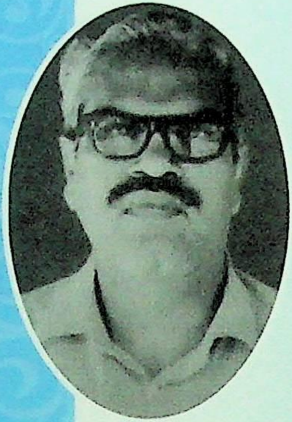

University of Jaffna

Prof.S.Mageswaran

Memorial Lecture – 2019

"Hydrogen Energy"

by

Professor R.M.G.Rajapakse

Department of Chemistry

University of Peradeniya.

on

Friday 22nd March 2019

at 3.00 p.m

at

Kailasapathy Auditorium

University of Jaffna.

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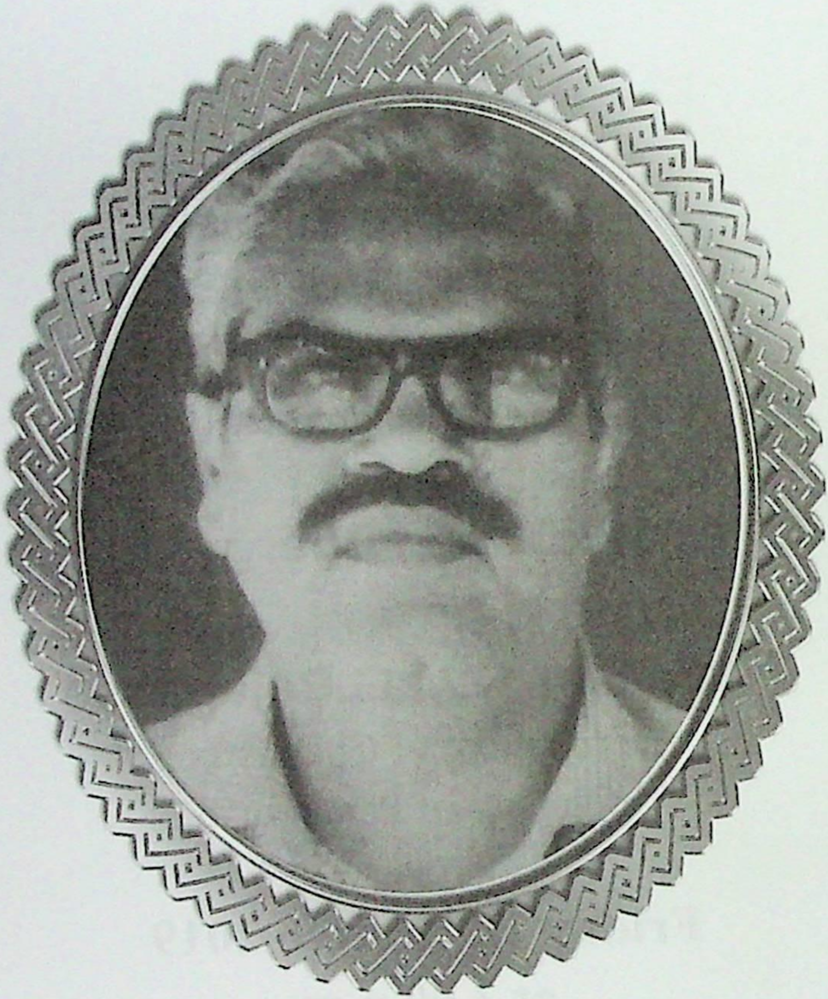

Prof.Sivapathasuntharam Mageswaran

Message from the Vice Chancellor

It is my honour and pleasure to welcome all of you to Professor Sivapathasuntharam Mageswaran Memorial Lecture.

Late Professor Mageswaran was well recognized for his academic records and dedicated service to this University and need to be considered as a role model by the academic society of this University.

He had taken keen interest about students and devoted his time for the improvement and upgrading of the Department of Chemistry. He was always maintaining the student discipline and took appropriate action to solve the issues.

I wish to thank Professor Rajapakse for agreeing to deliver Prof. S. Mageswaran Memorial Lecture titled on 'Hydrogen Energy' which is very useful to students and researchers and I wish Professor Rajapakse for every success in his endeavors to bring out the issues in his field.

Prof. R. Vigneswaran
Vice Chancellor

HYDROGEN ENERGY: EXPECTATIONS FOR CLEANER TRANSPORTATION

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HYDROGEN FUEL ENERGY

Clean food to eat, clean water to drink and clean air to breath are basic human needs. However, our struggle for the so-called better living standards contribute vehemently to depriving of our own basic rights and basic needs as is very correctly indicated by the Great Native American Chief Seattle in 1850s. The pollution of the environment; all segments including lithosphere, biosphere, hydrosphere and atmosphere, by anthropogenic origin is considerable. Even the so called environmentally friendlier solar energy conversion to electricity, with the aid of silicon solar cells, which are now wide-spreading, are by no means green since the production of one tonne of solar grade silicon mandatorily emit over ten tonnes of carbon dioxide gas to the atmosphere! Our struggle for energy and ever increasing demand for energy have hampered our environment in the highest possible adverse manner and fossil fuels used for transportation essentially stand out as a major source of air pollution. This article is aimed at browsing alternative fuels which are environmentally benign rather than detrimental.

Hydrogen gas is perhaps the cleanest energy resource available to humankind because the combustion of hydrogen gas produces water as the only product. As such, hydrogen-fuelled motor vehicles are the environmentally friendliest means of transportation, although, as of now, the cost of hydrogen-fuelled cars containing fuel cells are unaffordable to the common man simply due to their high cost. However, luxury cars such as Toyota Mirai, Mercedes-Benz F-Cell and FCV Honda are now in market (Figure 1). [2] - [4]

Figure 1: Hydrogen-powered motor vehicles available in the market. [2]

The Natural Abundance of Hydrogen in terms of mass of hydrogen per mass of Earth is 260 µg/g which means there are 6,700,000 H atoms per billion of all the atoms of the Earth. The Oceans of the Earth contains 10.82% by mass of hydrogen. Petroleum and organic matter contain significant fraction of hydrogen but the atmosphere contains only minute amounts of hydrogen not in the form of hydrogen gas but due to the presence of water vapour. As such, hydrogen as hydrogen gas is virtually non-existent even in the atmosphere since hydrogen gas is capable of escaping our atmosphere due to its lightness and high speed thus making it enable to overcome the gravity pull. [5]

PRODUCTION OF HYDROGEN GAS

Currently, the majority of hydrogen gas is produced from fossil fuels by the process known as steam reforming of hydrocarbons or by partial oxidation of methane and coal gasification. Only a small quantities of hydrogen gas is produced by other routes such as biomass gasification and electrolysis of water. The Production Capacity of Hydrogen in the United States alone is around 9 million metric tonnes per year and nearly half is used on-site for oil refining and the rest is mainly used in the production of ammonia from nitrogen gas in the Haber process and for the production of methanol by the reduction of carbon dioxide. In the year 2004 alone, 53 metric tonnes of hydrogen gas have been consumed worldwide. The global market for hydrogen and fuel cells is predicted to grow at a CAGR of around 14.9% over 2015-2020 and expected to reach 3010 million USD market in 2023. Water electrolysis is the splitting of water to hydrogen and oxygen gases using electricity and is by far the most expensive way of producing hydrogen gas due to the very high cost of electricity.

PHOTOCATALYTIC WATER SPLITTING

Better way to split water is not by using electricity directly in electrolytic cells but by using solar energy as energy source. Such Photocatalytic Water Splitting stands out to be very interesting subject if water can be split into hydrogen and oxygen gases just by suspending the catalyst in water and exposing the reactor to solar radiation [7] - [13]. Photocatalytic Water Splitting belongs to an Artificial Photosynthetic Process requiring, theoretically, only water, photocatalyst and solar energy photons. The reaction can be shown as depicted in Equation (1). The reaction requires at least 1.23 eV energy of photons (infrared photons) as per thermodynamic considerations but both half-reactions , i.e., oxidation of water to oxygen gas and reduction of water to hydrogen gas, demand considerable overpotentials thus making huge kinetic barriers for the reactions to take place from a photocatalyst irradiated by infrared photons impossible.

Considering the overpotentials required for H+(aq) reduction (at least 50 mV Pt) and water oxidation (at least 500 mV on Pt) the minimum energy required is around 1.80 eV and typically the semiconductors with band gaps in the range of 1.8 – 2.2 eV are the best photocatalysts for hydrogen generation . This process takes place naturally in complex biological pathways but industrial production of hydrogen gas is currently incompatible.

$$2H_2O(l) \xrightarrow{\text{Photon Energy}>1.23\text{ eV}} 2H_2(g) + O_2(g) \qquad (1)[7]$$

Photocatalytic water splitting is stemmed from the discovery of Fujishima and Honda, in 1974[7] where they have demonstrated that an electrochemical cell ultraviolet light irradiated titanium dioxide single electrode photoanode coupled with Pt comprising of cathode are capable of producing oxygen and hydrogen, respectively, from water. Since then innumerable efforts have been devoted on the photocatalytic splitting of water and numerous modifications have been effected. The use of nanoparticles of TiO_2 in place of a flat sheet enabled a huge increase in surface area of the catalyst though the efficiencies obtained are still in the upper limit of a few micromoles per minute. TiO_2 is a wide band gap semiconductor (Eg = 3.20 eV) and the illumination of ultraviolet radiation of energy ≥ 3.20 eV results in the excitation of valence band electrons to the conduction band (e^-CB), thus creating positively charged lattice sites known as holes in the valence band, (h^+VB). The majority of these electron-hole pairs thus 3 generated undergo recombination generating heat and lower energy photons. Only a minute fraction is therefore available for useful redox reactions. The reaction scheme depicted below demonstrate these processes.

$$\mathrm{TiO_2} \overset{h\nu}{\rightarrow} \mathrm{h^{+}_{VB}} + \mathrm{e^{-}_{CB}}$$

$$\mathrm{h^{+}_{VB}} + \mathrm{e^{-}_{CB}} \rightarrow \Delta + \mathrm{h\nu'}$$

At the Photoanode $\mathrm{4h^{+}_{VB}} + \mathrm{2H_2O} \rightarrow \mathrm{4H^{+}} + \mathrm{O_2}$

$$\mathrm{e^{-}_{CB}} \rightarrow \mathrm{e^{-}_{Pt}}$$

$$H^{+}_{at\ the\ anode} \xrightarrow{\text{electrolyte}} H^{+}_{at\ Pt\ cathode}$$

At the Pt cathode $\mathrm{2e^{-}_{Pt}} + 2H^{+}_{at\ Pt\ cathode} \rightarrow \mathrm{2H_2}$

TiO2 is by far the most studied photocatalyst for water splitting since the potential of the top of the VB of TiO2 is well below the standard electrode potential of water oxidation (+1.23 V wrt SHE) and the bottom of the CB of TiO2 is well above the standard potential of H+ reduction (0 V wrt SHE)[7]. Hence, on theoretical grounds, at least under standard conditions, the h+-e- pairs generated in TiO2 photocatalyst are able to split water to O2 and H2 gases. Although, this is the case, the efficiencies of water splitting by solar energy irradiated TiO2 have been very low due to three reasons: (i) the band gap of TiO2 is large (3.20 eV) so that only UV radiation of wavelength ≤380 nm are effective which accounts only for 5% of the incident solar radiation on Earth surface, (ii) majority of h+-e- pairs photogenerated undergo recombination very quickly generating heat and luminescence allowing only minute fraction to do useful half-reactions and (iii) very large and positive standard molar Gibbs Energy of Reaction (1) (+ 237 kJ mol-1) making the backward reaction highly spontaneous. In addition, the overpotentials required for oxidation of water to oxygen gas and reduction of water to oxygen gas are considerably high thus demanding extra potentials for the reactions to proceed at appreciable rates thus making both reactions kinetically very slow at the above potentials.

One way to extend the life-time of photogenerated h+-e- pairs is to deposit islands of metal catalysts such as Pt, Au, Pd, Rh, Ni, Cu or Ag on TiO2 nanoparticles. The Fermi Levels of these metals are more positive than the potential of the bottom of CB of TiO2 nanoparticles and hence photogenerated electrons can be transferred to metal islands while holes remaining in the VB of TiO2 so as to separate the photogenerated h+-e- pairs. The metal deposition is indeed shown to improve the photocatalytic water splitting efficiency of TiO2 photocatalysts. Use of sacrificial electron donors such as oxalic acid, methanol, formic acid, formaldehyde etc. were also shown to improve photocatalytic hydrogen generation efficiency of TiO2 since these substances are easier to oxidise than water. Addition of carbonate salts to water has resulted in improved hydrogen generation due to the suppression of the back reaction. Use of metals in the form of quantum dots (Nanoparticles whose all three dimensions are confined to the nanoscale of 1 nm to 100 nm) enables to harness size-dependent properties, particularly, size-dependent optical and electrical properties such as Surface Plasmon Resonance (SPR). Gold and silver quantum dots exhibit SPR in the visible range as exemplified by the versatile colours of these nanoparticles depending upon their size and shape. SPR enables the quantum dots to absorb in the visible region for electronic excitation. Since the Fermi Levels of these quantum dots are more negative than the potential of the bottom of the CB of TiO2 nanoparticles, the 4 excited electrons in the quantum dots can be injected to the CB of TiO2 thus enabling increased water reduction to generate hydrogen. This is shown in Figure 2.

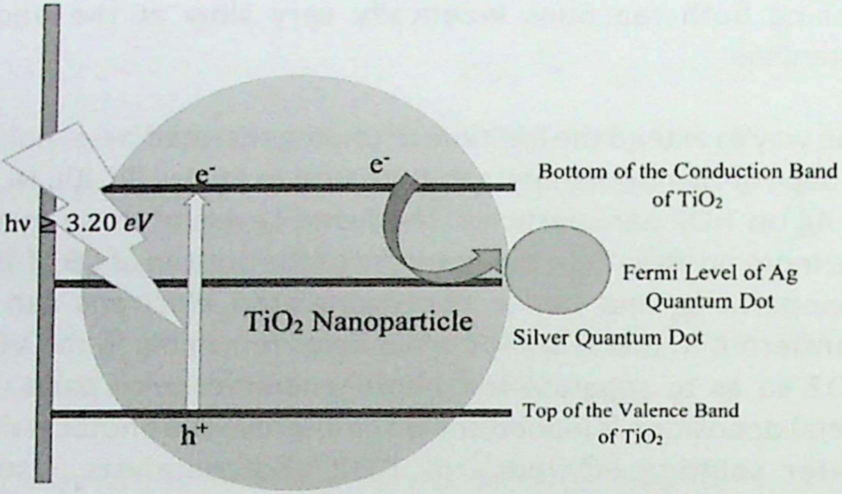


Figure 2: Ultraviolet irradiated excitation of VB electron to CB of TiO2 nanoparticle and visible light induced surface plasmon electron injection from silver quantum dot to the CB of TiO2 nanoparticle.

Band positions depend on the energies of the atomic orbitals those overlap to form the valence and conduction bands of semiconductor materials. For TiO2 the VB has O 2p character while CB has Ti 3d character which giving rise to a band gap of 3.0 eV for rutile and 3.2 eV for anatase. Figure 4 shows overlapping of atomic orbitals to form energy bands in TiO and TiO2 where half-full t2g CB of TiO makes it a full conductor possessing metallic conduction. Since the t2g CB of TiO2 is empty and that top of VB is formed by filled O 2p orbitals creating a band gap of 3.2 eV in anatase form of TiO2, it behaves as a semiconductor with a band gap 3.2 eV (Figure 3).

Note that the band gap also depends on the atomic arrangement in the crystal structure. Band gap can also be tuned by utilizing size-dependent optical properties of semiconductors in the nanoscale.

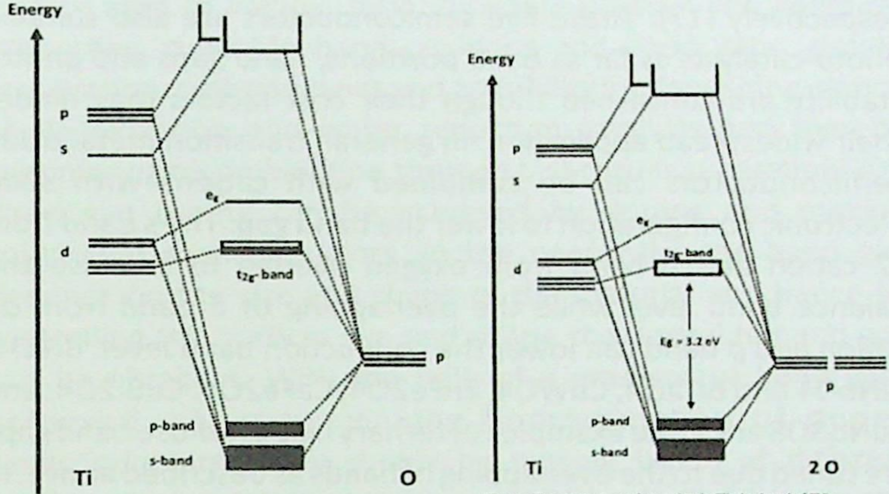


Figure : In the band structure for TiO a partially filled t_{2g} band can be seen. This gives TiO its metallic properties.

Figure : The empty t_{2g} and completely filled p-band of TiO_2 makes it a semi-conductor with a band gap of 3.2 eV. This is in the ultraviolet region.

Figure 3: Atomic orbital overlapping diagram showing metallic conduction of TiO and semiconducting properties of TiO2.

The atomic orbital overlapping contributing to band formation can be better explained taking ternary semiconductors with ABO4 structures. For instance, in BiTaO4 and BiNbO4 semiconductors top of the VB has characteristics of Bi 6s orbitals and bottoms of the CBs have Ta 5d and Nb 4d characters, respectively. Since the energy of Ta 5d is higher than that of Nb 4d, the bottom of the CB of the former is higher than that of the latter although the top of the VB is basically the same. This gives rise to a higher band gap for BiTaO4 (2.7 eV) when compared to that of BiNbO4 (2.6 eV)[16]. Both materials have the top of VB below (more positive than) water oxidation potential while the bottom of CB above (more negative than) the H+ reduction potential. Thus, both of them are possible semiconductor materials for photocatalytic water splitting. Similar considerations give rise to band gaps of InVO4, InNbO4 and InTaO4 semiconductors to be 1.9 eV, 2.5 eV and 2.6 eV, respectively [17]. These five semiconductors are also suitable photo-catalysts as far as band positions, band gaps and photo-stability are concerned though their cost factors may hinder their widespread application. In general, transition metal oxide semiconductors can be combined with cations with s2d0 electronic configuration to lower the band gap. The s band from s2 cation and p band from oxygen overlap to increase the valence band level while the overlapping of d band from d0 cation and p band can lower the conduction band level. BiVO4, BiNbO4 and BiTaO4, CuWO4, ZnFe2O4, CaFe2O4, CuBi2O4, and CuNb3O8 are some examples of ternary oxides whose band gaps are tuned due to the overlapping of bands as described above. In order to increase their electronic conductivities they can be doped with cations such as Ag+, V5+ or W6+ [51–53]. Instead of cation doping band gap tuning can also be achieved by anion doping. The atable 6 anions of the elements such as N, S, Se etc. (N3-, S2- or Se2-) have empty p orbitals which lie higher than those of O and hence the VB position moves up when N3-, S2- or Se2- are doped for O2- in oxide semiconductors. This strategy has been utilized in designing N-, S- or Se-doped visible light responsive TiO2 nanomaterials used in photocatalytic hydrogen generation. Other strategies for band gap tuning is by modifying the catalysts with silicon, group III-V semiconductors, and carbon-based materials. Semiconductors currently under investigation for photocatalytic H2 generation are mainly oxides and sulphides of metals in their highest oxidation state such as Ti4+, Zn2+, Nb5+, W6+, Ce4+, Ga3+, In3+, Ge4+, Sn4+, Sb5+, Ta5+ and so on. [18], [14],[19]

USE OF SEMICONDUCTOR NANOMATERIALS

Compared to bulk single crystal electrodes whose surface area is determined only by geometrical area nanomaterials of semiconductors offer several advantages which include large surface area to volume ratio, tuneable physical and chemical properties, tuneable band positions and band gaps, simple preparation methodologies and possibility for depositing islands of H+ oxidation and water reduction catalysts and thereby suppressing recombination through fast carrier separation[20]. Band gap tuning can be achieved by doping and making compound semiconductors. In the nanoscale, the band gap depends on the size and shape of the material and hence by controlling the particle size and shape the desirable band gap can be obtained. With the help of a gradient of band gaps achieved either by making homo-junction of doped semiconductors or by simply by making layers of different particle sizes tandem structures could be built to cover the absorption of the entire visible and UV spectra incident on the Earth surface. Another striking feature of nanomaterials is that the size scale of 1 – 100 nm is comparable to charge carrier scattering length of semiconductor nanomaterials. As such, carrier scattering loses are significantly reduced in the nanoscale when compared to the same in the bulk state thus enhancing carrier collection efficiency. Nanomaterial are characterized by increased oscillator strength thus enabling high absorption coefficient facilitating increased light absorption. As such, 0-d nanomaterials such as nanoparticles, 1-d nanomaterials such as nanotubes (NTs), nanorods (NRs) and nanowires (NWs) which confining to nanoscale in two dimensions with one dimension extending beyond 100 nm limit and 2-d nanomaterials such as nanoflakes (NFs), nanosheets (NSs), etc. which confining to nanoscale in only one dimension and other complex nanotechnological architectures of semiconductors have been used in photocatalytic hydrogen generation. Thin films of interconnected 0-dimensional nanoparticles (quantum dots, QDs, when the size is towards the lower end of the nanoscale) have shown efficient light absorption and consequent high photocatalytic efficiency. However, thin films of interconnected 0-d nanoparticles suffer from the disadvantage that the charge carriers have no direct transport as in 1-d nanomaterial but instead have to undergo random diffusion. This increases the charge transport length and thereby increasing the possibility for charge loses. 1-d nanomaterials have direct charge transport along their elongated dimension though they have comparatively lower surface area. As such, QDs have been deposited on vertically aligned 1-d nanomaterials to enhance surface area and light absorption and hence to increase both the catalytic sites and light absorption characteristics. In this respect, QDs of various materials such as CdS, CdSe, Co3O4, graphene, other carbon forms, graphitic carbon nitride, etc., have been used. Some 1-d and 2-d nanostructures of semiconductor materials used for photocatalytic hydrogen generation include TiO2 NRs and NTs, ZnO NRs and NWs, WO3 NRs, Nb2O5 NWs, Ta2O5 NWs, TaON NTs, MoS2 tipped CdS NWs, MoS2 NSs, SiC NWs, g-C3N4 NSs, carbon NTs (CNTs), and so on. Additionally, 3-d nanostructures such as dendritic α-Fe2O3 have also been used.[21], [22] 7

IMPROVING PHOTOCATALYTIC ACTIVITY AND SUPPRESSING ELECTRON-HOLE RECOMBINATION

In order to improve photocatalytic activity of the semiconductor material it should absorb in the visible range creating catalytic sites and electron-hole pairs produce should be effectively separated so as to suppress recombination [23]. The semiconductor must be stable against hole corrosion. Both the extension of light absorption to visible range and charge carrier separation could be achieved by doping with some transition metals in their zero-valent state such as Pt, Ag, Au, Cu, or as mixed oxides of Cr3+, Ru4+, Rh3+, Ni2+, and so on. Semiconductor nanoparticles can be decorated with islands of co-catalysts such as Pt as H+ reduction catalyst and RuO2 as water oxidation catalyst. In this case, photogenerated electrons in the CB of TiO2 are transferred to Pt and holes remaining in the VB are transferred to RuO2 thus separating photogenerated electron-hole pairs and thereby reducing their recombination. Pt acts as a catalyst for H+ reduction while RuO2 is a catalyst for water oxidation. [24]–[26]

Semiconductor materials containing transition metal cations with partially filled d-orbitals tend to undergo photo corrosion. As such, although ZnO and CdS are expected to perform well as photocatalysts for water splitting the holes produce react with their lattices thus corroding the catalysts as shown in Equations 6 and 7.

$$2h^{+} + CdS \rightarrow Cd2^{+} + S \qquad (6)$$

$$4h^{+} + 2ZnO \rightarrow 2Zn2^{+} + O2 \qquad (7)$$

These reactions compete with water oxidation reaction and a way to overcome this problem is to use sacrificial agents that are easier to oxidize than both water and semiconductor material. In the case of CdS, sacrificial agents used are S2-(aq), SO32-(aq) and so on. In the case of ZnO, easily oxidizable organic compounds such as methanol or ethanol is used. Photogenerated holes will then oxidize these solution species and the electrons will reduce H+ to H2. This will also solve the problem of semiconductor lattice destruction due to heat produced by the reaction between H2 and O2 gases produced as the latter is no longer produced. [27]

Another method to suppress semiconductor material oxidation is to use electronically conducting polymers. Truc et al. found that Ta3N5 undergoes hole corrosion according to Reaction (8).

$$2Ta_3N_5 + 30h^+ + 30OH^- \rightarrow Ta_2O_5 + 5N_2 + 15H_2 \quad (8)$$

They used polythiophene and polyaniline conducting polymers as sensitizers to increase the charge transfer efficiency and to prevent high recombination rates of the photo-excited electrons and holes of Ta3N5 photo-catalyst. This also led to the increase in electron-hole separation efficiency. Photogenerated holes are transported along the conducting polymer chains to prevent hole corrosion of the semiconductor material also. As such, Ta3N5/conducting polymer systems showed good photocatalytic activity for overall water splitting to produce both hydrogen and oxygen even under visible light irradiation. [28] Figure 4 shows band positions and band gaps of common semiconductors and the potentials corresponding to H+ reduction and H2O oxidation are shown in Figure 3. Note that semiconductors possessing the bottom of CB above H+ reduction potential and top of VB below water oxidation potential with a band gap in the range of 1.8 – 2.0 eV are the most suitable semiconductors for photocatalytic water splitting though hole corrosion and hence the stability and durability are yet another factors to consider when choosing a suitable semiconductor.

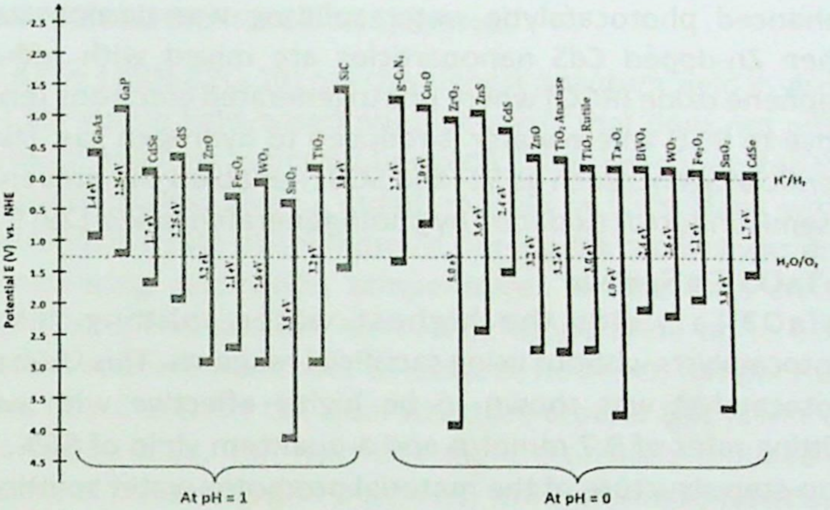


Figure 4: Band positions and band gaps of some common semiconductors at specified pH vales together with H+/H2 and H2O/O2 standard electrode potentials.

SEMICONDUCTING SOLID SOLUTIONS FOR PHOTOCATALYTIC HYDROGEN GENERATION

Cd1-xZnxS System

Solid solutions Cd1-xZnxS with different Zn concentration (0.2 < x < 0.35) has been investigated in the production of hydrogen from aqueous solutions containing SO32-/S2- as sacrificial reagents under visible light. Textural, structural and surface catalyst properties were determined by N2 adsorption isotherms, UV–vis spectroscopy, SEM and XRD and related to the activity results in hydrogen production from water splitting under visible light irradiation. It was found that the crystallinity and energy band structure of the Cd1-xZnxS solid solutions depend on their Zn atomic concentration. Hydrogen production rate was found to increase gradually when the Zn concentration on photocatalysts increases from 0.2 to 0.3.Subsequent increase in the Zn fraction up to 0.35 leads to lower hydrogen production.

Enhanced photocatalytic water splitting was demonstrated when Zn-doped CdS nanoparticles are mixed with reduced graphene oxide (RGO) where photogenerated electrons tend to move to RGO where water is reduced to hydrogen gas. Use of sacrificial agents such as S2- and SO32- enabled the prevention of semiconductor oxidation by photogenerated holes. [29] 9

NaTaO3:La System

NaTaO3:La yields the highest water splitting rate of photocatalysts without using sacrificial reagents. This UV-based photocatalyst was shown to be highly effective with water splitting rates of 9.7 mmol/h and a quantum yield of 56%. The nano-step structure of the material promotes water splitting as edges functioned as H2 production sites and the grooves functioned as O2 production sites. Addition of NiO particles as cocatalysts assisted in H2 production; this step was done by using an impregnation method with an aqueous solution of Ni(NO3)2•6H2O and evaporating the solution in the presence of the photocatalyst. NaTaO3 has a conduction band higher than that of NiO, so photogenerated electrons are more easily transferred to the conduction band of NiO for H2 evolution.[29]

K3Ta3B2O12 System

K3Ta3B2O12, another catalyst activated by solely UV light and above, does not have the performance or quantum yield of NaTaO3:La. However, it does have the ability to split water without the assistance of co-catalysts and gives a quantum yield of 6.5% along with a water splitting rate of 1.21 mmol/h. This ability is due to the pillared structure of the photo-catalyst, which involves TaO6 pillars connected by BO3 triangle units. Loading with NiO did not assist the photo-catalyst due to the highly active H2 evolution sites.[30]

$(Ga_{0.82}Zn_{0.18})(N_{0.82}O_{0.18})$ System

(Ga.82Zn.18)(N.82O.18) has the highest quantum yield in visible light for visible light-based photocatalysts that does not utilize sacrificial reagents as of October 2008. It has been reported that the photocatalyst gives a quantum yield of 5.9% along with a water splitting rate of 0.4 mmol/h. Tuning the catalyst was done by increasing calcination temperatures for the final step in synthesizing the catalyst. Increasing temperature up to 600 C tend to reduce the number of defects, however, temperatures above 700 C destroy the local structure around zinc atoms and thus undesirable. The heat-treatment ultimately reduced the amount of surface Zn and O defects, which normally function as recombination sites, thus limiting photocatalytic activity. The catalyst was then loaded with $Rh_{2-y}Cr_yO_3$ at a rate of 2.5 wt % Rh and 2 wt% Cr to yield the best performance.[31]

$BiVO_4$ and W-Doped $BiVO_4$

Bismuth vanadate based systems have been demonstrated to have high solar-to-hydrogen conversion efficiency of 5.2% which is by far the highest for metal-oxide photo-electrode. Other advantages include that it is a cheap catalyst and can be synthesized simply from wet chemical processes. W doping shifts the band positions downwards thus when $BiVO_4$ and W-doped $BiVO_4$ are brought into contact band bending occurs at the homojunction as shown in Figure 3. While both semiconductors generate photogenerated electron-hole pairs electrons are transported to $BiVO_4$and holes to W-doped $BiVO_4$ thus separating them for suppressing recombination. This is shown in Figure 5.

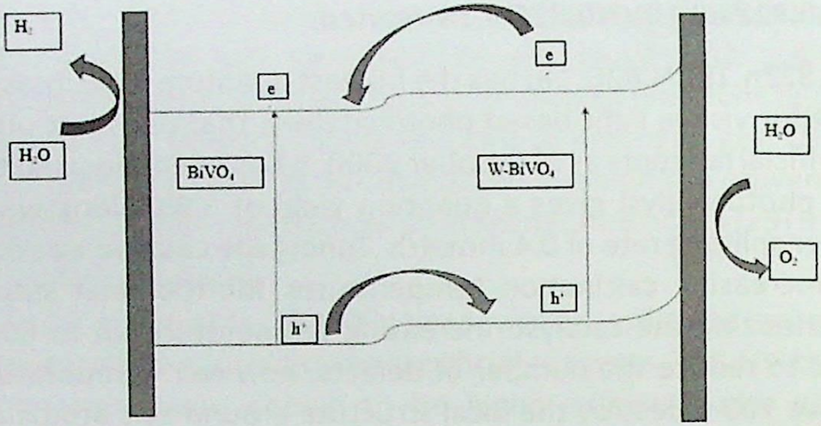


Figure 5: BiVO4/ W-BiVO4 homojunction facilitating electron injection from the CB of W-BiVO4 to the CB of BiVO4 while hole transport in the opposite direction thus separating electron-hole pairs.

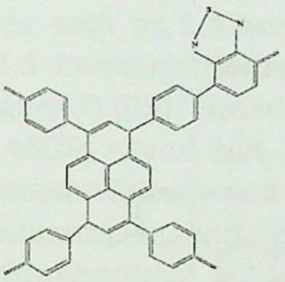
Gradient-doped W-BiVO4 were prepared by varying W percentage from 0 to 1%. Where the thin films of each of these semiconductor nanoparticles had graded band bending at the respective homojuntions and highly improved electron-hole separation was thus achieved. WO3 NRs decorated with BiVO4 particles and the latter coated with Co-porphyrins have also been used in photocatalytic water splitting. [32]

WSe2 based Systems

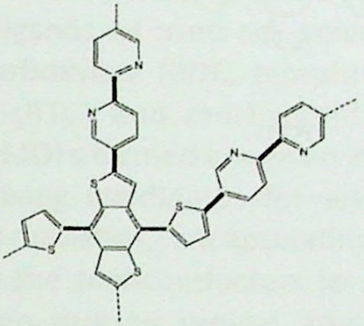
Tungsten diselenide stands out as a future hydrogen fuel production photocatalys as revealed by scientists in Switzerland in 2015. [33]

POROUS ORGANIC POLYMERS

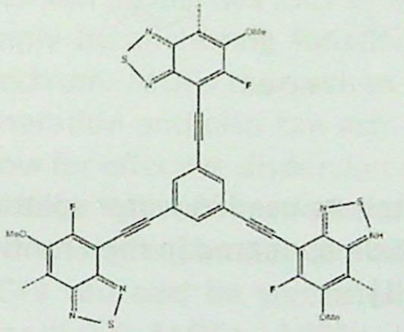
Porous organic polymers are considered to be emerging materials for photocatalytic water splitting. These materials have been reviewed recently and are depicted in Figure 6. Similarly electronically conducting polymers such as poly (fluorene-co-phenylene) derivatives have been used as photosensitizers in photo-driven hydrogen evolution in aqueous solution at pH 6 generating H2 gas at a rate of 429 mmol H2 gCP–1 h–1.



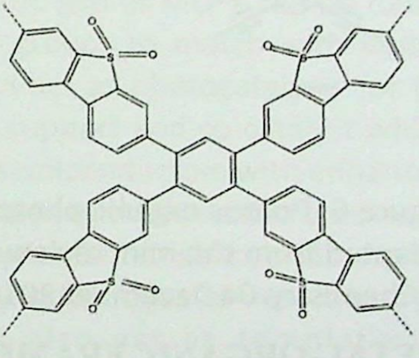
PyBt-2



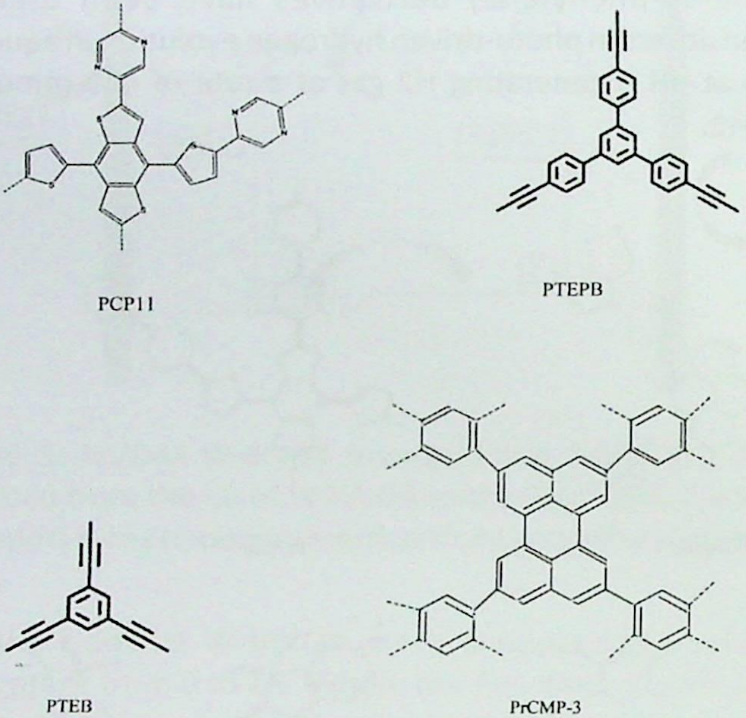
PCP4e



B-FOBT-1,3,5-E



DBTD-CMP1



PCP11

PTEPB

PTEB

PrCMP-3

Figure 6: Porous organic photocatalysts used in water splitting. Adapted from the mini review article appeared in the Frontiers in Chemistry, 04 December 2018,[1]

METAL-ORGANIC FRAMEWORKS

Metal-organic frameworks (MOFs) are attracting great attention recently as catalysts and solid supports in photocatalytic water splitting [34]. MOFs are highly porous materials with unique structures possessing structural versatility and high porosity with fascinating optical and electrical properties which are compounds consisting of metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional structures. They are a subclass of coordination polymers, which are porous, 3D-networked, crystalline materials composed of metal ions or clusters connected by organic linkers (Figure 7). The organic ligands included are sometimes referred to as "struts". Metal ions used are typically Al3+, Cu2+, Fe3+ and Zn2+but MOFs of other cations such as Ti4+, Cd2+ and Eu3+ etc. have also been synthesized. Ligands 13 used are polydentate ones such as 1,4-benzenedicarboxylate (BDC, terephthalate), 1,3,5-benzenetricarboxylate (BTC) and methylimidazolate (Figure 7) [35]. The respective MOFs formed are given in Figure 4. MOFs stand out as promising candidates for anchoring photosensitizers and catalytic moieties, encapsulating metal nanoparticles, and supporting the semiconductors to support photochemical H2 production due to typical advantages associated with MOFs such as large surface area, permanent pores and tuneable channels as well as desired physical and chemical properties [36] .The band gap of MOFs can be tuned simply by anchoring functional groups to match with visible spectrum. MOFs themselves can act as photocatalysts for H2 generation and also can acts as support and co-catalyst which allow for effective dispersion of semiconductors with enhanced the solar light absorption and promote the kinetic processes of both charge separation and catalytic reactions in hybrid systems. MOFs can also be sensitized by other dyes to result in dye-sensitized MOFs. MOFs can also act as templates in photocatalytic hydrogen generation.

Mahata et al. in 2006, first reported three novel MOFs, namely, [Co2(C10H8N2)][C12H8O(COO)2]2, [Ni2(C10H8N2)2][C12H8O-(COO)2]2·H2O, and [Zn2(C10H8N2)][C12H8O(COO)2]2 with three dimensional structures involved in photocatalytic degradation of dyes [37]. Mori and co-workers, in 2009 [38], reported, for the first time, photocatalytic hydrogen generation from water using the MOF [Ru2(p-BDC)2]n (p-BDC = 1,4-benzenedicarboxylate). Garcia in 2010, reported water-resistant

MOFs of Zr with ligands terephthalate (UiO-66) and 2-aminoterephthalate [UiO66-(NH2)] which are capable of photocatalytic hydrogen generation from methanol or water/methanol upon UV irradiation [34]. Horiuchi and co-workers reported a visible light responsive catalyst Ti-MOF-NH2 (titanium oxoclusters and 2-amino-benzenedicarboxylic acid) for photocatalytic H2 production from water [39]. The MOF exhibits a visible light absorption up to 500 nm due to chromophore in linking units and as such photocatalytic H2 production was performed under visible light irradiation by using triethanolamine (TEOA) as sacrificial electron donor and Pt nanoparticle as co-catalyst. Ti-MOF-NH2 exhibits a slight photocatalytic activity generating 3 ▯mol of H2 per hour [40]. One of the striking advantages of MOFs is that they can be used to integrate the organic dyes with non-noble metal into a single framework. Gd-MOF containing H4abtc (3,3',5,5'-azobenzene tetracarboxylic acid) and Gd3+ was used in visible light driven H2 generation. This MOF has light absorption onset at 530 nm with HOMO-LUMO gap of 2.35 eV which are ideal conditions for photocatalytic hydrogen generation [41]. There are several other recent discoveries which give insights into bright future of MOF for photocatalytic hydrogen generation.

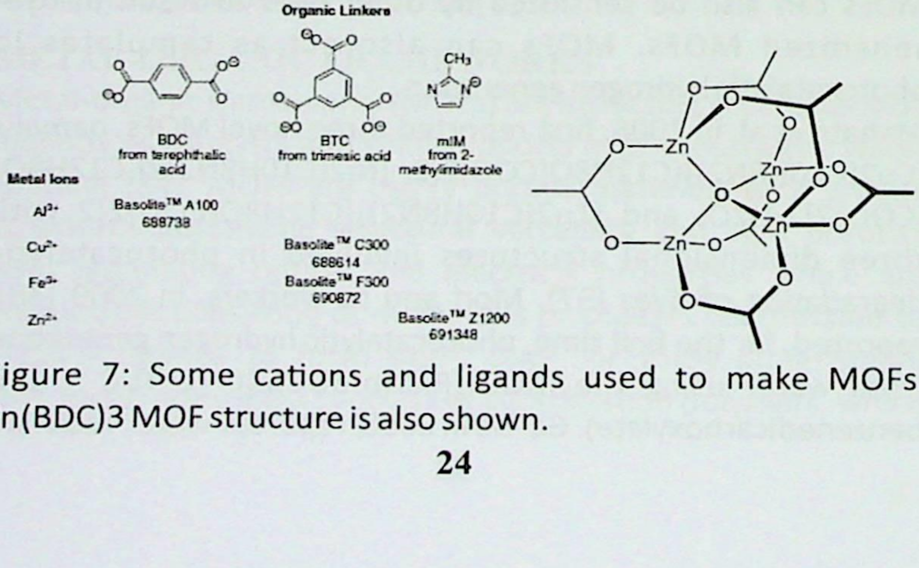


Figure 7: Some cations and ligands used to make MOFs. Zn(BDC)3 MOF structure is also shown.

PHOTON-UPCONVERSION BASED PHOTOCATALYSTS

The doping of TiO2 nanoparticles with various transition metal metal ions is another strategy that has been thoroughly investigated to create electronic energy levels within the band gap of TiO2 to enable the composite materials visible light responsive [41]. The same could also be achieved by non-metal doping such as N- or S-doping of TiO2 [42]. Water splitting by these composite catalysts have also been thoroughly investigated. The nanostructure and the crystallographic phase of TiO2 have been found to influence crucially on the efficiency of H2 photogeneration. However, the efficiencies so far achieved are below 1 mmol of H2 gas per hour for continuous illumination of solar radiation. We have combined the advantages of perfectly engineered nanostructures of TiO2, quantum dots of silver deposited on the engineered nanostructure of TiO2 and Nb(V) doping to make a photocatalyst that is capable of generating hydrogen gas highly efficiently giving rise to about 3 mL per minute which is by far the most active photocatalyst ever discovered. We made use simple and low-cost sol-gel technique followed by hydrothermal treatment and the powerful self-assembly of nanomaterials to form engineered architectures of long and thin nanowires of TiO2/Ag/Nb(V) photocatalyst which is grey-black in colour. The photocatalyst is capable of splitting distilled water when exposed to even stray light coming through the glass windows of the laboratory. This rate of water splitting is three orders of magnitude faster than the best recorded efficiency thus far. The fact that the catalyst is grey-black in colour and its ability to split water even under infrared irradiation suggest that the catalyst is capable of upconverting infrared photons to visible photons to aid in electronic excitations. The doping by Nb(V) has, therefore, introduced electronic energy levels within the band gap of TiO2 which are as close as the vibrational energy levels of TiO2. The catalyst is trifunctional in radiation absorption: UV absorption by TiO2 nanowires, Visible light absorption by Ag quantum dots and infrared absorption by doped Nb(V) ions. These collective radiation absorption and photon upconversion results in increased electron injection to the CB of TiO2 nanoparticles thus making the composite catalyst superior to everything else so far discovered. The self-assembled architecture of thin and long nanowires of TiO2 also influences positively towards efficient hydrogen generation. This photocataltst is found to be stable for months under ordinary ambient laboratory conditions. This, n number of IR photons can be added to give a visible photon as shown in Figure 8.

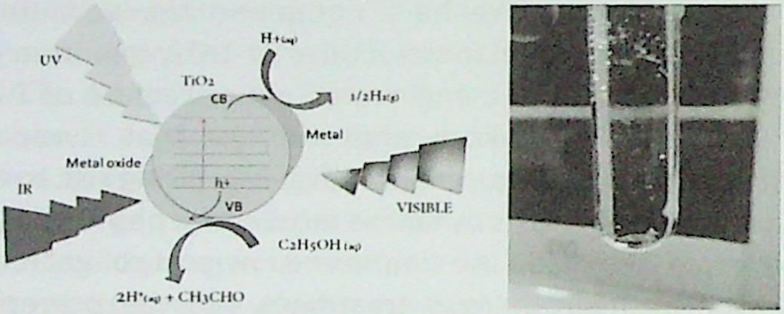


Figure 8: Schematic illustration of hydrogen evolution from TiO2 modified with cation doping for photon Upconversion and Ag QDs for SPR effect (left). H2 evolution in the dark by It-TiO2-AgQD system is shown in the right (right). 15

Ir(IV)-doped Ag QD attached TiO2 nanoparticles also show rapid hydrogen evolution when illuminated with visible and IR radiation. Here, Ir(IV) introduces a ladder of electronic energy levels which are comparable to vibrational energy levels of TiO2 which fall within the band gap of TiO2. As such, if this technology is upscaled to produce hydrogen from water at a rate required for producing hydrogen for use as motor vehicle fuel then the environmental pollution by emissions from exhausts of motor cars can be eliminated and we would be driving greener cars. We believe that it is not just a speculation but a grand reality and let us hope for driving greener cars in the very near future.

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