

## A Journey from CO<sub>2</sub> to Energetic Fuel

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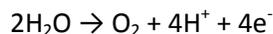
Energy is very crucial to obtain primary requirements of life as well as to sustain a comfortable and modern lifestyle. Energy demand is climbing day by day due to rapid industrialization, better quality life and increase in population. If such trend remains, then all resources of oils will be depleted in the coming years. We must rely on alternative renewable energy resources to maintain a standard of living. However, utilization of biomass provides many different ways for waste to useful energy resources by transforming forest, agriculture or municipal solid wastes to biofuels. The atmospheric concentration of CO<sub>2</sub> has awfully increased in the past century from the combustion of fossil fuels, which is the main source of global warming<sup>1</sup>. Many countries have tried to reduce CO<sub>2</sub> level by storing it in safe places such as oceans and depleted coal seams (CO<sub>2</sub> sequestration) but this method is highly expensive due to which it becomes a burden for those countries<sup>2</sup>. By keeping in mind that CO<sub>2</sub> is cheap, green and renewable feedstock, it can be converted into biofuels.

Many approaches have been developed for CO<sub>2</sub> reduction including electrochemical reduction, photochemical reduction and photo-electrochemical reduction. In electrochemical method, CO<sub>2</sub> can be converted electrochemically to formaldehyde, formic acid, methanol and methane employing various electrodes such as RuO<sub>2</sub>-coated diamond electrode<sup>3</sup>, poly-pyrrole electrode<sup>4</sup> and Cu electrode. But this method is economically unfavorable as it requires electricity.

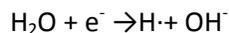
In photochemical reduction, excitation of an electron from the valence band to the conduction band takes place on irradiation with suitable visible light energy. The photo-generated electron can reduce CO<sub>2</sub> to formaldehyde, formic acid, methanol and methane. For CO<sub>2</sub> reduction, different semiconductors such as TiO<sub>2</sub>, WO<sub>3</sub>, ZnO, GaP, CdS and SiC were studied. Various types of photocatalysts such as SrTiO<sub>3</sub>, dispersed TiO<sub>2</sub> on glass, Cu loaded TiO<sub>2</sub> powder, zeolite modified TiO<sub>2</sub> were used for photocatalytic reduction of CO<sub>2</sub>. p-type InP/Ru complex polymer hybrid photocatalyst was found to be selective for the formation of HCOOH<sup>5</sup> and Bi<sub>2</sub>WO<sub>6</sub> nanoplates were found to be selective for reduction of CO<sub>2</sub> to CH<sub>4</sub><sup>6</sup>. An artificial photosynthesis system based on the enzyme coupled graphene photocatalysts for the formation of HCOOH from CO<sub>2</sub> under solar energy was investigated in which graphene is allowed to

covalently bind to the chromophore (as an electron donor). Once the absorption of the photon takes place, electrons get excited from the chromophore which reach to the Rh-complex via graphene due to which Rh-complex get reduced. Rh-complex works as an electron mediator and abstracts proton, transfer electrons and a hydride to  $\text{NAD}^+$  which gets converted into NADH. Now, this NADH converts  $\text{CO}_2$  into HCOOH in the presence of formate dehydrogenase. The transfer of the photo-excited electron becomes difficult because of the small energy difference between the conduction band of chemically converted graphene and the reduction potential of Rh-complex which results in very low efficiency of NADH regeneration<sup>7</sup>.

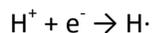
A highly efficient photo-electrochemical  $\text{CO}_2$  reduction under halogen light irradiation using electrolytes  $\text{KHCO}_3$  in cathodic chamber and  $\text{NaCl}$  in an anodic chamber for the formation of four main products formaldehyde, formic acid, methanol and methane takes place.  $\text{CO}_2$  reduction is achieved as the oxidation state of carbon changes from +IV to +II, 0, -II and then -IV i.e., from  $\text{CO}_2$  to formaldehyde, formic acid, methanol and methane respectively. The electrons and holes are generated as a result of excitation of solar cell by sunlight. Oxidation of the  $\text{H}_2\text{O}$  molecule at the anode takes place, which results in formation of oxygen ( $\text{O}_2$ ) and protons ( $\text{H}^+$ ) i.e.



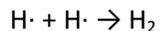
The photon-generated electron reacts with water adsorbed on the cathode (e.g. copper electrode), resulting in the production of hydrogen radical ( $\text{H}\cdot$ ) and hydroxyl ion ( $\text{OH}^-$ ) i.e.



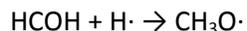
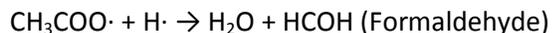
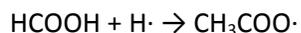
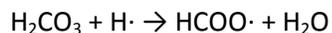
The proton is then transferred to the cathode and gets reduced to hydrogen radical, i.e.

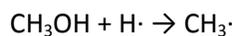
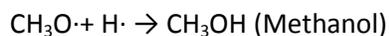


Recombination of hydrogen radicals yields hydrogen molecule, i.e.



A series of hydrocarbons with decreasing oxidation numbers such as HCOOH, HCHO,  $\text{CH}_3\text{OH}$  and  $\text{CH}_4$  are produced as a result of reaction between aqueous carbon dioxide molecules and hydrogen radical<sup>8</sup>, i.e.





Instead of using Pt and Cu as electrodes, we can also use GaN as photoanode and Indium as cathode in which light illumination of photoanode creates electron-hole pair which leads to H<sub>2</sub>O oxidation in an anodic chamber containing NaOH and CO<sub>2</sub> reduction in cathodic chamber containing KHCO<sub>3</sub> as an electrolyte. Effectiveness of GaN photoelectrode can be increased by using AlGaN/GaN heterostructure. Because of the pH difference of the two electrolytes, potential difference is generated. Now the reaction product HCOOH can be used as a renewable energy resource. This method has a maximum quantum efficiency of 28% at 300 nm without the need of any sacrificial material and photoelectrode degradation was also not observed<sup>9</sup>.

An efficient photo-electrochemical cell is also achieved by using single-crystal semiconductor as electrodes but here photo corrosion is a major problem. So an alternative to a photo-electrochemical system is to use a coupled photovoltaic-electrochemical system which utilizes metallic electrodes. The use of metal-based electrodes creates a system that can carry out a complex chemical process such as the multielectron, multi-proton reduction of CO<sub>2</sub>. Here n-GaN was used as photoanode and Indium as cathode for the conversion of CO<sub>2</sub> to HCOOH<sup>10</sup>. The conversion of CO<sub>2</sub> into potential chemical commodities using solar energy has numerous benefits which will provide us energy as well as very helpful in reducing the global warming problem. To store energy in a more convenient and highly usable form of high energy density liquid fuel, there is not any better option till now. Overall this idea has sparkling future due to its importance and eco-friendly properties.

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