

Conversion of carbon dioxide to methanol using solar energy

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Conversion of carbon dioxide into methanol or to any other value-added chemical using solar light (known as artificial photosynthesis) is of great importance from the point of view of energy crisis and global warming problem. This note discusses the methods and challenges that need to be addressed for realizing processes for converting carbon dioxide to value-added chemicals.

Several technologies have been proposed for utilization of carbon dioxide (CO₂), a greenhouse gas, and for improving the efficiency of energy conversion. The most successful of these types of reaction is the Sabatier process¹. This process involves the reaction of hydrogen with CO₂ at elevated temperatures and pressures in the presence of a nickel catalyst to produce methane and water (CO₂ + 4H₂ → CH₄ + 2H₂O). It was discovered by the French chemist, Paul Sabatier. It has been proposed as a key step in reducing the cost of manned explorations to Mars (Mars Direct) through *in situ* resource utilization. After producing water by combining hydrogen transported from the Earth and CO₂ taken from the atmosphere of Mars, oxygen would be extracted from the water by electrolysis and used as a rocket propellant. The stoichiometric propulsion fuel mix ratio is 1 : 8 between hydrogen and oxygen by weight (each pound of hydrogen requires 8 pounds of oxygen to burn), and if only the light hydrogen has to be transported and the heavy oxygen extracted locally, this would result in considerable weight savings which would have to be transported to Mars. Nevertheless, the expensive electrolysis technique employed in the Sabatier process for splitting water into oxygen and hydrogen is not economical to practice for vehicles that run on the road. Nevertheless, methanol is the most desired product of CO₂ as it can be transformed into other useful chemicals using conventional chemical technologies, or easily transported and used as fuel-like renewable energy²⁻⁸.

The electrochemical systems developed for reducing CO₂ to methanol involve high electrode over-potentials, which offer little or no advantage, since the quantity of fuel consumed during the synthesis of the reduction products far exceeds the fuel value of the products²⁻⁸. On one side the catalytic hydrogenation of CO₂ to methanol involves high reac-

tion temperatures and on the other side, the electrocatalytic reduction of carbon dioxide at Pd, Pt and Hg electrodes was found to be inefficient³. The endothermic nature of CO₂ reduction to methanol [CO_{2(g)} + 2H_{2O(l)} → CH_{3OH(l)} + 3/2 O_{2(g)}; H⁰ = 727 kJ mol⁻¹ and G⁰ = 703 kJ mol⁻¹] is responsible for the noted inferior product yields⁴. The economic production of value-added chemicals from CO₂ is possible only if solar energy is utilized. Solar energy can be harnessed for this purpose by: (1) artificial photosynthesis using homogeneous and heterogeneous systems; (2) electrochemical reduction using solar electric power, and (3) hydrogenation of CO₂ using solar-produced hydrogen in photoelectrochemical (PEC) cells⁴. The reduction of carbon dioxide into methanol in a PEC cell occurs in two steps. In the first step, water is oxidized to produce protons, electrons and molecular oxygen on the surface of the photoanode upon light irradiation (H₂O → 2H⁺ + 2e⁻ + ½O₂). This is the energy-consuming step, i.e. the light reaction of the natural photosynthesis. In the second step, the protons and electrons produced at the photoanode will be utilized to reduce CO₂ into methanol (CO₂ + 6H⁺ + 6e⁻ → CH_{3OH} + H₂O; E⁰ = -0.38 V) on the surface of the (photo) cathode. Since this latter step is an exothermic one, it does not need any energy (a dark reaction). This means the formation of protons and electrons by water oxidation at the photoanode surface is the most crucial and important step²⁻⁸. This two-step reaction was successfully demonstrated in a PEC cell over a p-type gallium phosphide semiconductor surface to obtain methanol together with formic acid (HCOOH) and formaldehyde². However, this process suffered from several limitations such as poor performance, instability of associated catalysts and semi-conductors in water, inefficiency of electrolytic systems, inferior reducing cathode materials, etc.

Photoreduction of CO₂ requires thermodynamic energy input of 1.5 eV. Greater energy input is required to make up for losses due to band bending (necessary in order to separate charge at the semiconductor surface), resistance losses, and overvoltage potentials⁴⁻⁶. Photoreduction of CO₂ at high efficiency is also hampered by a number of problems. Upon illumination of the semiconductor with light energy equal to or greater than that of the semiconductor bandgap, electrons are promoted from the valence band to the conduction band, creating electron-hole pairs at or near the interface. The electron-hole pairs are spatially separated by the semiconductor junction barrier, and are injected into the electrolyte at the respective electrodes to produce electrochemical oxidation and reduction reactions. If an electron or hole does not transfer to the substrate rapidly, recombination of electron-hole pairs can occur at surface defects or grain boundaries. Although the electrolyte-semiconductor interface has excellent characteristics for separation of charge and generation of high oxidation or reduction potentials when irradiated, it often has poor catalytic properties for reactions with significant activation energies⁴⁻⁶.

A major impediment to the exploitation of PEC cells in solar energy conversion and storage is the susceptibility of small-bandgap semiconductor materials to photoanodic and photocathodic degradation. The photo-instability is particularly severe for n-type semiconductors where the photogenerated holes, which reach the interface, can oxidize the semiconductor itself. In fact, all known semiconducting materials are predicted to exhibit thermodynamic instability towards anodic photodegradation⁴⁻⁶. Whether or not an electrode is photostable is decided by the competitive rates of the thermodynamically possible reactions, namely the semiconductor decomposition reaction

and the electrolyte reactions. Several efforts have been made to control the photo-instability of the semiconductor–electrolyte interfaces using surface-coating techniques^{6,7}. For example, the non-corroding layers of metals or relatively stable semiconductor films. These continuous metal films which block solvent penetration can protect n-type GaP electrodes from photocorrosion. However, if the films are too thick for the photo-generated holes to penetrate without being scattered, they assume the Fermi energy of the metal. Then the system is equivalent to a metal electrolysis electrode in series with a metal–semiconductor Schottky barrier. In such a system, the metal–semiconductor junction controls the photovoltage and not the electrolytic reactions. In other cases, the metal can form an Ohmic contact that leads to the loss of the photoactivity of the semiconductor. In discontinuous metal coatings, the electrolyte contacts the semiconductor, a situation which can lead to photocorrosion^{4–6}. Corrosion-resistant wide-bandgap oxide semiconductor (mostly TiO₂ and titanates) coatings over narrow-bandgap n-type semiconductors such as GaAs, Si, CdS, GaP and InP have also been shown to impart protection from photodecomposition⁵. One of two problems is currently associated with the use of optically transparent, wide-bandgap semiconducting oxide coatings: either a thick film blocks charge transmission, or a thin film still allows photocorrosion.

The chemical bonding of electroactive polymers to the semiconductor surface has also been found to affect the interfacial charge-transfer kinetics such that the less thermodynamically favoured redox reaction in the electrolyte predominates over the thermodynamically favoured semiconductor decomposition reaction^{2–8}. To date, emphasis has been placed on improving the catalytic properties of p-type electrodes, where photocorrosion by reductive processes is not a major problem. The over-voltage for the evolution of hydrogen from p-type electrode surfaces is normally quite large. It has been demonstrated, however, that the catalytic property of a p-type Si photocathode is enhanced for hydrogen evolution when a viologen derivative is chemically bonded to the electrode surface and Pt particles are dispersed within the polymer matrix⁶. The viologen mediates the transfer of the photogenerated electron to H⁺ by the platinum to form H₂. A thin platinum

coating directly on the p-type silicon surface also improves the catalytic performance of the electrode. Charge conduction is generally much higher in electrically conductive polymers than in typical electroactive polymers. Accordingly, work on charge conductive polymers in the field of photoelectrochemistry has been directed towards stabilization of electrodes against photodegradation in electricity-generating cells. Charge conductive polymers are known to protect certain semiconductor surfaces from photodecomposition, by transmitting photogenerated holes in the semiconductor to oxidizable species in the electrolyte at a rate much higher than the thermodynamically favoured rate of decomposition of the electrode. In a study, an n-type silicon semiconductor photoelectrode was coated with polypyrrole, a charge conductive polymer that has enhanced the stability of electrode against surface oxidation in electricity-generating cells⁶. An n-type GaAs was also coated with polypyrrole to reduce photodecomposition in the same cells, although the polymer exhibited poor adhesion in aqueous electrolyte^{6,7}. Despite the promising use of polypyrrole on n-type silicon to suppress photodecomposition, heretofore, whether or not conductive polymers in general could be used in conjunction with catalysts was unknown. Moreover, it can be seen that the discovery of uses for various polymer coatings on photoelectrodes has been on a case-by-case basis because of the empirical nature of the effects on any particular semiconductor and/or the interaction with a given electrolyte environment^{6,7}.

In another study⁵, both the electrode surfaces were modified with *N,N'*-dimethyl, 4,4'-bipyridinium (methyl viologen, MV²⁺), an electron mediator, to enhance the rate of PEC reactions and suppress photocorrosion and recombination. The role of the MV²⁺/MV⁺ system is to provide an oxidized material which is efficiently photoreduced and a reduction product which can efficiently transfer electrons to water or hydrogen ions at metal (platinum) catalysts to produce H₂. The problems with mediation via solutions of methyl viologen are the intense absorption of visible light by the MV²⁺ species, and the relatively low concentration of the mediator.

Several other transition-metal complexes have also been employed as photochemical and thermal catalysts because

they can absorb a significant portion of the solar spectrum, have long-lived excited states, can promote multi-electron transfer and can activate small molecules through binding⁶. In transition-metal complexes, a central metal has octahedral, tetrahedral, square-planar, square-pyramidal, or trigonal-pyramidal symmetry depending on the surrounding ligands. Reduced metal centres such as M^IL, in which the oxidation number of the central metal (M) is plus one and the ligand (L) has four coordinating atoms, typically have one or more vacant coordinate sites. These sites can be used to bind and activate CO₂ (or other small molecules). The oxidative addition of CO₂ to M^IL to form a metalcarboxylate, M^{III}L(CO₂[−]), stabilizes the CO₂ moiety through two-electron transfer. M^{III}L(CO₂[−]) can then react with H⁺ to form M^{III}L, CO and OH[−]. The systems that have been used for photochemical CO₂ reduction studies have been divided into the following steps: (1) Ru(bpy)₃²⁺ (bpy, 2,2''-bipyridine) as both the photosensitizer and the catalyst; (2) Ru(bpy)₃²⁺ as the photo-sensitizer and another metal complex as the catalyst; (3) ReX(CO)₃ (bpy) (X is a halide or phosphine-type ligand) or a similar complex as both the photo-sensitizer and the catalyst; (4) Ru(bpy)₃²⁺ or Ru(bpy)₃²⁺-type complex as the photo-sensitizer in microheterogeneous systems; (5) a metallophorphirin as both the photo-sensitizer and the catalyst, and (6) organic photo-sensitizers with transition–metal complexes as catalysts. Mechanisms believed to be involved in the above process are: (i) light absorption by a photo-sensitizer to produce the excited state; (ii) a quenching reaction between the excited state and an electron donor to produce a reduced complex, (iii) electron transfer from the reduced complex to a catalyst, and (iv) activation of CO₂ by the reduced catalyst⁶. However, the major products formed in this process are HCOOH and carbon monoxide.

In a study⁴, molybdenum was used as a cathode to reduce CO₂ to methanol selectively and with up to 80–100% Faradaic efficiency. However, the efficiency of molybdenum as catalyst needs to be tested in a PEC cell. In another study³, CO₂ was reduced to methanol over catalysed p-GaP in a PEC cell. More than 95% conversion and 100% methanol selectivity were noted. Since GaP undergoes photocorrosion, this process cannot be practised in a commer-

cial plant. In another study⁹, water was successfully photo-oxidized over cobalt oxide nanocrystals plus a sensitizer embedded in micro-channels of mesoporous silica. The micron-sized particles of cobalt oxide were found to be inefficient and not nearly fast enough to serve as photocatalysts. The yield for clusters of cobalt oxide (Co₃O₄) nano-sized crystals was about 1600 times higher than for micron-sized particles, and the turnover frequency (speed) was about 1140 oxygen molecules per second per cluster, which is commensurate with solar flux at ground level (approximately 1000 W/m²). In another study¹⁰, a water-soluble new inorganic metal-oxide cluster with a core consisting of four ions of the rare transition metal, ruthenium, was used to oxidize water. This catalyst was found to be stable in the reaction. In contrast to all other molecular catalysts for water oxidation, this catalyst does not contain any organic components. This is the reason for its stability in water. Nevertheless, the efficacy of this catalyst also needs to be tested in a PEC cell for the same reac-

tion without utilizing an organic photosensitizer.

On the basis of above discussions, the stable and efficient PEC cells for converting CO₂ into methanol could be realized by understanding: (i) the underlying mechanisms of oxidation of water and reduction of carbon dioxide at photoanode and photocathode respectively; (ii) the mechanisms involved in the photocorrosion of non-oxide based anode and cathode materials in water-based PEC cells; (iii) the interaction of conducting polymers/electroactive polymers with electrode materials, and (iv) the electron and ion transporting behaviour of water-soluble organics/catalysts.

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