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A Journey from CO_2 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_2 has awfully increased in the past century from the combustion of fossil fuels, which is the main source of global warming[1]. Many countries have tried to reduce CO_2 level by storing it in safe places such as oceans and depleted coal seams (CO_2 sequestration) but this method is highly expensive due to which it becomes a burden for those countries[2]. By keeping in mind that CO_2 is cheap, green and renewable feedstock, it can be converted into biofuels.

Many approaches have been developed for CO_2 reduction including electrochemical reduction, photochemical reduction and photo-electrochemical reduction. In electrochemical method, CO_2 can be converted electrochemically to formaldehyde, formic acid, methanol and methane employing various electrodes such as RuO_2-coated diamond electrode[3], poly-pyrrole electrode[4] 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_2 to formaldehyde, formic acid, methanol and methane. For CO_2 reduction, different semiconductors such as TiO_2, WO_3, ZnO, GaP, CdS and SiC were studied. Various types of photocatalyts such as $SrTiO_3$, dispersed TiO_2 on glass, Cu loaded TiO_2 powder, zeolite modified TiO_2 were used for photocatalytic reduction of CO_2. p-type InP/Ru complex polymer hybrid photocatalyst was found to be selective for the formation of HCOOH[5] and Bi_2WO_6 nanoplates were found to be selective for reduction of CO_2 to CH_4 [6]. An artificial photosynthesis system based on the enzyme coupled graphene photocatalyts for the formation of HCOOH from CO_2 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 NAD^+ which gets converted into NADH. Now, this NADH converts 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[7].

A highly efficient photo-electrochemical CO_2 reduction under halogen light irradiation using electrolytes $KHCO_3$ in cathodic chamber and NaCl in an anodic chamber for the formation of four main products formaldehyde, formic acid, methanol and methane takes place. CO_2 reduction is achieved as the oxidation state of carbon changes from +IV to +II, 0, -II and then -IV i.e., from 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 H_2O molecule at the anode takes place, which results in formation of oxygen (O_2) and protons (H^+) i.e.

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

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

$H_2O + e^- \rightarrow H\cdot + OH^-$

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

$H^+ + e^- \rightarrow H\cdot$

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

$H\cdot + H\cdot \rightarrow H_2$

A series of hydrocarbons with decreasing oxidation numbers such as HCOOH, HCHO, CH_3OH and CH_4 are produced as a result of reaction between aqueous carbon dioxide molecules and hydrogen radical[8], i.e.

$H_2CO_3 + H\cdot \rightarrow HCOO\cdot + H_2O$

$HCOO\cdot + H\cdot \rightarrow HCOOH$ (Formic acid)

$HCOOH + H\cdot \rightarrow CH_3COO\cdot$

$CH_3COO\cdot + H\cdot \rightarrow H_2O + HCOH$ (Formaldehyde)

$HCOH + H\cdot \rightarrow CH_3O\cdot$

$CH_3O\cdot + H\cdot \rightarrow CH_3OH$ (Methanol)

$CH_3OH + H\cdot \rightarrow CH_3\cdot$

$CH_3\cdot + H\cdot \rightarrow CH_4$ (Methane)

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_2O oxidation in an anodic chamber containing NaOH and CO_2 reduction in cathodic chamber containing $KHCO_3$ 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[9].

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_2. Here n-GaN was used as photoanode and Indium as cathode for the conversion of CO_2 to HCOOH[10].The conversion of CO_2 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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