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COURSE NOTES

CHEMICAL APPROACHES FOR HARNESSING SOLAR ENERGY

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Introduction

Most of mankind's present energy requirements are met by the consumption of past products of photosynthesis i.e. fossil fuels such as coal and oil and by the combustion of firewood. Even hydro-electricity and wind power are finally derived from the energy of the sun. The energy of the fossil fuel deposits on Earth is currently estimated to be equivalent to 40 x 10^{21} J while the present annual consumption of these deposits is about 3 x 10^{20} J. Thus it is inevitable that a major energy crisis is soon going to affect the world in the next century. The ability to synthesize fuels and chemicals from abundant renewable resources could have a significant impact on the energy budget of the entire world. Thus transformation of solar energy to usable forms by photochemical mechanisms is one of the great social as well as scientific challenges of today. Our dependance on fossil fuel reserves combined with political unrest in major oil producing areas such as the middle-east have affected the economies of developing and developed countries alike. Nevertheless the use of our most abundant resource, the sun, has increased only marginally over the last several decades. The Earth receives at its surface about 3 x 10^{24} J per year and it can be seen that the sun delivers to the earth in roughly four days, the proven energy reserves of fossil and nuclear fuels combined. It has been estimated that if only 0.1% of the earth's surface were covered with solar collectors operating at an average efficiency of 10% all of world's annual energy needs could be supplied by the sun.

However, there are two major drawbacks to the economic commercial utilization of solar energy. Firstly solar radiation is discontinuous and diffuse. Thus suitable storage systems are necessary for the effective utilization of solar energy specially during the night. Secondly, since the solar radiation falling on the earth is diffuse, large areas of collectors are required to capture and concentrate the radiation.

All our energy requirements, in theory, can also be met by growing biomass via natural photosynthesis. However, there are practical limitations in achieving this goal. The efficiency of solar energy conversion by plant photosynthesis is very low and seldom exceeds 1% on an annual basis, except in the case of a few plants such as sugarcane.

However, plants can also be used to produce other useful chemicals that can be used as fuel, perfumes, drugs and food. These, combined with the rapidly advancing science of biotechnology may provide new avenues for tackling the impending energy crisis. For example, a tree belonging to the leguminosae family of the genus Copaifera can be tapped to produce about 25L of a diesellike material in a 24h period. Production of such materials from plants is also a way of solar energy conversion to produce desirable chemicals.

Alcohol produced by the microbial fermentation of sugars from sugar cane is also an important by-product from plants. Alcohol mixed with gasoline under the trade name 'gasohol' is commonly used in countries such as Brazil and also to a limited extent in the USA.

Biomimitic Photosynthetic systems aimed at solar energy conversion may be completely synthetic or may be a combination of synthetic and biological molecules. The objective here may be the photolysis of water or generation of a reduced redox species which can be coupled to a catalyst to produce H_2 or reduce CO_2. Assemblies of porphyrins, quinones and carotenoids have been recently studied as possible model systems. Even combinations of semiconductors and biological molecules have been studied as components of artificial photosynthetic devices.

Photosynthesis is the secret of life. Understanding this marvellous process may significantly contribute to the survival of mankind.

Biological photosynthesis has the advantage of some three billion years of evolutionary development of elegant molecules which carry out highly specific reactions. Purely synthetic systems on the other hand are more flexible with higher solar efficiencies. They can be employed for the production of specific fuels and chemicals. Some processes of interest are photochemical water splitting to produce hydrogen, photofixation of molecular nitrogen and photoreduction of carbon dioxide to useful fuels such as methanol.

Chemical approaches to harnessing solar energy

There are various physical approaches of using solar energy. Solar drying, solar cookers are some of these. However, here we shall discuss only the chemical approaches of solar energy conversion.

1. Solar cell Technology

Photovoltaic solar cells convert light directly to electricity. Most of present day solar cells employ silicon metal doped with other impurities. Here silicon acts as a semiconductor where absorbed energy cause the excitation of an electron from the valence band to the conduction band of the semiconductor (appendix 1). The photogenerated electron can go through an external circuit where the absorbed energy is given out as electrical energy.

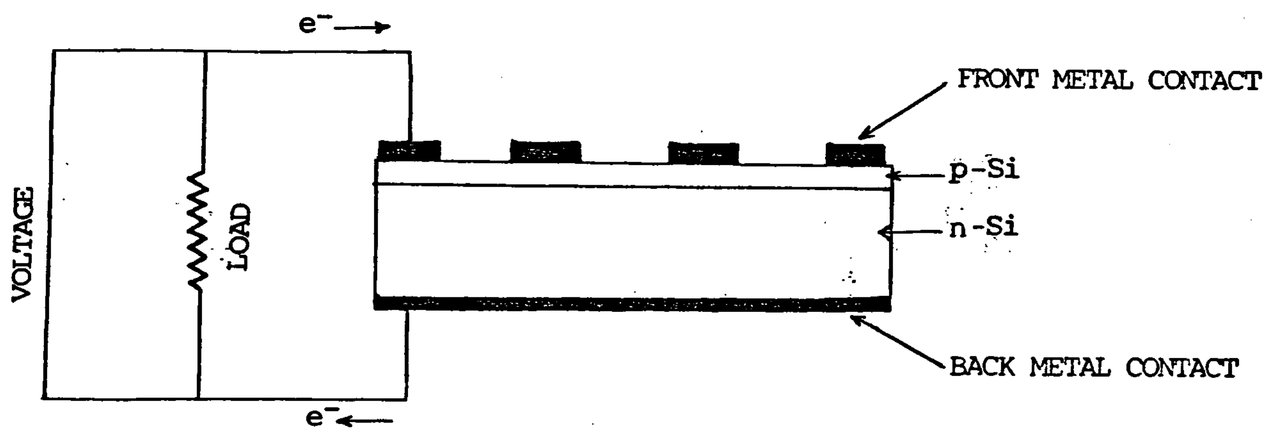

Fig. 1. A photovoltaic cell

These systems although simple are however costly to fabricate. It is essential to produce single crystals of silicon which are 100% pure. Such advanced technology is only available in the most developed countries of the world. Storage of electricity is also a problem in this method. At the present time batteries similar to those used in cars are used for this purpose.

However, considering the fact that certain remote villages in Sri Lanka are still not connected to the national grid, solar cell technology shows excellent promise for the rural electrification schemes for such villages.

2. Photochemical splitting of water

Fujishima and Honda in Japan first showed that water can be split into H_2 and O_2 using solar irradiation of TiO_2. Titanium dioxide is a semiconductor which produces electron-hole pairs upon irradiation. The electrons are used for the reduction of water to give H_2 while the holes oxidize water to O_2. However, the yields obtained with these systems are exceedingly small and have no commercial value. Attempts have been made in several laboratories to improve on the yields of H_2 by various chemical modifications. However, even to date there are no practically viable systems even on a laboratory scale.

Hydrogen as a fuel is attractive since its combustion product is H_2O which does not have the disadvantage of environmental pollution normally associated with the combustion of fossil fuels. However since H_2 is highly flammable, there are still some technological problems associated with its storage and transport.

3. Photochemical nitrogen fixation

The conversion of nitrogen to fixed forms such as ammonia and nitrate is essential for Agriculture and hence for sustaining life on Earth. With the current fertilizer prices pathways leading to alternative nitrogen fixation pathways have assumed great economic and sociological importance. The use of sunlight to convert nitrogen to fixed forms is an attractive method especially for the developing countries. Semiconductor catalysts are widely used for this purpose. Upon irradiation, such catalysts generate electron-hole pairs and the excited electron can be utilized for reducing nitrogen to ammonia. However, even here the yields of ammonia produced are far too small to be of any practical value.

A large number of semiconductor catalysts have been investigated as possible catalysts for the photosynthesis of ammonia. These include metal doped TiO_2 catalysts, metal titanates and hydrous ferric oxides and their modifications. Research carried out at the Institute of Fundamental Studies and the Universities of Ruhuna and Peradeniya have identified several superior catalysts based on hydrous ferric oxides for this purpose. Several factors that lead to catalyst poisoning and also valuable information concerning the mechanism of this interesting reaction have been discovered.

If a nitrogen-fixing solar cell can be developed its advantages are numerous especially for a developing country such as Sri Lanka. Even if the yields of ammonia are small the enrichment of soil nitrogen may be significant over a long period of time.

4. Photofixation of carbon dioxide

The reduction of CO_2 via multi-electron transfer reactions could produce formic acid, carbon monoxide, formaldehyde, methanol or methane. The exact products depend on the particular system used. It has been shown that CO_2 reduction takes place an illuminated semiconductors such as TiO_2, ZnO, CdS, GaP and SiC.

Other examples of photochemical reactions on semiconductors

(a) Depollution of water

Water contaminated with heavy metals such as cadmium, mercury, silver and platinum can be effectively decontaminated by passing it through a column containing TiO_2 coated glass beads. This process is highly efficient and could also be employed for the recovery of valuable metals, such as silver. Chlorinated hydrocarbons, pesticides and toxic organophosphorus compounds from insecticides can also be similarly decomposed. Here the products are harmless and this could be utilized to tackle the problem of contaminated drinking water.

(b) Oxidative decarboxylation of carborylic acids

It has been shown that platinum coated TiO_2 is an effective photocatalyst for the decarboxylation of carboxylic acids. For example,

$$CH_3COOH \qquad\qquad CH_4 + CO_2$$

(c) Amino acid synthesis

An interesting reaction, again catalyzed by Pt/TiO_2 and light is the synthesis of amino acids,

$$2CH_4 + NH_3 + H_2O \quad \overset{Pt - TiO_2}{\qquad\qquad} \quad H_2NCH_2COOH + 5H_2$$

This reaction is of interest in the chemical evolution of life. Devising other similar reactions remains a challenge to the photochemist.

(d) Photooxidation of alkanes, alkenes and alcohols

A wide variety of the above substrates have been photooxidized on irradiated semiconductors. The yields are generally good even for industrial applications.

(e) Photosynthesis of hydrogen peroxide

As early as 1911, it was shown that aqueous suspensions of ZnO produce H_2O_2 upon irradiation.

(f) Hydrogen production from organic materials

The direct photochemical splitting of water by semiconductors upon irradiation is not very efficient from a practical point of view. However, alcohols, hydrocarbons, cellulose and other waste materials when irradiated with semiconductors produce hydrogen with better efficiency.

CONCLUSION

From the above account it is clear that solar energy conversion via chemical means is a fruitful area of research. This type of research is especially relevant to countries such as Sri Lanka with its abundance of sunlight. Mankind will have to face up to the possibility of drying up reserves of fossil fuel. The logical source to look up would be towards the sun, which has been silently providing us with all our fuel and food silently over millions of years.

Appendix 1

Electrons, molecules and semiconductors

In the hydrogen molecule, the two electrons occupy a bonding orbital. When the molecule is electronically excited one of the electrons jumps into an antibonding orbital. In general, a polyatomic molecule with n atoms have 1/2 n bonding and 1/2 n antibonding orbitals. In a solid with an infinite array of atoms, the number of bonding and antibonding orbitals becomes so great, and the gaps between them is so narrow that they merge into separate bands. The bonding orbitals form a valence band while the antibonding orbitals merge into a conduction band. Electrons in a solid's valence band are localized around individual atoms in a solid lattice. The gap between the two bands (called the band gap) is the property that distinguishes a solid as a conductor, a semiconductor or an insulator (Fig. 1)

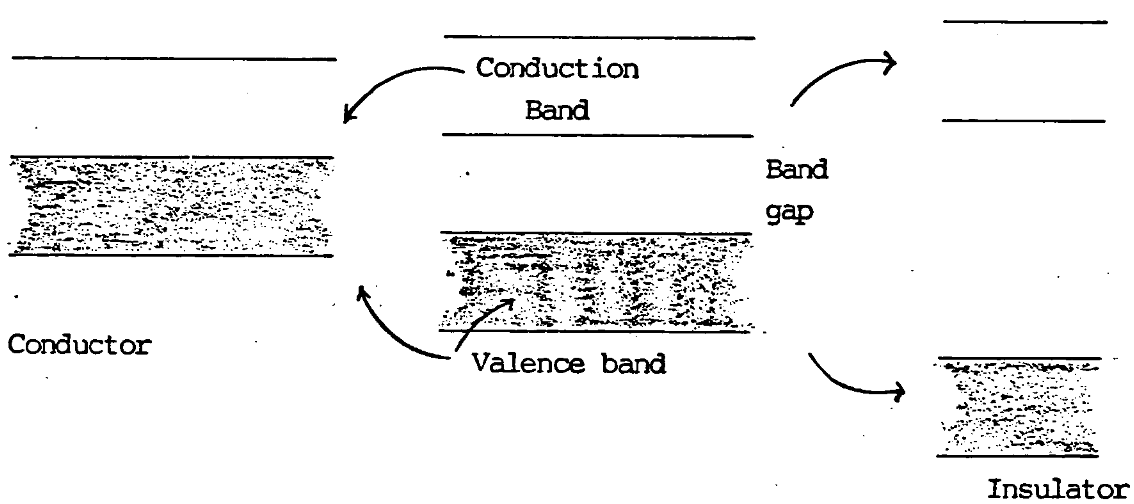

Fig. 2 Energy bands in a conductor, semiconductor, Insulator

Semiconductors have a narrow band gap compared to insulators. Thus heat or light energy can 'kick' the electrons up into the conduction band.