Conversion of CO₂ to methanol in aqueous medium on visible light active BiVO₄, Cu₂BiVO₆ photocatalysts and in CM-n-TiO₂ - Cu PEC by simultaneous electron and proton transfer reactions

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Abstract

Photocatalytic conversions of CO_2 to methanol were carried out in aqueous medium on visible light active bismuth vanadium oxide ($BiVO_4$) and on copper bismuth vanadium oxide (Cu_2BiVO_6) photocatalysts under illumination of light intensity of 1 sun (0.1 W cm^{-2}). The percent solar to methanol conversion efficiency (% STME) was found to be 2.78% on of $BiVO_4$ compared to 2.50% on Cu_2BiVO_6 photocatalyst under same illumination condition for 80 min reaction time. Such small difference in the photoconversion efficiencies can be attributed to similar band gap energies, absorption coefficient of light and particle sizes for both samples. At more than 80 min reaction time, the amount of methanol formation reduced drastically due to rapid uncontrollable back reaction on the same photocatalyst surface. Much higher solar to methanol photoconversion efficiency (% STME) of 5.83% was observed when CO_2 was reduced to methanol on Cu cathode and water was oxidized to O_2 on visible light active carbon modified titanium oxide (CM-n-TiO_2) photoanode in a photoelectrochemical cell (PEC) under minimal external bias of 0.3 V for the reaction time of 10 min. Methanol formation was found to be dependent on the way the CO_2 solution was prepared under pressure in deionized water and followed by addition of NaOH solution so that the most of the dissolved CO_2 remained intact in its molecular form. A mechanism of the photoelectrochemical reduction of adsorbed CO_2 (aq) to methanol was given in terms of multi electron and proton transfer reactions
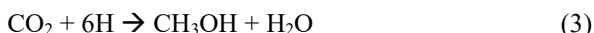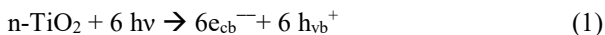
under illumination followed by removal of a water molecule from the intermediate.
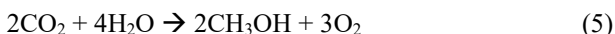
1 Introduction

It is an undeniable fact that carbon dioxide accounts for the largest share of the world's greenhouse gas emissions by its alarming increase in the atmosphere [1, 2]. Each year about 1.0×10^9 tons of carbon dioxide (CO_2) gas is added to the atmosphere, and during the next half century there will be about 50% increase in its concentration to reach to 600 ppm from its level in the year 2000. Such large-scale emission of carbon dioxide is believed to be essentially responsible for present changes in global climate system. One way to solve the CO_2 problem permanently would be to selectively convert it to a useful product such as liquid fuel methanol (CH_3OH). Transformation of CO_2 to methanol, a reusable source of energy, is carbon neutral that will benefit humans and save the environment. These conversions need energy infusion. This energy source should be one that does not add more CO_2, such as solar energy. On an estimate 5×10^{13} mol. of methanol would be needed to drive the car of the world on internal combustion engine and about half of that would be needed for cars powered by methanol run fuel cells [3]. Considering CO_2 emission at 2050 as 5×10^{14} moles, it is conceivable that fixing most of the CO_2 output as methanol provides a convenient hydrogen carrier for automotive fuel and in fuel cells as well [3]. Hence, the loop process of CO_2 capture and its direct solar reduction to methanol in aqueous medium on a photocatalyst surface or in a photoelectrochemical cell for its re-use will provide an ideal carbon neutral energy source that will minimize global warming and the dependence on world's depleting fossil fuel.

The process of reduction of CO_2 to methanol on a photocatalyst (e.g., $n\text{-}TiO_2$) surface in aqueous medium can be given as

$$n\text{-}TiO_2 + 6\ hv \rightarrow 6e_{cb}^- + 6\ h_{vb}^+ \tag{1}$$

$$6H^+ + 6e_{cb}^- + \rightarrow 6H \tag{2}$$

$$CO_2 + 6H \rightarrow CH_3OH + H_2O \tag{3}$$

$$6OH + 6h_{vb}^+ \rightarrow 3/2\ O_2 + 3H_2O \tag{4}$$

Overall reaction is given by addition of Equations (1)–(4) as

$$2CO_2 + 4H_2O \rightarrow 2CH_3OH + 3O_2 \tag{5}$$

However, in a photoelectrochemical cell (PEC) water oxidation to oxygen at photoanode can be used to facilitate the reduction of carbon dioxide to methanol at the dark cathode or photocathode according to following reactions.
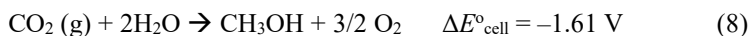
At the photoanode (with photogenerated holes, h^+ as in Equation (1):

$$3H_2O + 6h^+ \rightarrow 3/2\ O_2 + 6H^+ \qquad E^o_{red}\ (anode) = -1.23\ V \tag{6}$$
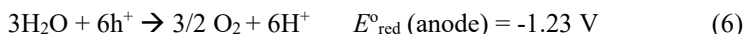
At the cathode or photocathode (with photogenerated electrons, e⁻ as in Equation (1):

$$CO_2 \text{ (g)} + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad E°_{red} \text{ (cathode)} = -0.38 \text{ V} \qquad (7)$$
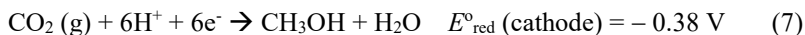
The overall reaction is obtained by combining reactions (6) and (7) to give:

$$CO_2 \text{ (g)} + 2H_2O \rightarrow CH_3OH + 3/2 \, O_2 \qquad \Delta E°_{cell} = -1.61 \text{ V} \qquad (8)$$

This reaction (8) which involves 6 electron and 6 proton transfer process (see reaction 7) is accessible in aqueous medium in a photoelectrochemical cell (PEC) having appropriate photoelectrodes under sunlight illumination. Any process to be thermodynamically feasible the photocatalysts or photoelectrodes must supply the needed voltage under sunlight illumination. Hence, the main challenge for CO_2 reduction involves the search for suitable photocatalysts or photoelectrodes that can absorb both UV and visible light, can generate sufficient photovoltage and importantly be highly specific to convert CO_2 to useful fuel, methanol (CH_3OH) and not other non-fuel organics. Most widely tested photocatalyst used for the reduction of CO_2 was the n-TiO_2 nanoparticles and the reaction product was mainly methane, CH_4. The photocatalytic reduction of CO_2 to methanol was reported on combined visible light active p-type Cu_2O and n-type SiC in the form of nanocrystallites (p-Cu_2O/n-SiC) and reported yield of 36 μ mol. h⁻¹. gcatal.⁻¹ [4]. This indicates that Cu acted as an effective catalyst for the reduction of CO_2 specifically to methanol. Liu *et al*. [5] reported selective ethanol formation from photocatalytic reduction of carbon dioxide in water using visible light active $BiVO_4$ photocatalyst. The photocatalyst Cu_2BiVO_6 was found visible light active during oxygen evolution reaction on it [6].

Barton *et al*. [7] reported a selective solar-driven reduction of CO_2 to methanol using a pyridine catalyzed UV and visible light active p-GaP as photocathode based photoelectrochemical cell but no results on amounts of methanol produced was reported under white light illumination. Le *et al*. [8] reported electrochemical reduction of CO_2 to CH_3OH at copper oxide surfaces. Photocatalyst such as bismuth vanadium oxide ($BiVO_4$) were found both UV and visible light active [9]. Carbon modified titanium oxide (CM-n-TiO_2) thin film was found to absorb both in the UV and in the visible regions of solar spectrum during water splitting reaction [10].

In this study we have investigated both UV and visible light active nanoparticulate photocatalysts such as bismuth vanadium oxide ($BiVO_4$) and also copper bismuth vanadium oxide (Cu_2BiVO_6) for the reduction of CO_2 to methanol in an aqueous medium. We have also used CM-n-TiO_2 as the photoanode and Cu-metal as the cathode for the reduction of CO_2 to methanol in a photoelectrochemical cell (PEC) in an electrolyte solution that was made by mixing equal volumes of pressurized carbonated water and already prepared 5.0 M NaOH.

2   Experimental

2.1 Synthesis of photocatalyst BiVO₄ in a 125 mL Parr bomb

A 0.075 M $Bi(NO_3)_3 \cdot 5H_2O$ solution was made by dissolving 0.9095 g of it in 25 mL of 4.0 M HNO_3 under magnetic stirring for 2 hrs. Also a 0.075 M NH_4VO_3 solution was prepared by dissolving 0.2194 g of it in 25 mL of 2.0 M NaOH under magnetic stirring for 2 hrs. This alkaline solution of NH_4VO_3 was added drop wise to acidic $Bi(NO_3)_3 \cdot 5H_2O$ solution and stirred for 1 hr. The pH of the solution was adjusted to 7 with dilute HNO_3 and dilute NaOH. This solution was then poured in a Parr bomb (Figure 1) and then heated at 200°C for 6 hours in an electric oven. The solid product $BiVO_4$ was filtered after the Parr bomb was cooled to room temperature. The yellow precipitate of $BiVO_4$ nanoparticles was vacuum dried overnight in room temperature.

Figure 1:   125 mL Parr bomb.

2.2 Synthesis of photocatalyst Cu₂BiVO₆ in solid phase

0.932 g of Bi_2O_3, 0.640 g of CuO and 0.468g of NH_4VO_3 were mixed by grinding together in an agate mortar and heated at 750°C for 20 hrs followed by cooling to room temperature. This procedure gave a brown Cu_2BiVO_6 nanoparticles.

2.3 Synthesis of carbon modified titanium oxide (CM-n-TiO₂) thin films

Ti metal sheets (0.25 mm thick, 99.5% from Alfa Co.) were cut to an area of ~1.0 cm². These metal samples were cleaned in a sonicator for three fifteen min. intervals with acetone; acetone: double de-ionized water (1:1 ratio) and finally in double de-ionized water. After drying in air at room temperature, carbon modified titanium oxide (CM)-n-TiO_2 thin films were synthesized by flame oxidation of the cleaned Ti metal samples at 850°C for 15 min. using a custom designed multi-holed large area flame (Knight, model RN. 3.5 XA WC) under controlled oxygen and natural gas flows. Most importantly, the flame was kept facing downward to minimize the excess airflow from the surrounding. A thermocouple (Thermolyne Corp K-type Thermocouple, PM-20700) was used to measure the temperature of the flame and was maintained it constant by controlling the oxygen and natural gas flow rates using FL-1807 and FL-1806 flow meters (Omega Engineering) respectively. The flame oxidation temperature of 850°C was kept constant for 15 min. by controlling the flow rates of oxygen (1.5 L/min to 2.0 L/min) and the natural gas (2.0 L/min).

2.4 Preparation of aqueous solution of CO₂

CO_2 (g) was dissolved in deionized water under pressure in a pressure cell (Figure 2) at room temperature or used pressurized carbonated water made in a commercial carbonator. Equal volumes of this carbonated water (20 mL) and 5.0 M NaOH (20 mL) were added to make the electrolyte concentration of 2.5 M NaOH of volume 40 mL. Note that the aqueous solution of CO_2 in carbonated water was made basic by the addition of already prepared NaOH solution to minimize the competitive reduction of proton to hydrogen gas. Carbon dioxide dissolves in water as

$$CO_2 \text{ (g)} \leftrightarrow CO_2 \text{ (aq)} \tag{9}$$

It is expected that most of the carbon dioxide remains as solvated molecular form of CO_2 since at 25°C the concentration of CO_2 (aq) is more than 600 times higher [11] than that of H_2CO_3(aq) such that

$$[CO_2 \text{ (aq)}] = 600 \times [H_2CO_3 \text{ (aq)}] \tag{10}$$

Under pressure more carbon dioxide can be dissolved in water which are trapped by water molecules to form solvated molecular CO_2 (aq). The small amounts of carbonic acid that are formed make the aqueous CO_2 solution acidic. However, rapid dissolution of gaseous CO_2 (g) occurs when it is dissolved directly in sodium hydroxide solution to form $NaHCO_3$. Hence, it is expected that when CO_2 solution is made directly in aqueous NaOH solution, the [CO_2 (aq)] will be lower than the [HCO_3^- (aq)].

2.5 Setup for photochemical experiments

A 100 mg of photocatalyst $BiVO_4$ was added to a mixture of 25 mL of 5.0 M NaOH and 25 mL of CO_2 saturated (carbonated) water. The total volume of the solution became 50.0 mL of 2.5 M NaOH. This 50 mL of 2.5 M solution having 100 mg catalyst in it was magnetically stirred and irradiated with light through a transparent glass window (see Figure 3) having intensity of 0.1 W cm⁻² from a 150 watt Xenon lamp for 60 min. After 60 min. a 1.0 mL of the solution having reaction products was heated to 90°C in GC vial prior to GC analysis using headspace. This procedure was then repeated for 80 min., 100 min. and 120 min. reaction times. No other GC peaks other than the methanol peak was observed in solution phase. Negligible amount of methanol was detected in the gas phase. The amounts of methanol formed were obtained from the observed GC peak areas using the GC peak area of methanol standard. This procedure was also used for photocatalyst, Cu_2BiVO_4 for reaction time of 80 min.

2.6 Setup for photoelectrochemical experiments

To carry out the photoelectrochemical experiment, a 20 mL of CO_2 saturated water (carbonated water) was mixed with an equal volume (20 mL) of 5.0 M NaOH to prepare the electrolyte with an overall NaOH concentration of 2.5 M having total volume of 40 mL.

Figure 2:   Pressure cell.

Figure 3:   Setup for photochemical experiments.

The PEC consisted of a two-compartment quartz glass cell (see Figure 4). A 20 mL of this electrolyte solution was poured in each compartment. We used Saturated Calomel Electrode (SCE) as the reference electrode and the CM-n-TiO$_2$ thin films as the photoanode (working electrode) of surface area 0.65 cm^2 into the compartment 1. In compartment 2, a 3.0 cm^2 piece of Cu mesh was used as a counter electrode (cathode) for the reduction of CO$_2$ to methanol. This Cu mesh was cleaned in 1M HCl for 10 min. prior to use. Both compartments were connected by the salt-bridge made of the same electrolyte soaked glass wool thread. The photoanode (CM-n-TiO$_2$) was exposed to light intensity of 0.1 W cm^2 from a 150 watt Xenon lamp and also from a solar simulator (Thermo Oriel model 81192) for different set of experiments.
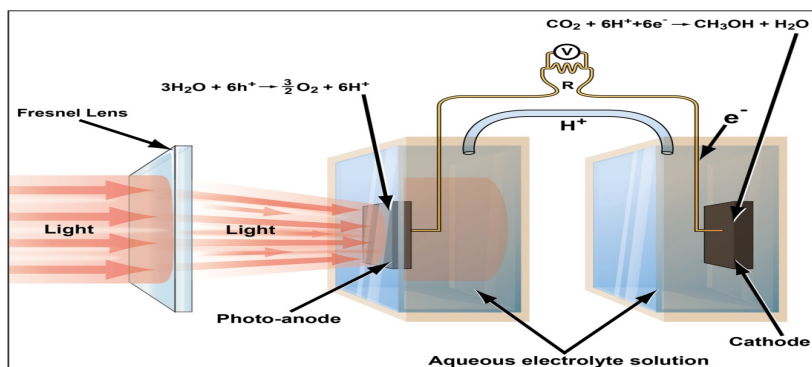

Figure 4:   A schematic diagram of a two-compartment photoelectrochemical cell (PEC), having the same electrolyte solution (2.5 M NaOH). Both compartments were connected by a bridge containing the same electrolyte having glass wool separator.

We altered the shapes of the Cu-mesh counter electrode (cathode at which reduction of CO$_2$ to methanol occurred) in an attempt to elucidate how its three-dimensional form might affect the production of methanol (MeOH). The configurations included: open, folded once, folded twice, rolled into a tube, and rolled into a compact tube. The only configurations that produced appreciable amounts of MeOH was the one folded once, and rolled into a tube.

2.7 Gas chromatographic analysis

The identification and quantification of the methanol production was carried out using a Shimadzu GC-2010 plus gas Chromatograph using headspace at elevated temperature of 90°C.

3 Results and discussion

3.1 Photochemical experiments

3.1.1 Photoconversion of CO_2 to methanol by visible light active BiVO₄ photocatalyst

For the observed GC peak areas using the observed peak area of 136 for 1.0 mM methanol as standard the methanol concentrations and its rates of formation of methanol, r_{MeOH} (in moles per g. catalyst per second) were determined. The solar to methanol conversion efficiency, % STME for photochemical reduction of CO_2 to methanol in aqueous medium was calculated using the expression,

$$\% \text{ STME} = [(- \Delta H^\circ_{MeOH} \, r_{MeOH}) / (P_{light} \times A_{light})] \times 100 \qquad (11)$$

where $\Delta H^\circ_{MeOH} = - 726$ kJ mole^{-1} is the standard heat of combustion of methanol, $P_{light} = 0.1$ W cm^{-2} is the intensity of light used and A_{light} in cm^2 is the cross sectional area in the reaction chamber on which light was exposed, r_{MeOH} is the rate of methanol production as the number of moles of methanol produced per gram catalyst per second that can be calculated using,

$$r_{MeOH} = (n_{MeOH} / m_{cat}.t_{reaction}) \qquad (12)$$

where n_{MeOH} is the number of moles of methanol formed in reaction time, $t_{reaction}$ (in seconds) and m_{cat} is the mass of the catalyst used (in grams).

Solar to methanol conversion efficiency values for the conversion of CO_2 to methanol were calculated using Equations (11) and (12) and given in Table 1. The number of moles of methanol formed per gram catalyst was plotted as a function reaction time in Figure 5.

Table 1: The results of photochemical reduction of CO_2 to methanol using BiVO₄ as nanoparticulate photocatalyst. A 50 mL, 0.1 g and 10 cm^2 were used as the reactant volume, weight of the BiVO₄ catalyst, and the area exposed to light per g.cat respectively. GC standard peak area of 136 for 1.0 mM Methanol (MeOH) was used.

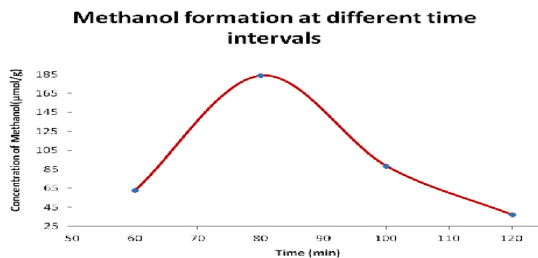| Reaction time, t reaction (min)	GC area found for MeOH	Molarity of MeOH formed (mM)	Moles of MeOH formed (μ mol. gcat^{-1})	Rate of MeOH formation, r_{MeOH} (mol. g. catal. s^{-1})	Percent solar to MeOH efficiency (% STME)
60	17	0.125	62.5	1.74×10^{-8}	1.26
80	50	0.368	183.8	3.83×10^{-8}	2.78
100	24	0.176	88.2	1.47×10^{-8}	1.06
120	9.5	0.07	35.0	4.86×10^{-9}	0.35

Methanol formation at different time intervals

Figure 5:   Methanol concentration (μ mol. gcatal^{-1}) as a function of reaction time.

It is observed in Table 1 and Figure 5 that the highest yield of methanol was observed for 80 min. reaction time on BiVO$_4$ photocatalyst but decreased at higher than 80 min. reaction time. We observed solar to methanol efficiency, % STME of 2.78% on BiVO$_4$ photocatalyst for 80 min. reaction time under illumination of 1 Sun from a Xenon lamp as shown in Table 1. The % STME reduced to 0.35 % for 120 min. reaction time. This may be due to rapid uncontrollable back reaction on the same photocatalyst surface.

3.1.2 Photoconversion of CO_2 to methanol Cu_2BiVO_6 photocatalyst

For the observed GC peak area of 45 for methanol using the observed GC peak area of 136 for 1.0 mM methanol standard, the methanol concentration was found to be 0.331 mM in 50 mL of reaction mixture having 0.1 gram Cu_2BiVO_6 photocatalyst exposed to light intensity of 0.1 W cm^{-2} for 80 min. reaction time. This then converts to rate of methanol formation, r_{MeOH} as equal to 3.45 x 10^{-8} mole methanol per second per gram catalyst. Using r_{MeOH} = 3.45 x 10^{-8} mole. s^{-1}. gcatal.$^{-1}$ in Equation (11) we found % STME = 2.50% for this photocatalyst. This value is comparable to 2.78% found using BiVO$_4$ photocatalyst.

3.2 Photoelectrochemical experiments

3.2.1 The percent solar to methanol conversion efficiency (% STME)

The percent solar to methanol conversion efficiency (% STME) for photoelectrochemical reaction in a PEC can be expressed as [10],

$$\% \text{ STME} = [j_p(E°_{rev} - E_{app})/P_{light})] \times 100 \qquad (13)$$

where photocurrent density, j_p (amps cm^{-2}) at the photoanode can be calculated from the number of moles of methanol, n_{MeOH} formed in the PEC using Faraday equation such that

$$j_p = (n_{MeOH} \times n_e \times F)/ (A_{photoelectrode} \times t_{reaction}) \qquad (14)$$

F is the Faraday constant = 96485 C mole^{-1}, n_e = 6 is the number of electron transferred for the reduction of CO_2 to methanol in aqueous medium (see Equation 7), $A_{photoelectrode}$ is the area in cm^2 of photoelectrode, CM-n-TiO$_2$ (e.g. 0.65 cm^2) that was exposed to light, $t_{reaction}$ is the reaction time in seconds and P_{light} is the

intensity of light ($0.1 W\ cm^{-2}$), $E°_{rev}$ is the reversible potential for CO_2 reduction to methanol = 1.61 volt and the potential applied, E_{app} can be expressed as [10],

$$E_{app} = (E_{meas} - E_{aoc}) \qquad (15)$$

where E_{meas} is the measured potential with respect to reference electrode (SCE) at which the electrochemical CO_2 reduction reaction was carried out under illumination of light and E_{aoc} is the potential vs SCE at the open circuit condition under the same illumination. We used E_{meas} = -0.3 V/SCE and E_{aoc} was found to be -0.6 V/SCE which gives the applied potential, E_{app} = 0.3 V. The percent solar to methanol conversion efficiencies, % STME were calculated using the Equations (13) and (14) and the results are given in Table 2.

Table 2:   The results of photoelectrochemical reduction of CO_2 to methanol (MeOH). A 20 mL and $0.65\ cm^2$ were used as reactant volume and CM-n-TiO_2 area respectively. GC standard peak area of 180 for 0.5 mM MeOH was used. The results in first two rows were obtained under Xenon lamp light whereas the result of last row was obtained under solar simulated light.

Reaction time, t reaction (min)	GC peak area found for MeOH	Molarity of MeOH (mM)	Moles of MeOH formed	Photocurrent density, j_p (amps cm^{-2})	Percent solar to methanol efficiency, % STME
10	54	0.150	3.00×10^{-6}	4.45×10^{-3}	5.83
20	55	0.153	3.06×10^{-6}	2.27×10^{-3}	2.97
10	51	0.142	2.83×10^{-6}	4.20×10^{-3}	5.50

It is observed in Table 2 that % STME decreased from reaction time of 10 min. to reaction time of 20 min. This observation can be attributed to back reaction also occurring in the two-compartment PEC. The use of carbonated water and the alkaline electrolyte solution under electrochemical applied potential of 0.3 V facilitated the methanol formation with high yield and high solar to methanol efficiency (e.g. 5.83% for 10 min. reaction time. This is much higher compared to those on photocatalyst nanoparticles (e.g. 2.78%) for the reaction time of 80 min. This is because the applied potential helped to overcome the thermodynamic barrier of this reaction and also the use of two-compartments PEC helped to minimize the back reaction to some extent. Note that only 0.32% difference in % STME was observed when light source of solar simulator (row 3 results) was used instead of xenon lamp (row 1 and 2 results) was used for 10 min reaction time.

3.3 Mechanism of CO_2 reduction to methanol

If CO_2 dissolves in water mainly in the form of HCO_3^- or CO_3^{2-} anions then the reduction of these anions becomes highly unfavorable due to their highly negative reduction potential. High negative potential is required for these anions due at least in part to the kinetic restrictions imposed by the structural difference between the linear CO_2 molecule and nonlinear bicarbonate and carbonate anions. Also, the reduction of CO_2 by single electron transfer to form CO_2^- radical anion is unfavorable due to its reduction potential of -1.90 V vs NHE due to a large reorganization energy between linear CO_2 molecule and non-linear bent radical anion. High reduction rate requires overpotential of up to 0.6 V, due at least in part to the kinetic restrictions imposed by the structural difference between the linear CO_2 and its nonlinear radical.

An alternative more favorable pathway is to reduce CO_2 through multiple electron-multiple-proton (six electrons and six proton) transfer process. This is because proton coupled multi-electron and proton transfer steps are generally more favorable than the single electron reduction reaction since in the former more stable molecule methanol is formed. The mechanism of reduction of the dissolved and surface adsorbed molecular CO_2 to CH_3OH is straight forward: addition of four nascent reactive H atoms formed by the reduction of H^+ at the cathode to saturate two C=O bonds in CO_2 (O=C=O) to form $OH-CH_2-OH$ and releasing a water molecule to form formaldehyde as $CH_2=O + H_2O$ and then addition of two more nascent hydrogen atoms to surface adsorbed formaldehyde ($CH_2=O$) to form CH_3OH.

3.4 UV-Vis spectra

The UV-Vis spectra of photocatalysts $BiVO_4$ and Cu_2BiVO_6 are given in Figure 6 and Figure 7 respectively. Though their absorption pattern looks different both photocatalysts show visible light absorption.
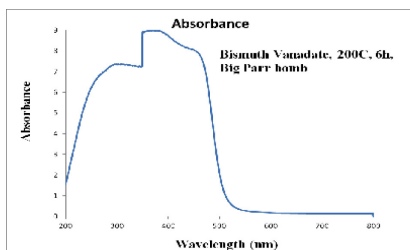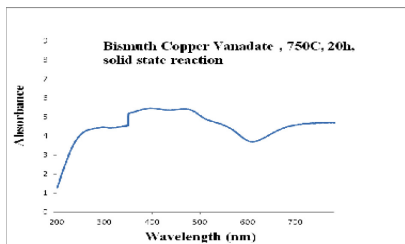

Figure 6: UV-Vis spectrum of $BiVO_4$.

Figure 7: UV-Vis of Cu_2BiVO_6.

3.5 Scanning Electron Microgram (SEM)

The SEM picture of $BiVO_4$ is shown in Figure 8. A layered like structure is observed in this SEM picture. The SEM picture of CM-n-TiO_2 film in Figure 9 shows nano-wall like micro-structured morphology having high surface area, which in turn contributed in enhancing the rate of water oxidation at CM-n-TiO_2 photoanode and thereby facilitated the CO_2 reduction to methanol at the Cu cathode.
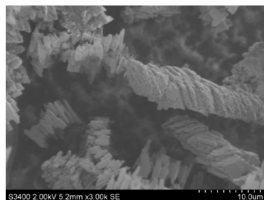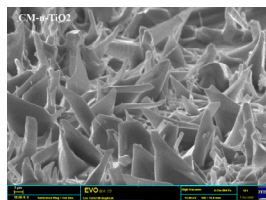

Figure 8: SEM Image of $BiVO_4$.

Figure 9: SEM image of CM-n-TiO_2 film.

3.6 NMR and GC-MS

We have also identified the methanol by NMR analysis and also confirmed by GC-MS by finding its molar mass of 32.0 g /mole.

4   Conclusion

We could observe the reduction of CO_2 to methanol in an aqueous medium when either $BiVO_4$ or Cu_2BiVO_6 photocatalyst nanoparticles was exposed to light with low yield and low photoconversion efficiency compared to those in CM-n-TiO_2 llCu photoelectrochemical cell. The yield of methanol on photocatalyst particles was found to increase with reaction time but drastically decreased when reaction time was drastically increased further. This is due to rapid uncontrollable back reaction on the same photocatalyst surface. It should be pointed out that we could successfully enhance the production of methanol by direct reduction of CO_2 using CM-n-TiO_2 as photoanode under illumination of 1 sun and Cu-metal as the dark cathode. Notably, no methanol formation was observed when CO_2 was dissolved directly in NaOH solution. Future studies on nanoparticulate photocatalyst must involve methods for rapid removal of product methanol from the reaction mixture prior to its conversion back to reactants, CO_2 and H_2O. For example, by passing the CO_2 gas through the reaction mixture and collect the product methanol in a cold trap. Use of pressurized carbonated water in 2.5 M NaOH in which H^+ concentration is low, helped to minimize the competitive H_2 gas evolution at the cathode. The use of two compartments PEC connected by a salt bridge also helped to reduce the rate of back reaction and hence enhanced the methanol production by direct reduction of CO_2 having higher percentage of solar to methanol

efficiency. Future studies should involve Nafion membrane between the photoanode and cathode compartment to block the back reaction.

Acknowledgement

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