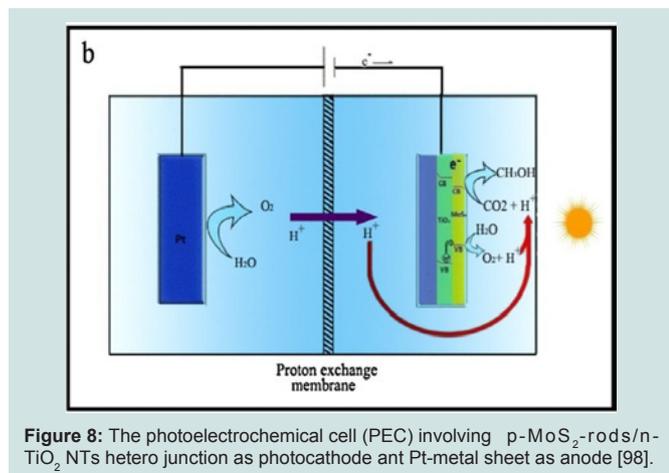


Figure 8: The photoelectrochemical cell (PEC) involving p-MoS₂-rods/n-TiO₂ NTs hetero junction as photocathode and Pt-metal sheet as anode [98].

to methanol formation and the total yield was quite low.

One dimensional wedged or compact nitrogen-doped CuO was prepared on Cu substrate by its anodization. The resulting CuO semiconductor exhibited an energy band gap of 1.34 eV [97]. The photoelectrocatalytic reduction of CO₂ produced predominantly methanol with a current efficiency of 84.4% which was about 15 times higher compared to 5.84 % on bare CuO film. However, the methanol output (600 μmol. L⁻¹. cm⁻². h⁻¹) was 139 times higher than that on the regular CuO film (4.33 μmol. L⁻¹. cm⁻². h⁻¹). This highly enhanced photo response of wedged nitrogen doped CuO compared to regular undoped CuO film can be attributed to the fact that nitrogen sites acted as the active center for CO₂ adsorption and as well as enhanced surface area of wedged sample.

Hydrothermally synthesized highly ordered TiO₂ nanotube arrays (TiO₂NTs) were decorated by MoS₂-rods to produce MoS₂-rods/TiO₂ NTs heterojunction [98], the band gap of which was found to be 1.55 eV. The rate of photoelectrochemical reduction of CO₂ using MoS₂-rods/TiO₂ NTs / Pt PEC enhanced more than two folds compared to that on the regular TiO₂ NTs /Pt PEC. Also, the faradaic efficiency or current efficiency increased by 2.65 times and the methanol yield increased by 2.29 times from 263.25 μmol. L⁻¹. cm⁻². h⁻¹ to 603.75 μmol. L⁻¹. cm⁻². h⁻¹. This marked enhancement of methanol yield on MoS₂-rods/TiO₂ NTs heterojunction can be attributed to low band gap visible light active Mo-S₂-rods and lowering the recombination rate of the photogenerated carriers due to p/n junction produced at the p-type MoS₂ and n-type TiO₂ interface. This advanced photoelectrochemical cell (PEC) to produce methanol isV shown in Figure 8.

Electrochemical reduction of CO₂ to alcohol was achieved using a self-organized TiO₂ nanotube arrays (TNAs) photoanode [99]. Electrochemical anodization method was used (applying 20 V for 2 h at 30 °C) to fabricate the self-organized TiO₂ nano tube arrays (TNAs) with Ti foils as anode in 1 M (NH₄)₂SO₄ electrolyte solution containing 0.5 wt% NH₄F. The photocatalytic conversion of CO₂ and H₂O to alcohols predominately methanol and ethanol was carried out using the annealed TNAs under Xenon lamp illumination. The generation rate of methanol and ethanol were found to be 10 and 9 nano mol. cm⁻² h⁻¹, respectively. Such low rates are due to absorption of only UV light by the regular n-TiO₂ synthesized by anodization of

Ti metal foil. As well as due to the sluggish O₂ evolution on Pt catalyst used as anode.

Layered CuO/Cu₂O semiconductor nanorods was prepared by thermal oxidation of Cu-foil to CuO and followed by electrodeposition of p-Cu₂O on it [87]. These nanorods photoelectrochemically reduced CO₂ to methanol with 95% faradaic efficiencies. This high percentage of Faradic efficiency indicates high selectivity of CuO/Cu₂O for photoelectrochemical reduction of CO₂ to methanol. However, such p-type copper oxide semiconductors will be eventually transformed to their corresponding metals under the cathodic polarization condition and hence their photocatalytic activity will be completely diminished as was observed by other authors [94].

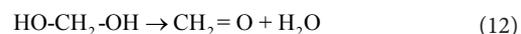
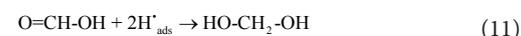
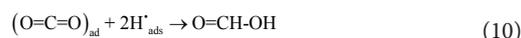
p-CuInS₂ thin film photocathode with co-catalyst pyridinium ion was found to reduce CO₂ to methanol with 97 % the faradaic efficiency[84]. Yield of methanol was reported to be as high as ~ 200 μmol.L⁻¹.cm⁻². h⁻¹.

Wang et al. [100] reported the photoelectrochemical reduction of CO₂ on amine-functionalized TiO₂ supported on Ni-Foam (amine-functionalized TiO₂/Ni-Foam) as a photocathode and BiVO₄ as photoanode. Methanol was the main product and the rate of which was found to be ≤ 153 μ mol. h⁻¹.cm⁻². This value was found to be 15 times higher than that on bare TiO₂/Ni-foam photocathode.

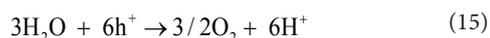
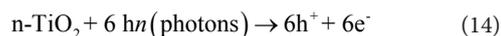
Mechanism of reduction of CO₂ to Methanol in a PEC

One possible mechanism for the reduction of adsorbed (CO₂) ad to methanol (CH₃OH) in aqueous solution involves adsorbed hydrogenradicals, H[•]_{ads} on the cathode surface generated by coupled electron and proton transfer reactions followed by saturation of double bonds in CO₂ (O=C=O) by the hydrogen radicals, formation of formaldehyde and H₂O and then CH₃OH formation by further saturation of the double bond in formaldehyde (CH₂ = O) by hydrogen radicals (see equations 9 -13):

At the metal cathode (M):



Oxygen separation from H₂O occurs at the counter photoelectrode (e.g., n-TiO₂ photoanode) as:



Addition of (Equations 9-15) give the overall reaction,



Summary and Conclusion

Numerous studies were carried out on photocatalytic conversion of CO₂ in aqueous medium to various organic products or fuel. Most of the studies generated limited yield of methanol on photocatalyst surface under light illumination. Thus, future challenges involve the

Table 1

Photocatalyst	Products	Rates of Product yield
Cu ₂ O[69]	Methanol	21.8 μmol. g ⁻¹ cat.h ⁻¹
SiC [69]	Methanol	30.6 μmol. g ⁻¹ cat. h ⁻¹
Cu ₂ O / SiC [69]	Methanol	38.2 μmol. g ⁻¹ cat. h ⁻¹
Bi ₂ S ₃ / CdS[70]	Methanol	122.6 μmol. g ⁻¹ cat. h ⁻¹
Bi ₂ S ₃ /TiO ₂ NTs[55]	Methanol	45.0μmol. g ⁻¹ cat. h ⁻¹
Zn-Cu-Ga-LDH[71]	Methanol	0.17 μmol. g ⁻¹ cat. h ⁻¹
Cu decorated GO[66]	Methanol	3.0μmol. g ⁻¹ cat. h ⁻¹
Ru-polyazine [67]	Methanol	82.0μmol. g ⁻¹ cat. h ⁻¹
BiVO ₄ [72]	Methanol	27.6 μmol. g ⁻¹ cat. h ⁻¹
Fe ₂ O ₃ -TiO ₂ Nanoparticles [58]	Methanol	45.6 μmol. g ⁻¹ cat. h ⁻¹
Nitrogen doped TiO ₂ [59]	Methanol	23 μmol. g ⁻¹ cat. h ⁻¹
Ag/TiO ₂ [60]	Methanol	30.0 μmol. g ⁻¹ cat. h ⁻¹
Cu-TiO ₂ /ZSM-5[64]	Methanol	50.1μmol. g-1 cat. h-1
Co-TiO ₂ /ZSM-5[64]	Methanol	35.21 μmol. g-1 cat.
Mo-Clusters Cs ₄ [Mo ₅ Br ₁₄][103]	Methanol	271.0μmol. g-1 cat. h-1
Mo-Clusters TBA[Mo ₅ Br ₁₄][103]	Methanol	229.0μmol. g ⁻¹ cat. h ⁻¹
Cu(II) imidazolate[104]	Methanol	342.5 μmol. g ⁻¹ cat. h ⁻¹
Graphene OxideGO-3[105]	Methanol	0.172 μ mol. g ⁻¹ cat. h ⁻¹
Ni-TiO ₂ /ACF [106]	Methanol	493.2 μ mol. g ⁻¹ cat. h ⁻¹
Cu/CM-n-TiO ₂ [77]	Methanol	518.6 μ mol. g ⁻¹ cat. h ⁻¹ under UV 177 μ mol. g ⁻¹ cat. h ⁻¹ under natural sunlight.
Cu/CM-nTiO ₂ [78]	Methanol	582.0 μ mol. g ⁻¹ cat. h ⁻¹ under UV 182.0 μ mol. g ⁻¹ cat. h ⁻¹ under natural sunlight.
Photoelectrodes		
N-doped CuO[97]	Methanol	600 μmol. L ⁻¹ .cm ⁻² . h ⁻¹
Un-doped CuO[97]	Methanol	4.3μmol. L ⁻¹ .cm ⁻² . h ⁻¹
MoS ₂ rods/TiO ₂ NTs heterojunction[98]	Methanol	603.8μmol. L ⁻¹ .m ⁻² . h ⁻¹
CuInS ₂ photocathde with pyridinium as co-catalyst[84]	Methanol	200 μmol. L ⁻¹ .cm ⁻² . h ⁻¹
Ni-Foam-supported and amine functionalized TiO ₂ photocathode [100]	Methanol	≤ 153 μ mol. L ⁻¹ .cm ⁻² . h ⁻¹

identification of photocatalysts that can absorb both UV and visible lights of the solar spectrum, preferentially adsorb the dissolved CO₂, limit the competitive hydrogen evolution reaction and as well as minimize the generation of non-fuel reduction products.

Nanoparticulate photocatalysts have the advantage that coupled CO₂ reduction and water oxidation take place on the same particle. This aids in reducing the recombination of photogenerated carriers due to minimal transport distance prior to their reaction with the species at the particle-solution interface. Furthermore, nanoparticles with hetero-junction have the added advantage of generating the photo voltage that helps efficient separation of photoexcited electron-hole pairs prior to their recombination. In addition, the high surface

area of the nanoparticles enhances the yield. Conversely, the limitations of the photocatalysts are the low yield and consequently the low photoconversion efficiency. Under sunlight illumination, the photocatalysts are unable to generate high enough photo voltage to enhance the yield of CO₂ reduction to methanol in aqueous medium (see Equation 3). This intriguing limitation dictates the use of only UV-light active photocatalysts of high band gap. Also, there is no simple way to minimize the reverse reaction that oxidizes the newly formed methanol on the same particle surface unless methods are developed to separate the product continuously from the reaction chamber.

On the other hand, the photoelectrochemical reduction of CO₂ to

methanol in aqueous medium has several advantages. This is because, in addition to solar energy, a minimal amount of energy from the external sources will be possible to utilize. The added advantage is that the external energy source could be from renewable solar or wind power. Alternatively, the use of appropriate combination of p-type and n-type semiconductor photoelectrodes will enable the CO₂ reduction without the need of external bias [101, 102]. In this case, both photoelectrodes will supply the needed photovoltage to enhance the reaction rate.

Moreover, for the photoelectrochemical method to be efficient, the appropriate cathode or photocathode materials on which the dissolved CO₂ is preferentially adsorbed will need to be identified. Furthermore, photoanodes are to be selected such that they can efficiently separate oxygen from water equations 14,15 and can absorb most of the photons of the solar spectrum.

From the survey in this review it looks obvious (Table 1) that Cu or Mo containing materials such as p-CuInS₂ [84], CuO [97] or Cu₂O [69] or MoS₂-rod/TiO₂ NTs heterojunction [98] act as specific cathode or photocathodes for the reduction of CO₂ mainly to methanol at low applied potential. Similarly in presence of homogeneous catalyst, pyridinium, the p-GaP photocathode efficiently reduces CO₂ to methanol in aqueous medium [63]. It is also observed in (Table 1) that Bi₂S₃/CdS [70], Mo-Clusters Cs₂ [63] [Mo₆Br₁₄] [103], Mo-Clusters TBA[Mo₆Br₁₄] [103], Cu(II) imidazolate [104] are the high methanol yielding photocatalysts. However, among the photoelectrodes N-doped CuO [97], MoS₂ rods/TiO₂ NTs heterojunction [98] were found to have the high rates of methanol formation due to affinity of CO₂ to preferentially adsorb on nitrogen sites.

Future studies may focus in identifying appropriate ratios of aqueous-non-aqueous mixed solvents where the dissolution of CO₂ mainly in the molecular form is enhanced. The detailed studies should be made on the effect of the concentration of alkaline electrolyte (e.g. NaOH or KOH) on the yield of methanol. In depth study is also needed in finding the effect of the combination of various amounts of pressurized carbonated water (where CO₂ dissolves mainly in the molecular form) and the concentrated NaOH solution on the yield of methanol.

In a photoelectrochemical cell appropriate membrane should be used to separate the anode and cathode compartments to stop the reverse reaction by blocking movement of methanol formed. Also, for photocatalytic reaction on photoactive nanoparticles the product methanol must be removed continuously by passing an inert gas and be collected by cold trap to avoid back reaction.

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