

The Relevance of Photocatalysis for Energy Conversion and Storage

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Abstract

Photocatalysis is an emerging area of research in energy conversion and storage. In this sense, the production of fuels by the photocatalytic water splitting and reduction of carbon dioxide and dinitrogen assumes importance. The prospects of these three reactions in this context are evaluated. The prospects of storage of hydrogen and carbon dioxide in solid-state materials are also considered.

Introduction

The Science of catalysis has seen many facets and changes in the last century. The two important factors for sustaining the living beings on this earth are energy conversion and environment. Though the science of catalysis, in general, contributes to both these issues, a new and recent domain called 'Photocatalysis' a misnomer or not, plays a vital role in fulfilling these two functions. Photon assisted process has taken new dimensions in many ways like photo-electrochemical decomposition of water for fuel hydrogen production ^[1] and the conversion of one of the most inert (stable) molecules namely carbon dioxide into value-added chemicals ^[2] in addition to decomposition of dyes ^[3] and chemicals in water treatment. In reality, the photons are activating the solid catalyst by

altering the potential of charge and the catalytic reaction takes place only on the surface sites of the photo-active materials. It must be admitted that there are still views that many of these challenging processes of energy conversion have reached the time window where these could have happened have now come to an end ^[1]. Despite this pessimism, there is still scientific curiosity on these processes and still there are persistent attempts to make these processes commercially feasible.

This situation is generally assumed to have started from the initial publication of Fujishima and Honda ^[4], though there were attempts in this direction before this period ^[5]. In the near future, the energy conversion process will center around four simple molecules, namely water, dinitrogen, carbon monoxide and carbon dioxide ^[6]. Though the activation of these small molecules was known for a long time, (positively systematically from the 1950s) the transformation of these molecules for energy conversion has not still reached the stage of economic and commercial feasibility sometimes even led to frustration among the proponents. It appears that it is time one analyzes this situation to propose the direction in which these processes will become economically feasible. The purpose of this presentation is an attempt in this direction to bring out the reasons for this situation and also to seek remedies for the same, though one cannot assume getting appropri-

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ate answers and success in this difficult task.

Photocatalysis – Some Basis

One of the reasons for this obsession on this topic is the available nature of solar energy even some of the shortcomings like the diurnal and intermittent nature and non-uniform distribution of this form of energy [7]. Photocatalytic materials are mostly centered around semiconducting solids since available and exploitable photon sources (natural or artificial) can provide energy range (1-3.5 eV) for changing the potential energy of the active species (electrons or holes). The re-

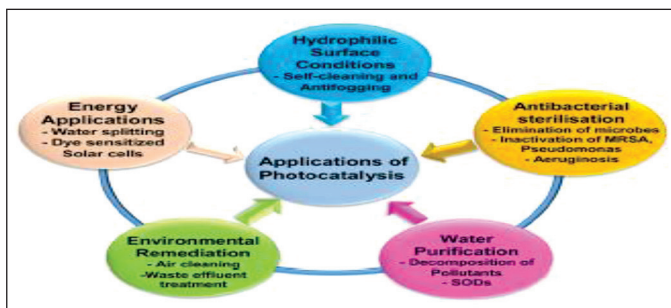


Fig.1. Main envisioned applications of photocatalysis [reproduced from ref. 9].

alized catalysis action is due to these activated species (excitons) and not the photons and in this sense the term photocatalysis appears to be a misnomer. However, these excitons may recombine within the lifetime of these species and thus not utilized in promoting the surface catalyzed reaction. This may be one of the reasons for the inconsistency often reported in the results [8].

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it more energetically sustainable and eco-compatible. The possible applications of photocatalysis is pictorially shown in Fig.1.

Typical processes taking place on semiconducting solids in photocatalysis can be summarized by the following steps:

- (1) Photon absorption (governed by the photon absorption coefficient usually termed as molar extinction coefficient) to generate electron-hole with sufficient potential to promote the desired redox reaction.
- (2) Recombination of the charge carriers within the semiconducting solids.
- (3) The separated charges have to migrate to surface reaction sites.
- (4) The redox reactions with charge transfer taking place on the generated surface sites.

There are still some challenges in photocatalysis.

These aspects including the kinetics and the energy of the photon source have been discussed frequently in literature [10]. The enthusiasm that this field evoked in the early days slowly wanes these days for various reasons like the efficiency of this technology in the energy conversion process especially hydrogen production from the photocatalytic splitting of water and converting carbon dioxide to chemicals and fuels. In the following, the prospects of photocatalysis for fuel production from the most of the four molecules are considered.

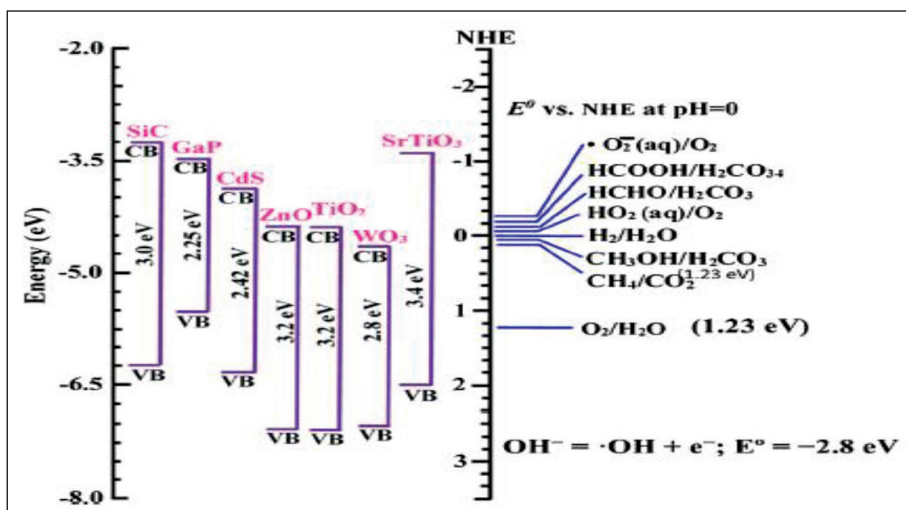


Fig.2. The positions of conduction band bottom and top of the valence band of typical semiconductors.

Table 1. Typical results (in the units of micromoles per hour per gram on photo-splitting of water [abstracted from 11]

Typical Photocatalysts	Hydrogen production rates in micromoles per hour per gram
Ta doped TiO ₂	11.7
Pt/C-TiO ₂	5713.6
Pt/TiO ₂	932
CuS/ZnCdS	7735
CdS/ZnS	239,000
Ni/CdS/g-C ₃ N ₄	1258
CdS/WS/graphene	1842
Au/TiO ₂	647,000
MoS ₂ /CuZnS	202

Photocatalytic splitting of water

The essential energy requirements for the decomposition of water is that hydrogen evolution potential has to be less negative with respect to the bottom of the conduction band edge while oxygen evolution reaction potential should be less positive as compared to the valence band top edge. This situation is pictorially represented in Fig 2 (though in this figure other reactions also are shown).

The selection of the semiconductor for hydrogen and oxygen evolution reactions in water decomposition is based on the energy portions of these two edges.

The conduction band bottom and valence band top positions and the values of band gaps shown in the figure as static positions but they may alter depending on the interface depending on the nature of the interface. This situation if it were to exist, then the observed results have to be analyzed differently. Though the efficiency of the photocatalytic decomposition of water splitting has not yet reached the levels in order this process can be exploited commercially, there are persistent efforts to increase this parameter by sensitizing the semiconductor in the form of coupled semiconductors or doping the semiconductor or dye sensitization and others. These attempts are mainly to alter and match the energy requirements for the process probably because the process is not only dependent on energy matching but also other factors like geometric and site symmetry may be responsible. 'Bandgap engineering' is one of the concepts probably over-emphasized in photocatalysis. It may be possible that even harnessing with wide band semiconductors may provide energy conversion necessary for all the living beings.

Typical selected results on the hydrogen produc-

tion rate on semiconducting solids by photo-splitting of water are assembled in Table 1. It is seen from the results given in Table 1, that the hydrogen production rate has not yet reached the stage of commercial exploitation. It appears that identifying the appropriate photocatalyst for water splitting has not yet reached the desired stage.

Photocatalytic Reduction of Carbon dioxide

The listing of simple reactions in relation to the reduction of carbon dioxide are given below:



Essentially, these reactions are dependent on the activation of the inert carbon dioxide molecule.

Even though the molecule of carbon dioxide can be associated with oxygen, carbon or mixed coordination as shown in Fig.3, the conversion of this molecule into a fuel or chemical depends on the proper activation of the molecule at the appropriately formulated active site (typically a stepped surface sites) on the catalyst surface. The inertness of carbon dioxide is reflected in the values of Gibbs free energy as seen from the data shown in Fig.4. The capture and utilization of carbon dioxide have become an important component of today's research efforts as revealed in the statements of Prof. Olah (one of the Nobel Prize winners) namely "Carbon dioxide. ... can be chemically transformed from a detrimental greenhouse gas causing global warming into a valuable, renewable and inexhaustible

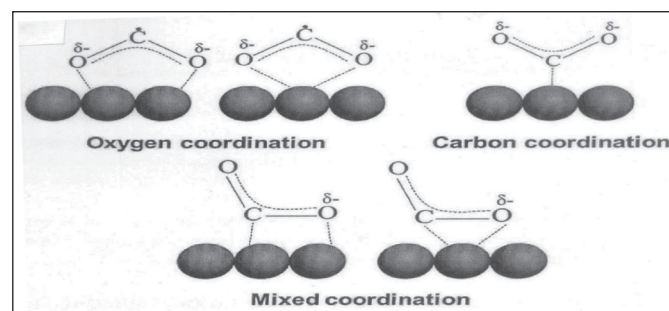


Fig.3. Possible modes of activation of carbon dioxide on solid surfaces through the coordination nature.

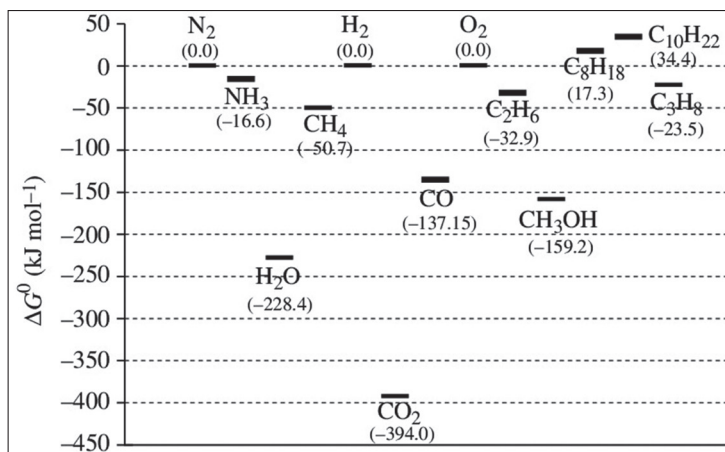


Fig.4. Values of Gibbs free energy of formation for selected (typical) chemicals [data base from <http://webbook.nist.gov/chemistry/name-ser.html>]

carbon source of the future allowing environmentally neutral use of carbon fuels and derived hydrocarbon products”.

The prospects of the utilization of carbon dioxide in combination with hydrogen (like water) will be a source of fuel production in the future is reflected in the cycle presented in Fig.5. The main process in the conversion of carbon dioxide is the production of synthesis gas by tri-reforming reaction one of the typical reaction is $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ 247/3 kJ.mol⁻¹. This may become one of the important steps in the reforming reaction as well in the utilization of carbon dioxide shortly.

The Reduction of Dinitrogen

One of the current exploited processes in the reduction of dinitrogen is the ammonia synthesis which goes under the name of the Haber Process at high temperatures (623-823 K) and pressures (150-350) atmospheres. However today the ammonia production

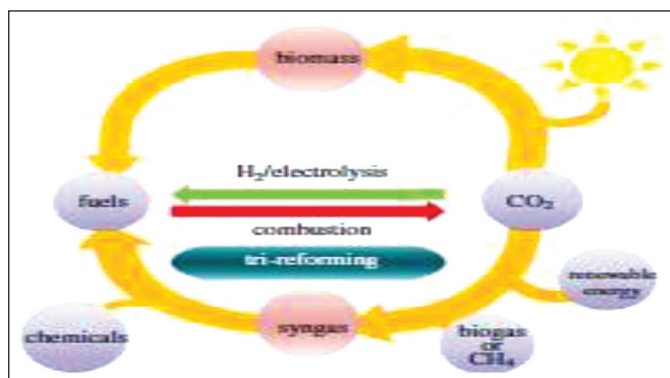


Fig.5. The possible cycle for fuel and chemical production from carbon dioxide [ref.12]

The original DOE (Department of Energy) recommendation is that at least a solid should take up at least 6.5 weight percent so that the cost of energy will be comparable to the present-day economy, even though there can be other issues concerned with solid-state hydrogen storage.

alone requires nearly 1% of the total energy by this universe. There have been attempts in the past to formulate a catalytic process for reducing dinitrogen at low temperatures and 1 atm. However, reduction of dinitrogen, probably the most stable diatomic molecule known, by protons and electrons or by dihydrogen to ammonia under these conditions appears to be more difficult than it was conceived. It appears to be possible to reduce dinitrogen catalytically at a single molybdenum center due to intellectual advance in the minds inorganic, bioinorganic and biological scientists. There are many issues in this reduction reaction. Are there many ways and processes to reduce dinitrogen to ammonia under mild conditions? Is molybdenum as believed the most efficient metal for dinitrogen reduction?

There is yet another domain for this reduction reaction. The problem for Nitrogen Reduction Reaction (NRR) is the lack of effective electrocatalyst for effecting this reaction under ambient conditions. This situation may be due to high overpotential for dinitrogen reaction and/or the low Faradaic efficiencies for ammonia formation. This situation is due to the fact that electrochemical reduction of dinitrogen takes place at negative potentials and in this sense, the dominant reaction is the competing hydrogen evolution reaction thus reducing the selectivity. This situation for NRR has multiple dimensions in the sense that formulating intrinsically reactive and selective electrocatalyst, interface engineering controlling the proton/electron transfer rate and also to decouple the nitrogen fixation and ammonia formation steps [13].

Storage

Energy storage can be achieved in various ways. Gas storage is one of them especially for hydrogen and carbon dioxide in solid-state materials [14]. Let us first consider the storage of hydrogen since it is known for a long time. Metals can take up hydrogen as metal hydrides, the familiar one is palladium hydride. The orig-

inal DOE (Department of Energy) recommendation is that at least a solid should take up at least 6.5 weight percent so that the cost of energy will be comparable to the present-day economy, even though there can be other issues concerned with solid-state hydrogen storage. So far no metallic or intermetallic systems have been identified which can store hydrogen to this extent. This situation has to be carefully analyzed and as most of the structures of solid-state materials (metals and intermetallics) normally consists of a polyhedron and only one hydrogen atom can be contained in each of the polyhedra and hence in these systems the storage cannot exceed 2 to 3.5 weight percent if the metal is from the transition group. Low atomic weight metals like magnesium and others may be able to store a higher percentage (>6.5 weight %) but they have other issues to be addressed. In this connection, layered structures (like carbon) can be considered as alternative materials but still the desired levels of storage have not been achieved in these materials as well.

A similar situation exists in the case of carbon dioxide capture and storage. Even the introduction of the Metal-organic framework (MOF) or the corresponding COF structured materials, though initially showed promise, have not reached the expected levels of storage. It appears that more innovative thinking and execution are required in this direction.

Summary

Today, energy conversion processes depend on the generation of hydrogen by splitting of water, in the conversion of carbon dioxide into value-added fuels and reduction of dinitrogen under ambient conditions. In this article the prospects of these three processes becoming economically viable are examined. Also, the storage of hydrogen and carbon dioxide in solid-state materials is briefly considered.

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