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Hydrogen production from wastewater by photo-electrolysis using ligand-free semiconductor Nano-composite of TiO_2 modified by Au: A brief review

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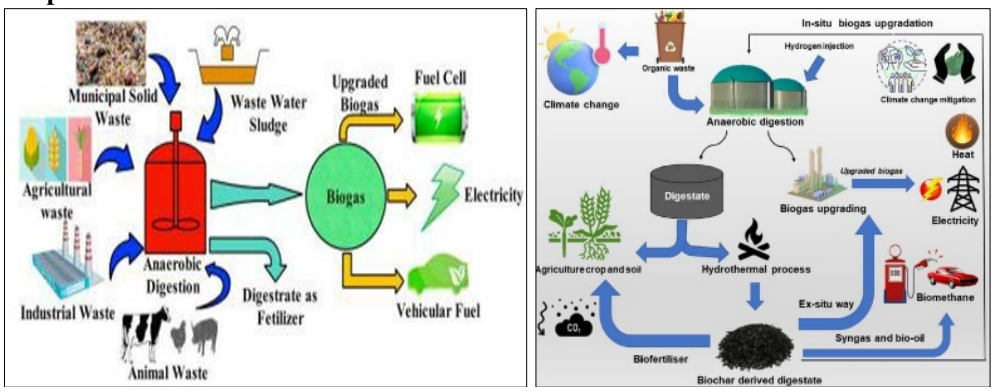
Abstract
The global climate risks and energy requirement issues have forced the world to adopt renewable resources and reduce the over-dependence on fossil fuel. Hydrogen is found to be the best alternative in current decades, and most of the countries are trying to explore it into technology within 2025. Industrial sources of environmental pollution generate huge amounts of industrial wastewater containing various recalcitrant organic and inorganic pollutants that are hazardous to the environment. And industrial wastewater can be regarded as a prospective source of energy and valuable raw materials for hydrogen production. Conventional sewage treatment systems are often not efficient enough for the complete degradation of pollutants and they are characterised by high energy consumption. The chemical energy that is stored in the wastewater is unexploited. A solution to these problems is the photo-electrocatalytic depletion of waste water to produce hydrogen which leads to energy generation. TiO_2 has been used as a photocatalyst since the 1970s due to its low cost, earth abundance, and stability. There has been a wide range of research activities in order to enhance the use of TiO_2 as a photocatalyst using dopants, modifying the surface, or depositing noble metals. Ligand-free semiconductor nano-composite of TiO_2 modified by Au is one of the best routes of water depletion techniques. This paper presents a general brief overview of the semiconductor Au doped TiO_2 materials applied as photoelectrodes in the treatment of wastewater. It deals with the alternative/cost-effective synthesis process of ligand-free Au/TiO_2 nano-composite, fundamentals of photo-electrocatalytic reactions and the mechanism of waste water treatment as well as parameters affecting the treatment process.

Graphical Abstract



Keywords: Nano-composite, photo-electrocatalysis, wastewater depletion, green H_2 generation

Introduction
The Renewable energy sector is at a hardcore demand in the current world's economical strategy. The Renewable Energy uses low energy efficiency, consumption and energy sources that are continually being replenished by the natural environment reducing the amount of VOCs. NOx, CO_2 and SOx gases in the air. Renewable energy sources turn these fuels into useful energy forms - most often hydroelectricity, but also heat, chemicals, or mechanical power. Today, we primarily use fossil fuels to heat and power up any industrial or domestic sectors, even fuel our cars.

It's convenient to use coal as the best fossil fuel, crude oil and natural gas for meeting our energy needs, but the supply source of these fossil-fuels are not abundant enough, rather limited. They are being continually used more rapidly than being created and we're eventually running short of them increasingly. And because of the safety concerns and waste disposal problems, the countries will retire much of its nuclear capacity as soon as possible. Whichever in the meantime, the world's energy requirements are expected to increase by 45% during the next 20 years. Renewable energy can fill that gap. Even if we had an unlimited supply of fossil fuels, using renewable energy sources is better and cleaner for the environment. It is the green technology that deals with very little generation of pollution from pollutants. Burning fossil fuels, however sends CFCS & greenhouse gases into the atmosphere, trapping the sun's heat and contributing to global warming. Other pollutants are released into the atmosphere, soil, and water due to burning fossil fuels. These pollutants take a dramatic toll on the environment and on humans. Mainly the Sulphur dioxide (SO_2) and nitrogen oxides (NOX) released from acid acid harms plants and water bodies. Nitrogen oxides also contribute to smog formation. The acidification of water bodies leads to wastewater generation from the industrial grades as well as domestically. This review paper particularly focuses on the production of a green alternative source from the generated wastewater by the photoelectrocatalytic degradation of wastewater treatment/ purification using some certain catalysts based on Ligand-free Semiconductor nano-composite of TiO_2 Modified and Au nanoparticles. In this process, semiconductor nanoparticles produce a slight electricity supply for the water splitting, removing the hazardous metal oxide ions from the water and therefore makes it a renewable and clean energy source for Green Hydrogen Production. Now, this renewable energy supply will also help us develop energy efficiency, independence and security. It is plentiful and this technology is an improved form for the generation of electricity and for carbon free Hydrogen Production. For the development of reliable and quality efficient. Cost effective technologies to produce hydrogen is very important in the context of CO_2 and climate change Mitigation. Hydrogen is a converted gas, mainly obtained by the OHCU (Oxy Hydro Cracking) and SMR (Steam Methane Reforming) in the large scale Industrial operations with the help of Nanocatalysts. Therefore industry uses the produced hydrogen for everything from removing Mercury, Sulphur, nitrogen from the crude oil to manufacture of vitamins. Its combustion does not emit carbon dioxide into the atmosphere, this fuel could drive the energy output from the earth. Since there is no abundant supply of hydrogen gas, this lightweight gas has to be produced for zero carbon emissions fuel future. Thus, the choice of water as the raw material to produce hydrogen using sunlight, and photoelectrochemical cells with PEM (Proton Exchange Membrane) (electrodes) by the photoelectrocatalysis or water depletion using TiO_2 with modified Gold Nanoparticles is the novel approach for the new generation green hydrogen production for a Cleaner Sustainable Environment. The design of efficient systems for splitting water into hydrogen and oxygen driven by Photo-electrolysis using Ligand-free PEM Semiconductor Nano-composite is among the most extensively challenging underpinning the long term potential of hydrogen as a clean, sustainable fuel. Hydrogen is found to be the most efficient energy carrier and can be obtained from different sources of raw materials mainly water. The overall water splitting results on oy 5% of global industrial hydrogen being produced by Electrolysis of water.

Photocatalytic water splitting technology by using Nano sized TiO_2 can produce negative emissions and low cost and environment friendly Hydrogen using renewable resources such as solar energy widely available and can fulfil the future needs and requirements of energy related problems. TiO_2 NPs is highly recommended because of its high efficiency semi conductivity and no reaction with the compounds over which it is applied. It also has a large surface area as a semiconductor photocatalyst nanocomposite.

Though TiO_2 has several drawbacks, therefore utilisation of TiO_2 as a direct photocatalyst can have reduced absorption capacity of visible UV radiation and fast recombination of photoexcited electron holes (e-/h+) pair. The activity of the electron hole pair mobility is restricted to the UV ray absorbance which is only approximately 4-6% of the solar spectrum. The general photo-electrocatalytic activity of TiO_2 is very limited especially under the visible range of light spectrum irradiation. This is due to its wide bandgap. TiO_2 represents excellent physicochemical properties and has Crystalline phases with gap energies between 3.2 eV and 3.1 eV, and are n type semiconductors leading to a small UV light range absorption, resulting in low solar energy utilisation efficiency. In general, TiO_2 is intrinsically an n type semiconductor but it can be doped with TiO_2/Au/ to form nanohybrid p- semiconductor by adding some acceptor impurities by doping titanium dioxide (TiO_2) lattice with gold (Au) nanoparticles and supporting with modified single-walled carbon nanotubes (SWCNTs). All the synthesised samples showed anatase-structure TiO_2 as evaluated by XRD. Therefore, to add an extra absorption capacity, and reduce the band space between the two electron holes and they could carry charge, modified Gold Nanoparticles have been added with TiO_2 that provides an important property of all transparent homojunction fabrication for light harvesting and energy storage. As a photocatalyst, TiO_2 has been widely applied in the photoelectrocatalytic degradation of various organic pollutants and also wastewater treatment.

The photocatalytic activity of TiO_2 is strongly affected by two important factors:- poor visible light absorption-based methods and high charge carrier recombination rate. Due to these reasons, the presence of a co catalyst is generally a noble metal that is required for photo-electrocatalytic hydrogen production. The presence of these metals on the surface of semiconductors promotes hydrogen evolution as they play the role of "charge accumulators", being centres of electrons release necessary for proton reduction that leads to improved charge carrier separation and to a higher photocatalytic activity. Among the noble metals, Gold (Au) also allows exploiting the surface Plasmon Resonance (SPR) effect with increased quantum dots that enhances visible light absorption and charge generation around the TiO_2 surface. Also, the combination of a good interaction between Au and TiO_2 and Au SPR effect allowed obtaining high photo-electrocatalytic Hydrogen Production performance under solar/ visible light irradiation. Thus, Gold is the ideal co catalyst for TiO_2 for water splitting reactions. The solar based photo-electrocatalytic conversion can be considered to be an easy and sustainable route for preparation of Gold based photocatalysts.

The photoelectrocatalytic (.PEC) degradation process has been extensively used in the field of decontamination and Purification of drinking water and wastewater due to its

environmental friendliness and considerable efficiency. Au/ TiO_2 nano-composite structures have been the promising class of PEC Materials. Though uniformly synthesising Au/ TiO_2 composites is difficult without the use of surface ligands, which may hinder the understanding of their intrinsic PEC properties. For the proper detoxification of wastewater, highly ordered ligand free Au/ TiO_2 nanotubes (NTs) with the high homogeneity properties and homogeneous composition has to be prepared successfully and carefully controlling the synthesis conditions. The physicochemical properties of Au/hoTiO_2 NTs with different Au contents and Concentrations were characterised by SEM XRD - Scanning Electron Microscopy, X Ray Diffraction, X Ray Photoelectron Spectroscopy (XPS) and UV- Visible Diffuse Reflectance Spectroscopy, EIS- Electrochemical Impedance Spectroscopy, life - time of Photogenerated electrons, decolonization of Methyl Orange (MO) and photo-current. Hence, by comparing the different Trapping agents, the decolonization mechanism of MO is also discussed which may cast light on understanding the inherent properties of Au/ TiO_2 nano-composites.

Thus, this present review elucidate the various aspects and esearches related to the mechanism of TiO_2 as nano photocatalyst for photo-electrocatalytic depletion for the effective solar hydrogen production via photocatalytic activity of water splitting. Also, In this work,we report the improved photoelectrochemical (PEC) properties of TiO_2 (P25) nanoparticles based on photoelectrodes. The TiO_2 nanoparticles are deposited on the Au substrate (TiO_2/Au ho) via the spin-coater, which is treated by the thermal annealing approach in a vacuum. The annealed homogeneous TiO_2/Au Photo-electrode shows 0.55 mAcm^–2 of photocurrent density and 0.30% of conversion efficiency at an applied potential of 0.35V (Approximated values obtained from XRD), which are higher than those of as-annealed TiO_2/Auho photoelectrode in the air. The improved PEC performance is attributed to high oxygen vacancy density with more active sides, while TiO_2 nanoparticle was annealed in a vacuum (101 torr) with low oxide concentration conditions. Based on these findings, we suggest that the thermal annealing process might serve as another approach to improved photoconversion efficiency and stability of the TiO_2 nanocomposite materials and their hybrid compounds-based PEC application.

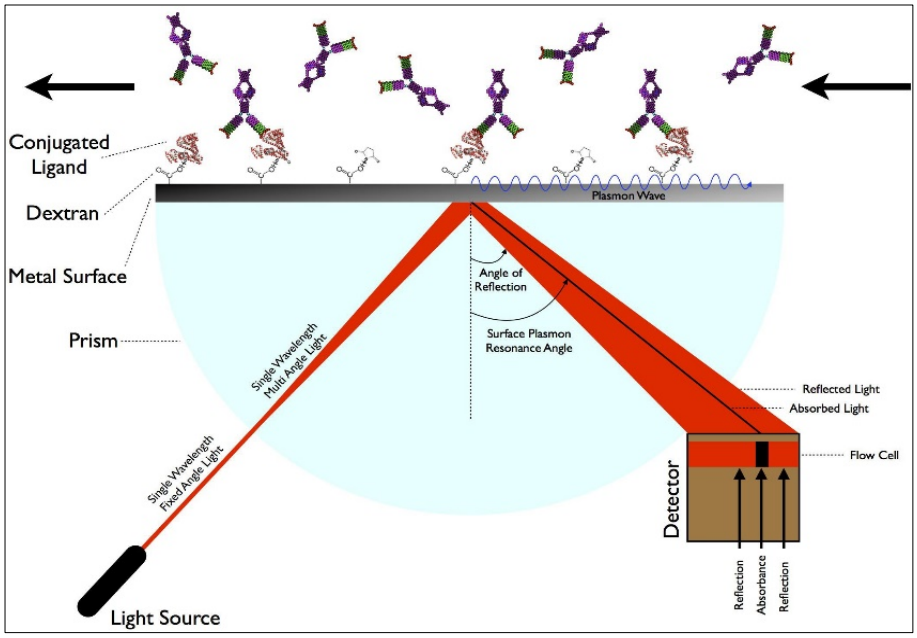


Fig 1: Surface Plasmon Resonance (SPR) for the detection of the conjugated ligands in the presence of incident light

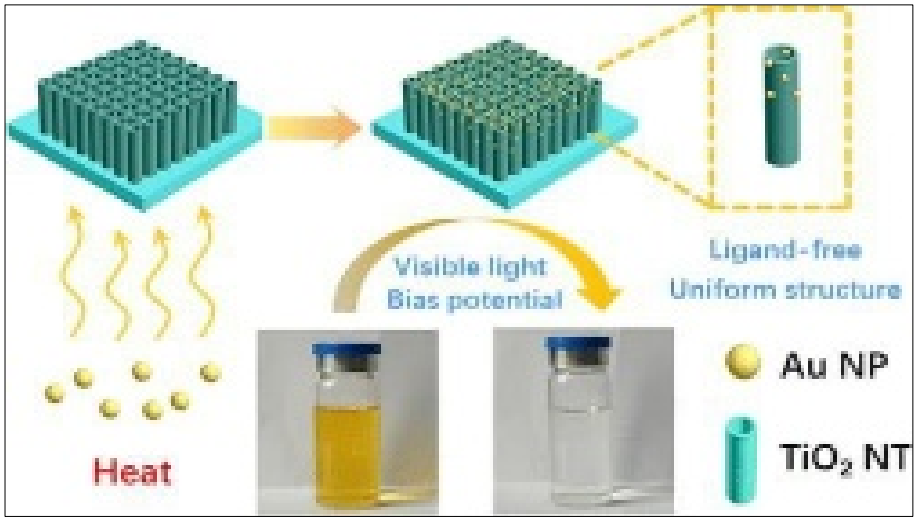


Fig 2: Ligand Free TiO_2 Nano-composites assisted by solar and UV Visible Light potential for purification. (Image Adapted from Reference)

Fig 3: UV Visible Light Spectrometer for potential for purification of Sample. (Adapted from IIT (ISM) DHANBAD Synthesis Laboratory)

General Routes for Hydrogen Production

Bio-Hydrogen: This fuel has been in the limelight for its tremendous potential in terms of being a clean and renewable energy currency. It has the highest gravimetric energy density when compared to other elements. It is also compatible with electrochemical and combustion processes for energy conversion without producing carbon-based emissions that contribute to environmental pollution and climate change. Biohydrogen can be produced by the processes of electrolysis of water, thermo-catalytic reformation of hydrogen-rich organic compounds, and other biological processes. Production of Hydrogen I'd mainly done either using fossil fuels or through the Renewable Energy Sources which is figured. The widely used process used mostly in the industrial sectors is the Steam Methane Reforming (SMR). Methane is a widely used fuel in this process due to its high hydrogen- to -carbon ratio (H:C) among the hydrocarbons groups; therefore the generated by- products are reduced. The Steam Methane Reforming (SMR) process is generally made up of two steps as presented below.

- The initial step is the reformation process. In this stage, methane gas mixes with steam (H_2O) at the beginning, which is moved over a catalyst bed reactor with a high pressure of 1.5- 3 MPa and a temperature range of 700- 900 °C to form a combination of carbon monoxide (CO) and hydrogen.
- The second step involves the shift reactions where there is the reaction of additional steam with the CO from the initial phase to produce additional hydrogen and CO_2 by Oxyfuel combustion.

CH_4+H_2O -> $CO+ 3H_2$
$CO+ H_2O$ -> $CO_2 + H_2$

-
- Coal Gasification is another thermochemical method for the generation of Hydrogen that uses fossil fuels. In this method, the coal is taken through a partial oxidation at high pressure, ~5 MPa with the subsequent reaction of steam with hydrogen and temperature assistance of steam and oxygen to yield the combination of CO_2, CO and CH_4 with other compounds. Hydrogen and CO mostly cooperate with the temperatures beyond 1000 °C and pressures of 1 bar. The process is represented in equations.

$C+½\ O_2$ -> CO
$C+ H_2O$ -> $CI+ H_2$

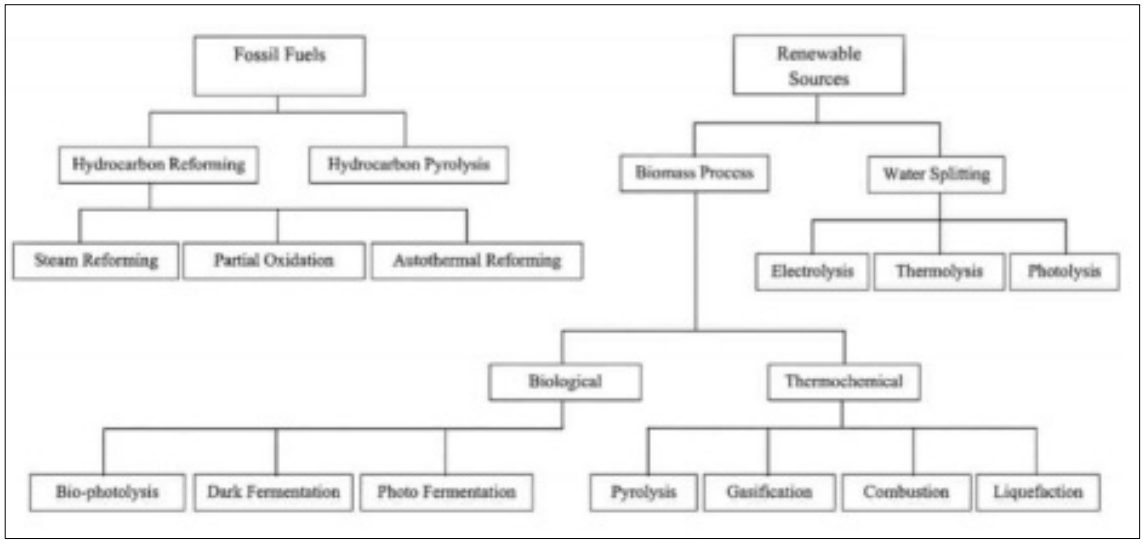
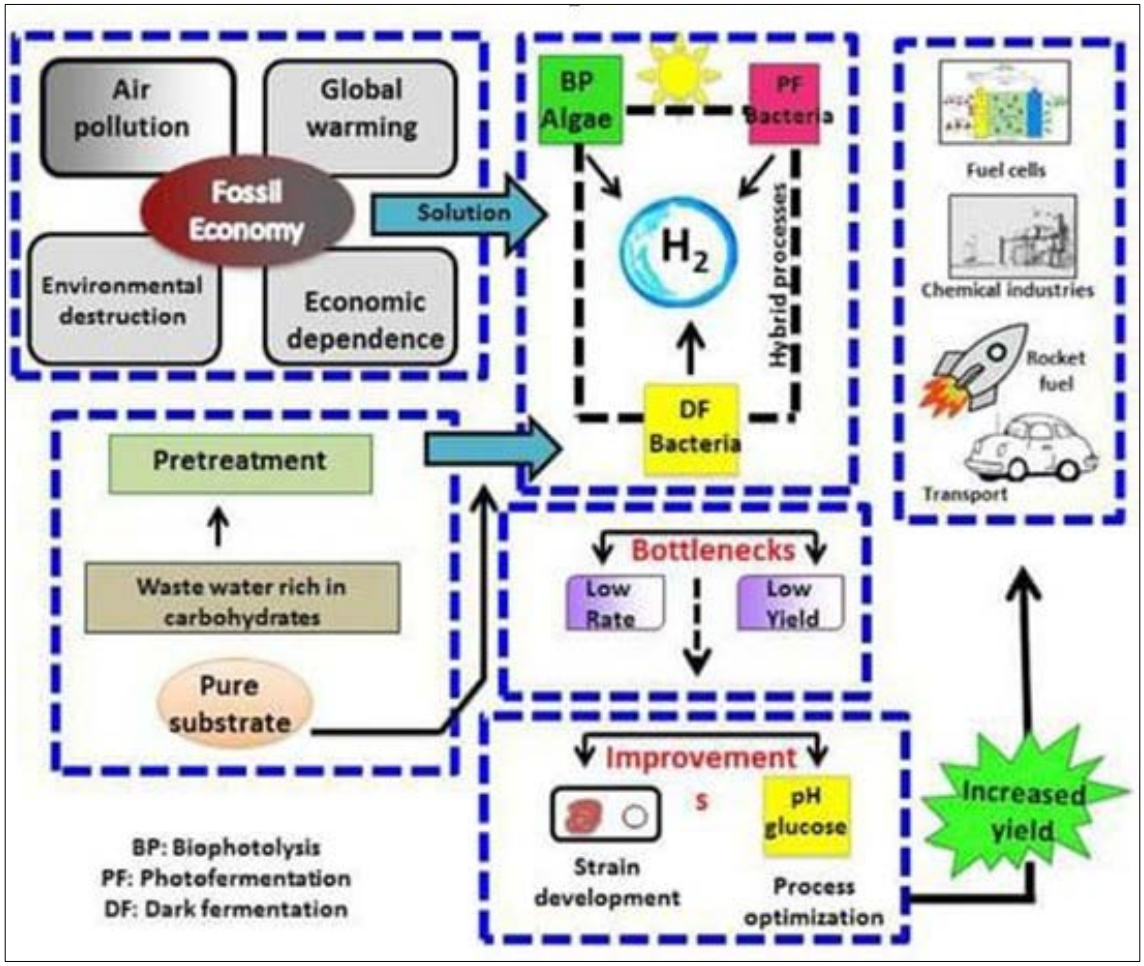


Fig 4: Various Routes to Hydrogen generation (Adapted from Reference)

This Study thus focuses on the hydrogen production pathways from renewable energy (RE) with the uses of some catalysts.



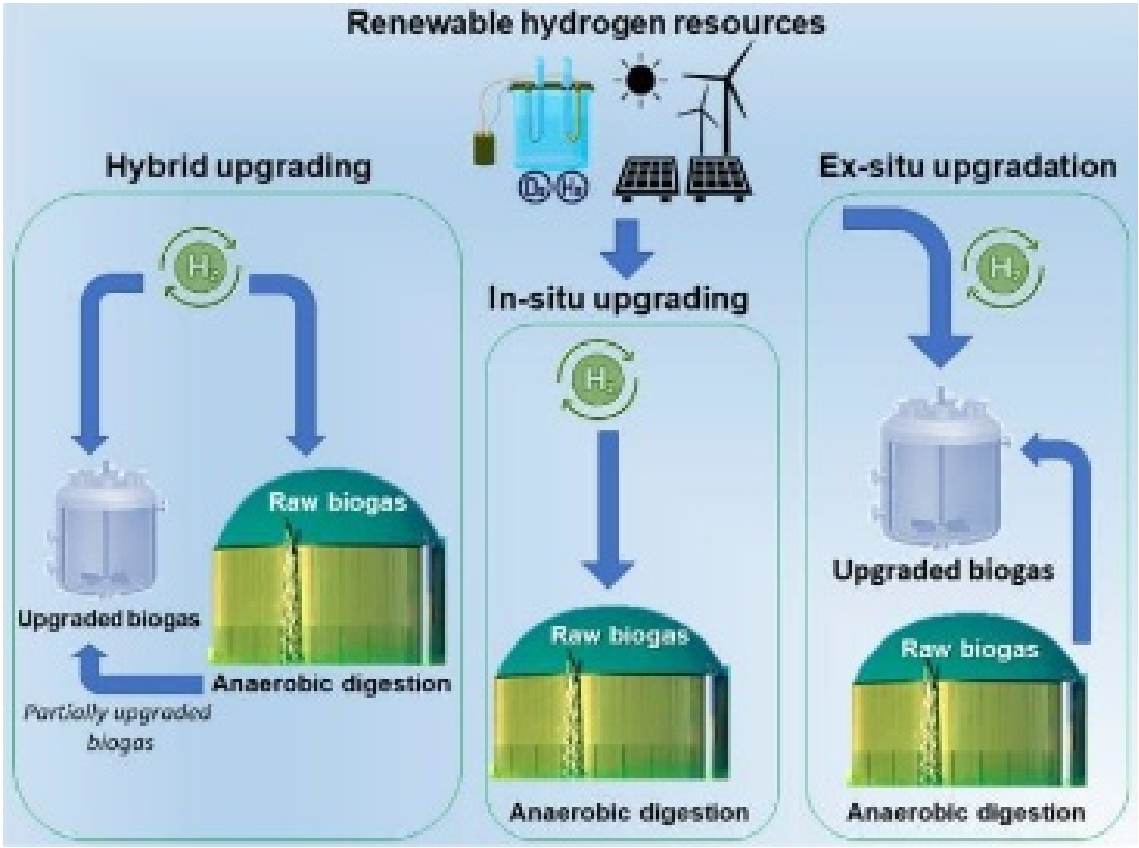


Fig 5: Hydrogen production pathways

Water Splitting

Water is the most abundant source for the Green Hydrogen Production since it's composed of Oxygen and hydrogen. With the help of sufficient external energy or electricity supply, the compound can be easily split into molecules of

Oxygen (O_2) and Hydrogen (H_2). Several technologies could be applied to split up the water. Some of the technologies are.

Electrolysis of Water for Hydrogen Production
In this process, water acts as a reactant, which is dissociated into oxygen and water using electrodes, and DC current.

Anode: H_2O -> 1/ $2O_2$ + 2H± + 2e-
Cathode: 2H± + 2e- -> H_2

Overall: H_2O-> H_2 + 1/ $2O_2$

Among the several Water Electrolyte used for water Electrolysis Systems PEM Electrolysis (Proton Exchange Membrane), Solar Water Splitting and Photocatalytic Water splitting technology are the most widely known for hydrogen production. They have the same principle but the operating conditions and catalysts used are different. Some of them are discussed below.

Photolysis of Water for Hydrogen Production
Water can release hydrogen under photochemical conditions, which occurs when water molecules absorb heat and light energy at a rate of 285.56 kJ/ mole of water from UV Visible Light radiation The dissociation of the H- O Bonds by the photons is called Photolysis, which occurs about 200 nm. This process is semi- Thermally Conductive in nature and in presence of chemical autocatalysts such as acidified KMno4 and, Pt, Au, Rh or Pd. Au is the most accelerating catalyst among the other noble metals.

KMNO4 (x)Z±+ H_2O -> Mn+2 (Z+1) + H + OH- 2H -> H_2

Here, Potassium permanganate (KMnO4) crystals are dissolved in water and forms a purple colour solution and acts as a strong oxidising agent therefore without producing any toxic byproducts.

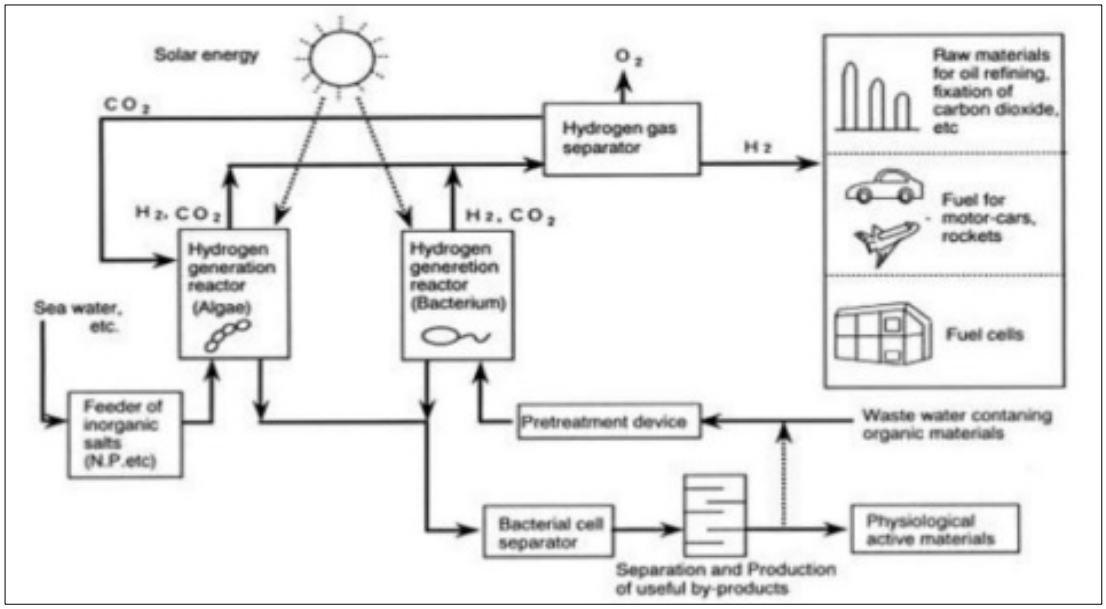


Fig 6: Overall Schematic flowchart of Hydrogen Production

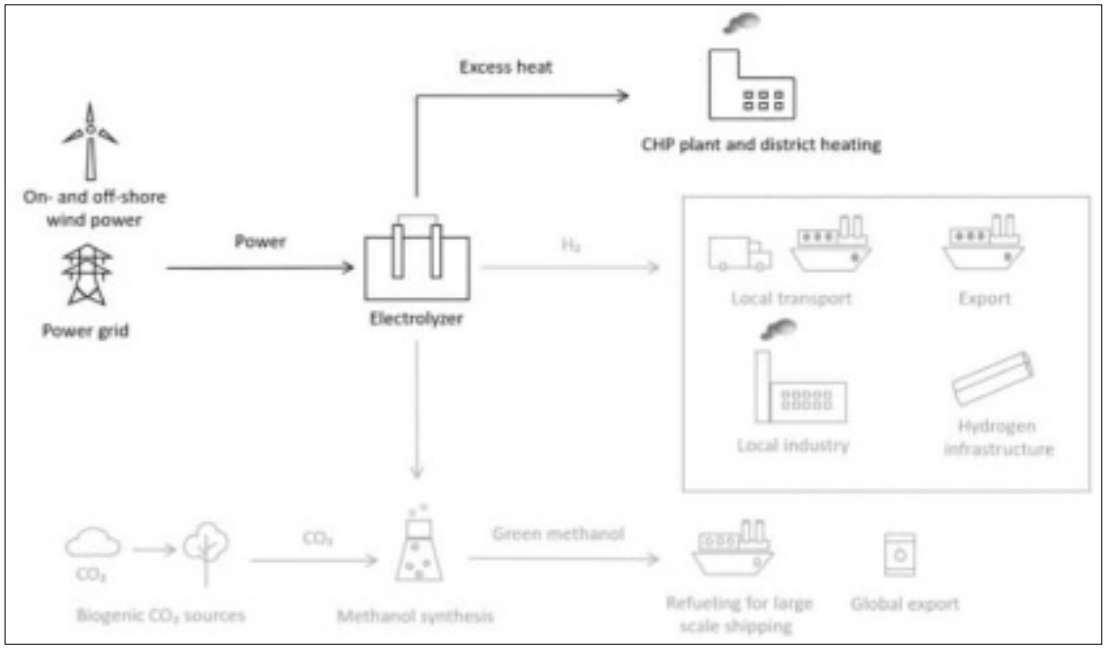


Fig 7: Schematic flowchart of Hydrogen Production Hub

Proton Exchange Membrane (PEM) Electrolysis

Hydrogen Production from proton Exchange Membrane (PEM) Electrolysis provides a better and promising solution for storage and utilisation of the renewable energy resources. Major Thermodynamic energy and exergy analysis has been conducted to optimise and investigate the performance analysis and Thermodynamic electrochemical characteristics of hydrogen production by a PEM Electrolyzer plant. PEM produces external irreversible heat losses like AD current loss. PEM electrolysis has an electrical efficiency of about 80% in working application, in terms of hydrogen produced per unit of electricity used to drive the reaction.

Hydrogen is the most efficient energy carrier, therefore in terms of sustainability and environmental impact, PEM Water Electrolysis is considered as most likely promising techniques for high pure and efficient Hydrogen Production from Renewable resources. It emits only oxygen as by product without any carbon emissions. The produced hydrogen (H_2) and Oxygen (O_2) are directly used as fuel cells for industrial applications. Nowadays the production of Green and Clean Hydrogen has increased the rate of PEM Water Electrolysis to a greater extent.

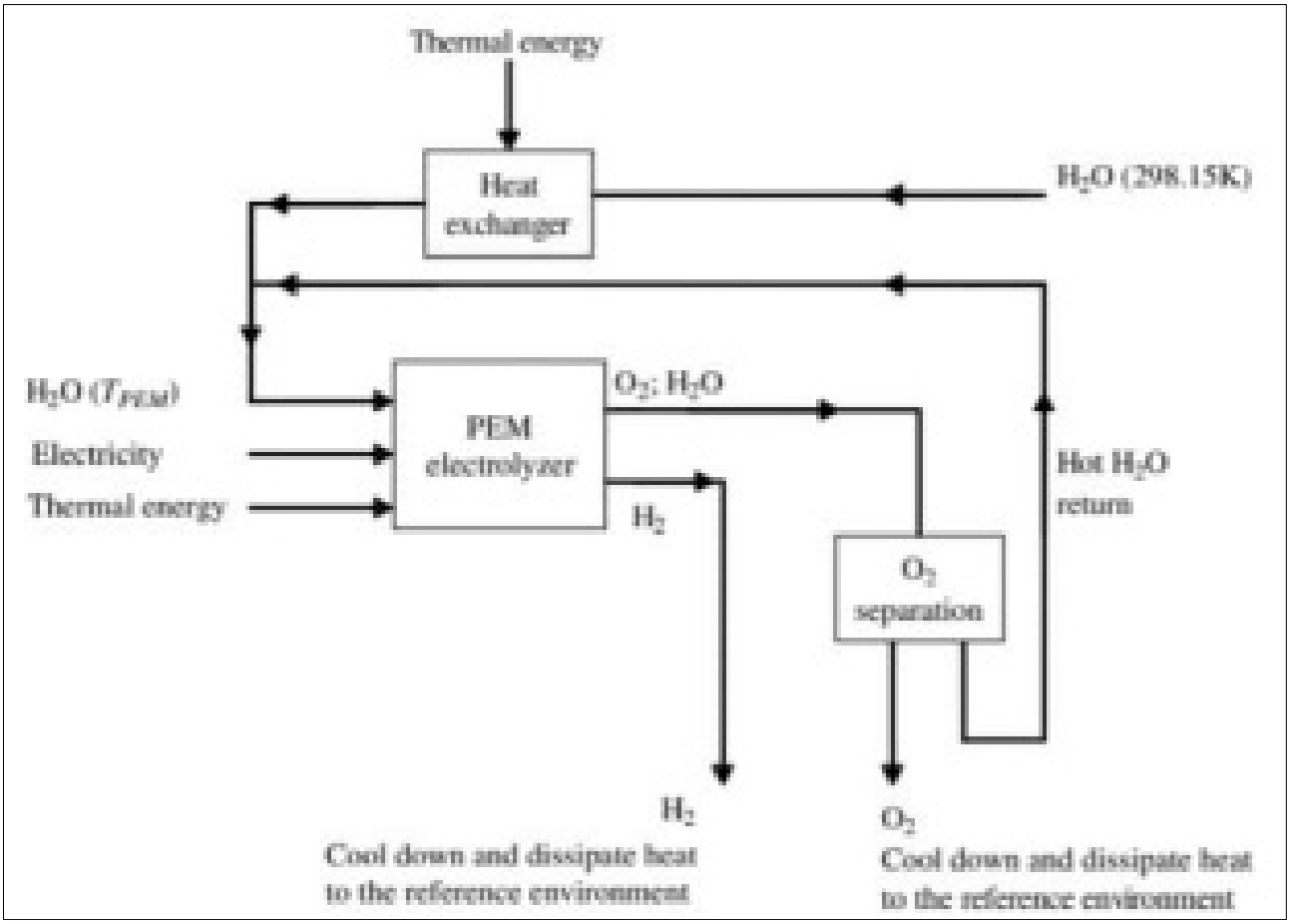


Fig 8: Schematic flowchart of PEM Electrolyzer Plant for Hydrogen production

The First PEM Water Electrolysis was idealized by Grubb in 1966 to overcome the drawbacks of normal solid oxide Electrolysis and alkaline water solution. PEM Water Electrolysis technology is similar to the PEM. Fuel cell technology where mainly *Naflon- poly sulfonated Membranes* was used as a proton conducting Electrolyte. These proton Exchange Membranes have many advantages such as lower gas permeability, high proton conductivity (0.1+/- 0.02S cm-¹), lower thickness (300 pm) and high pressure operations. In terms of sustainability and environmental impact, PEM Water Electrolysis is considered as the most favourable method for converting renewable energy to high pure and low cost effective hydrogen. Another promising PEM Water Electrolysis has great advantages such as compact design, high current density (2Acm-²), high efficiency, fast response, small CO_2 footprint, and easily operational under lower temperatures (20-100°C) and produces ultrapure sustainable hydrogen and oxygen as the byproduct. Additionally, balancing PEM Electrolysis plants are very simple, which is more attractive for industrial applications. The state- of- the-art electrocatalysts for PEM Electrolysis are highly active noble metals such as Pt/ Rd/ Pd as the Hydrogen Evolution Reaction (HER) at the cathode and RuO_2 / IrO_2 at the anode as the oxygen evolution reaction (OER) which makes it more expensive than alkaline water Electrolysis. Thus, the major challenge of PEM, Electrolysis, is to implement the cost reduction process in the market to maintain high efficiency. There are certain advantages of PEM Electrolysis which includes.

- High current density
- Compact Design of the Electrolyser system
- Quick Response from the Electrolytes
- Greater Hydrogen Production rate with high quality/ purity of the gases (99.99%).
- Higher energy efficiency (80- 90%).
- Higher Dynamic Operations

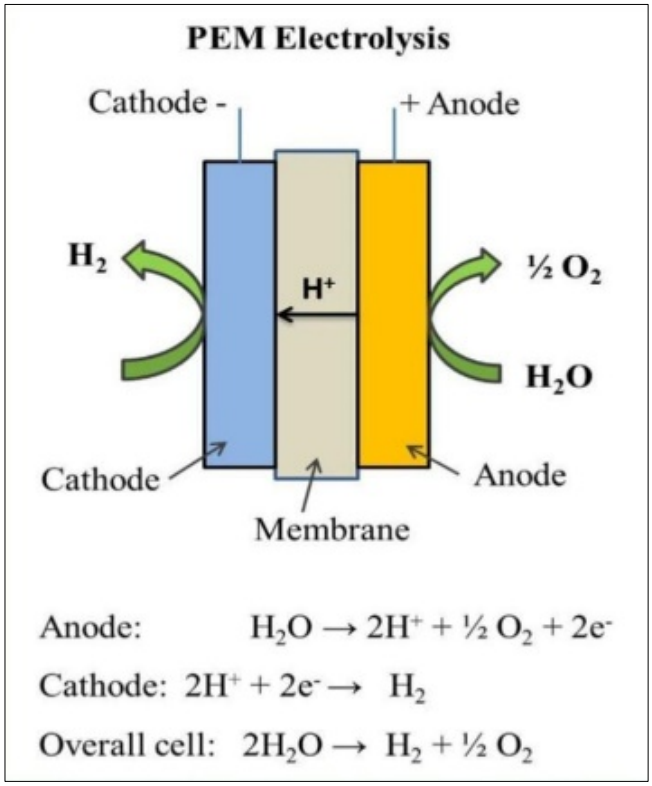


Fig 9: Schematic Illustration of PEM ELECTROLYZER

Principle of PEM Water Electrolysis

IN PEM Electrolysis, water is electrochemically split into hydrogen and oxygen driven by their respective electrodes I.e Hydrogen at the cathode and oxygen at the anode. PEM Water Electrolysis is accrued by pumping of water to the anode where it is split up into oxygen (O_2), protons (H±) and electrons (e-). These protons are travelled via the proton conducting membrane to the cathode side. The electrons exit from the anode through the external power circuit which provides the driving force (fuel cell voltage) for the reaction. At the cathode side, the protons and electrons recombine to produce biorenewable hydrogen at the end result.

Electrocatalysts for Hydrogen Evolution Reaction (HER)

The challenges towards hydrogen evolution reaction (HER) in PEM Electrolysis were mainly focused on the development of electrocatalytic conversion at the cathode separated by Electrocatalysts.

Though Pt/ Ir are the high cost metals, Platinum (Pt) or Pt based materials were mostly used as a standard catalyst for the Hydrogen evolution reaction (HER) as an active carbon support for improving stability, efficiency and biocompatibility. Pt provides the excellent HER activity and also exhibits outstanding stability in the acidic environment. Thus, highly dispersed carbon supported Pt - Based materials are currently benchmark catalysts for HER in PEM Water Electrolysis. To maintain the economic viability, increasing the specific performance and durability of the electrocatalysts, it is necessary to decrease the Pt loadings on carbon.The electrochemical active surface area is generally developed by the dispersed carbon nanoparticles in order to enhance the surface area and thereby decrease the Pt loadings. The electrocatalyst was then hosted in gas diffusion electrodes based on large surface area cost effective electronic carriers such as carbon nanotubes/carbons black. Later on many researchers initiated to use of different carbon blacks (CB) as support materials for platinum based catalyst as a standard electrocatalyst towards the HER. Though, the lower Pt loading on carbons are still indicates the significant portion of the overall system value, mainly due to the performance degradation or corrosion of the carbon support. Pt/C as cathode electrode and Ir, Ru as anode electrocatalysts along with an electrode surface area of 50-150 cm2 coated on Nafion 115 membrane. The noble metal loading varied between 0.2 and 0.4 mg cm2 and operated the electrolyser at 20 bar pressure and at 70-80 temperature. Nowadays Pd based electrocatalysts have shown increasing the significant interest towards the hydrogen evolution reaction because, palladium which is earth abundant and low cost compared to platinum, also shows remarkable electrocatalytic activity for several oxidation and reduction reactions.Pd activated carbon also tested for the HER with different weight loadings but unfortunately the obtained performance has not compared with the conventional Pt electrodes. The Pd carbon nanotubes (Pd/CNTs) have also been evaluated towards the HER though acceptable difference has not obtained compared to Pt/CNTs.Carbon nanotubes are generally used as an electron carrier support material for noble metal catalysts since they are generally known as having superior electron conductivity and corrosion resistance than conventional carbon blacks. Afterward, for better electrocatalytic activity and stability, hetero atom (N, P, S and B) doped carbon nanoparticles have been widely used as an electron carrier support material for noble metal electrodes in oxygen reduction reactions and hydrogen evolution reactions.The obtained Pd/N-CNTs results have shown comparable electrocatalytic activity than commercial Pt/C towards the HER and also exhibited almost similar electrochemical performance than conventional Pt/CB.Hence, Pd- based electrocatalysts can be used as alternatives to Pt-based catalysts for HER. In order to further reduce the cost of HER catalysts produced by using the other carbon-supported electrocatalysts, especially those only consist of earth abundant materials and low cost, such as AuNi-C, MO_2C/CNTs, Ni_2P/CNTs, Co-doped FeS_2/CNTs, WO_2/C nanowires and CoFe nanoalloys encapsulated in N-doped graphene etc., have been extensively studied in potential HER electro catalysts for alternative to Pt. However, these carbon supported Pt free HER catalysts that have actually been tested in PEM water electrolysis are rarely reported. In summary, in PEM water electrolysis alternative to Pt-based catalysts for HER several electrocatalysts have been developed and studied towards the HER. However, most of the catalysts belonging to the main family of metals with support of Nano carbons have been developed. Among these catalysts MoSx and Pd-based nano carbons appears to be the most capable electro catalysts in terms of electro catalytic activity and stability.

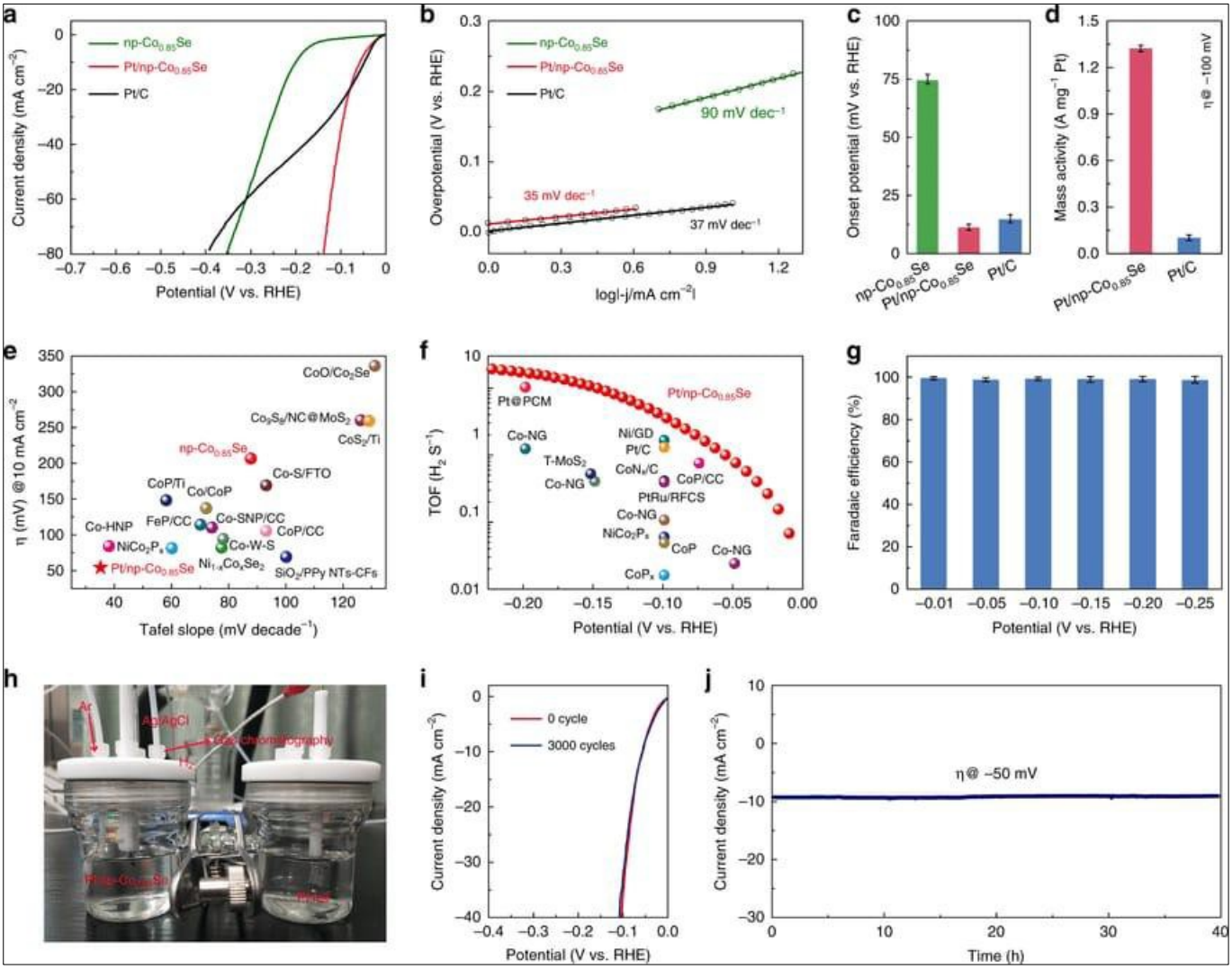


Fig 10: Report on HER (Hydrogen Evolution Reaction)

Thus, PEM Water Electrolysis technology is a unique way for Clean Hydrogen (H_2) production using the HER electrocatalysts as the fast accelerating materials for water splitting. HER electrocatalysts are more efficient and stable at large current densities. Therefore in PEM water electrolysis, emerging robust and stable electrocatalysts have been used but keeping in mind the commercial viability, in order to improve the Renewable energy based PEM Electrolyzers should be more cost effective and ecofriendly.

Solar PV Electrolysis

A number of solar hydrogen projects have been designed for hydrogen production to supply vehicle refuelling stations by using electricity from Solar Photovoltaic (PV) Panels and commercially available PEM electrolyzer for water splitting. Solar PV panels cover a large surface area of approximately more than 130m²per vehicle based on the system efficiency and estimated cost of Photovoltaic systems alone but the cost was effectively higher than the normal established plants for Hydrogen Evolution. Solar hydrogen have often consisted of power grid- tied systems in which PV modules were connected to the inverter electrodes to produce AC current which was then fed to the power grid. Power was extracted from the Grid through an independent circuit and converted to DC Current to operate the PEM Electrolyser. And produce hydrogen. These power grid- tird systems have the advantages of supplying ant desired amount of power from the utility to meet their needs, the additional cist of the inverters, power conditioning electronics, connection costs, utilisation efficiency fees, and the losses each time power is converted between the DC & AC, make them less efficient and more costly than the normal stand- alone systems. The Stand-Alone PV Electrolysis Systems for the solar hydrogen fuel production, have consisted of an array of the photovoltaic modules that supply DC Electricity through storage and power conditioning systems to the PEM Electrolyzer. The PV Modules are connected to a charge controller, storage batteries and a DC- DC power Converter to supply DC Current to an Electrolyzer consisting of a series of catalyzed electrodes to split up the water (H_2O) and therefore produce Hydrogen fuel and Oxygen. PV modules of a conventional and non - optimal system are mainly designed to supply green hydrogen by using most efficient voltage for operating the electrolyzer to split up the water bond. Euro-IV Hydrogen is now the new optimised Hydrogen produced from Solar Electrolysis of water by the European Standards. The PV Modules usually consist of a number of number of solid Crystalline silicon Solar cells (C- Si) solar cells (often 36 cells) connected on a series to produce additional electricity with a potential of about 18 V appropriate for charging 12 Volt lead acid storage batteries when operated at their maximum power point. (Vmpp), where they deliver their highest power under load. If any mismatch is found between the Vmpp and the operating voltage (Voper) of the electrolyzer, the efficiency of the PV System decreases sharply. The Pzv Power circuit in the battery system is

generally connected to a DC- DC Converter to change the PV Voltage to the characteristic operating voltage of the Electrolyser. The additional resistance imposed by the voltage converters and batteries in these systems also leads to significantly reduced efficiency. Thus, small Photo electrochemical (PEC) Devices, consisting of electrodes with its integrated PV and electrolytic functions, have been tested for practical usage but proven to be less effective than the PV Electrolyzer systems for the collection and storage of Hydrogen for Vehicle fueling and refilling stations as they operate at approximately one atmospheric pressure (1 atm) with a low energy density under normal conditions.

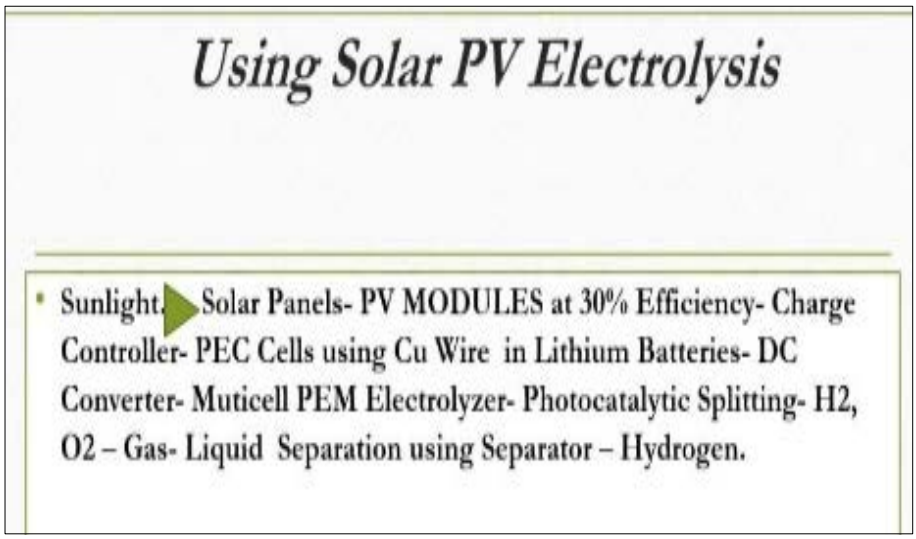


Fig 11: Overall Schematic flowchart of Solar PV Electrolysis for Hydrogen Production

Strategic Optimization of PV Electrolysis

Major improvements in solar powered electrolysis are needed to increase the efficiency and reduce the cost of the system and make it more practical for hydrogen generation. Since PV electricity generation and electrolysis are coupled to produce solar hydrogen, the electrical efficiency of the PV system must be multiplied by the efficiency of the electrolysis system for converting electricity to hydrogen fuel energy to find the overall efficiency of solar hydrogen generation (Eq. (1)). Both efficiencies need to be optimised for maximum system efficiency.Solar H_2 efficiency ¼ PV efficiency electrolysis efficiency.

Two strategies for improvements were chosen for testing the PV Electrolyzer System. Simplification of the PV-electrolysis system by removing the charge controllers, storage batteries, and DC–DC converters were done to reduce cost as well as electrical resistances in the system. The PV module was then connected directly to the electrolysis system to maximise the efficiency of the system by designing the solar module to give its maximum power at a voltage that would match the fixed voltage required to operate the complete electrolysis system (electrolyzer). Studies were conducted to design each part of the PV-electrolysis system including the solar modules and electrolysis system (electrodes and the electrolyte) to optimise the efficiency of the overall system.

One way to simplify the circuit was to eliminate the power converters (inverters and DC–DC converters) that add both to circuit resistance and system cost. Since each of these solid state power converters is about 90–95% efficient and costs approximately $100/kW, removing them from the design significantly improved the efficiency and cost. Instead of relying on a DC–DC converter to raise or lower the PV output voltage to the voltage level needed to operate the electrolyzer, the PV system was designed with the correct number of solar cells in series to generate the optimum electrolysis voltage. This system design constitutes direct connection PV-electrolysis. An optimised PV-electrolysis system was designed and built using PV modules directly connected to a multicell electrolyzer system Tests of systems incorporating a variety of PV modules were used to optimise the system efficiency.

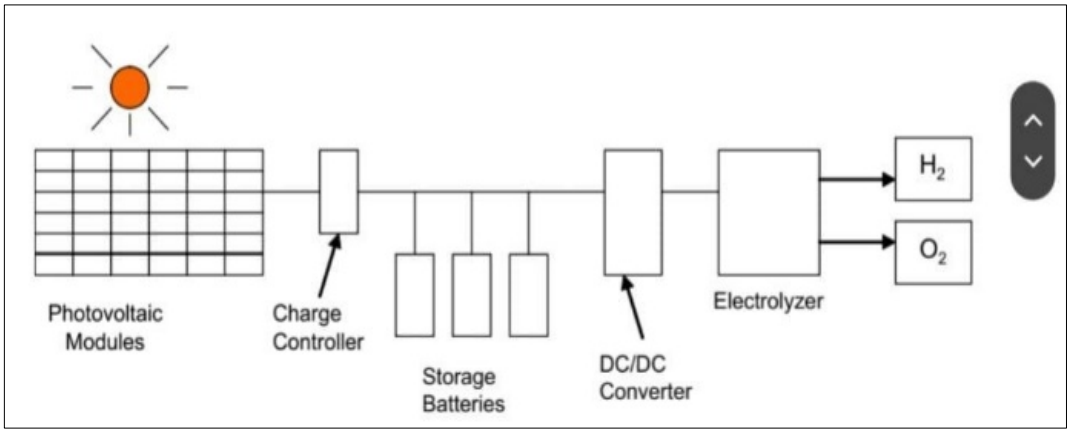


Fig 12: A Conventional Photovoltaic electrolyzer hydrogen generation system made from a non optimised photo-electrocatalytic (PV) power supply, electrolyzer and other hardwares

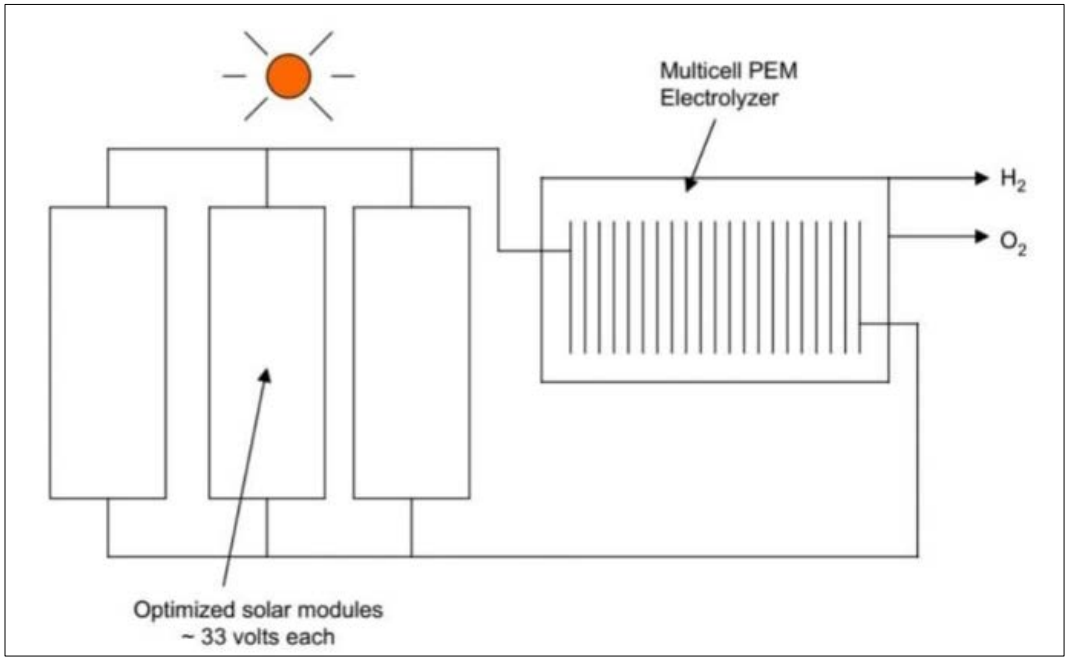


Fig 13: Optimised Design dor a PV Photovoltaic Electrolysis system using solar cells with the optimum Electrolysis potential connected in parallel to a PEM (Proton Exchange Membrane multicell (20 electrolysis cells in series) electrolyzer

Photo catalytic Water Splitting technology For Hydrogen Evolution using semiconductor TiO_2 Nano composites

The photocatalytic water splitting technology for Hydrogen production has been an widely established method reported since 1972. It is thus regarded as the most promising methods for Solar Energy Storage and Utilisation for future clean energy evolution by using several new devices like PEM Electrolyzer. The semi conductor based photocatalysis can be mainly described based on the difference between the concentration of the band gaps and band structures. When the energy output of the irradiated light photons is larger than that of the band gap energy of the semi conductor, electrons on the valence bond (VB) may be activated and jump directly to the Conduction band (CB) with the positive holes,left behind. The electrons on CB may either return to the VBTM to recombine with the alternative positive holes, or react with the adsorbed species on the surface of semiconductors. When the potential of electrons on CB is more negative than the redox potential of H_2/ H_2O, the separated electrons are now capable of water reduction to Hydrogen. The photocatalytic activity for hydrogen production has been realised not only by water splitting but also photocatalytic reforming (PR). The minimum requirements for photo-electrocatalytic protection of Hydrogen Production are.

- The electrons on the Conduction Band (CB) of the Semiconductor were capable of reducing protons to form Hydrogen.
- The holes on the valence Band of the semiconductor were capable of water oxidation or R- OH to release protons.

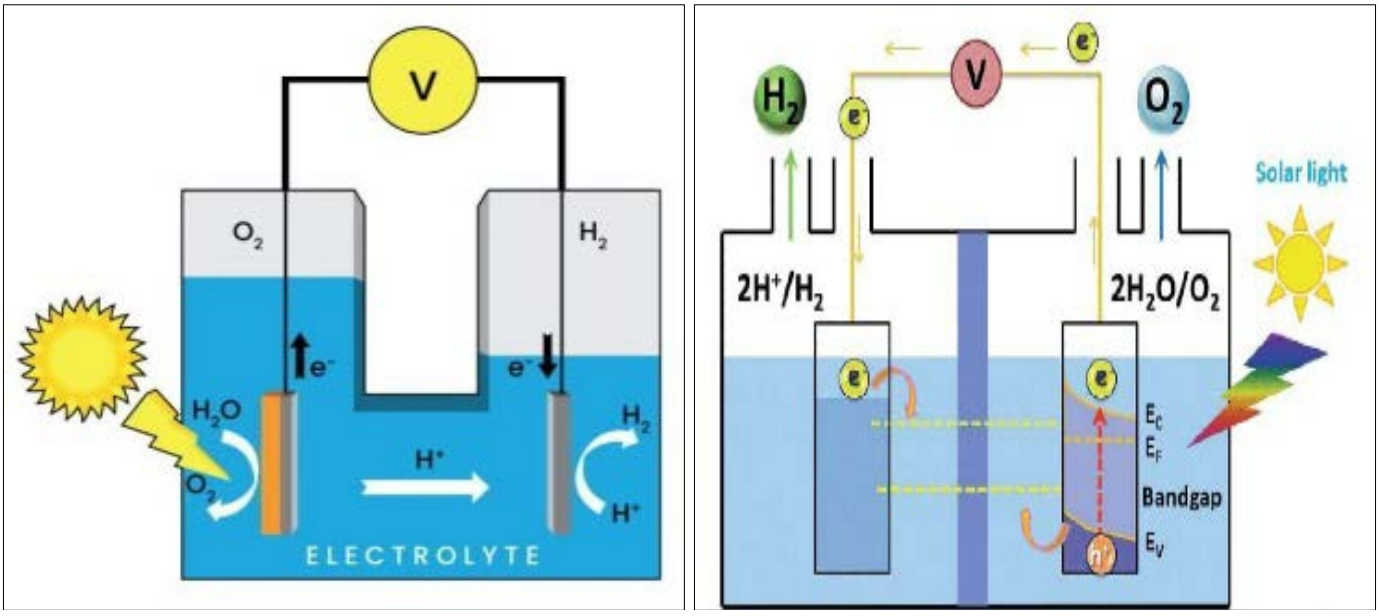


Fig 14: Atypical photoanode based photochemical cell for water splitting [9]

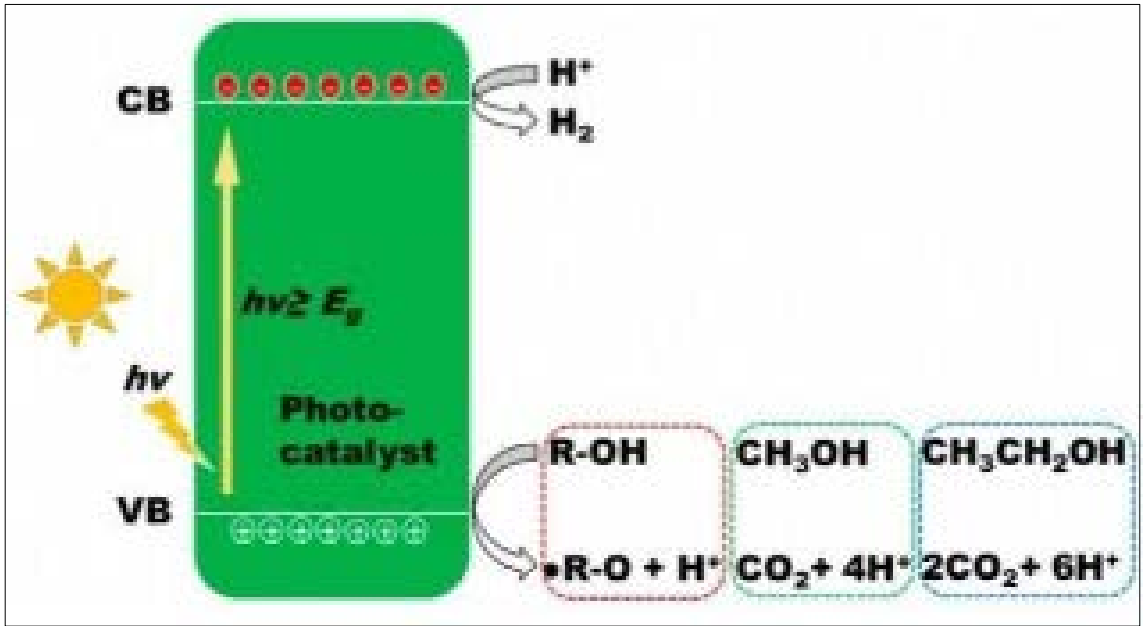


Fig 15: Photocatalytic Water splitting for hydrogen production

Photocatalytic Reforming of Methanol using TIO_2 as the Catalyst

Methanol is thr most widely used compound in performing the photocatalytic Reforming. Unlike the photoelectrocatalytic degradation of water, the products of photo-electrocatalytic reforming of organic compounds were Hydrogen (H_2) and Carbon Dioxide (CO_2), instead of H_2 and O_2.

$CH_3OH + H_2O$ hv> $CO_2 + 3H_2$

Reaction Pathways for Photocatalytic Reforming of Methanol using Au- TiO_2 involves the following processes.

- Photogeneration of charge carriers (electron holes).
- Adsorbed species on the surface of the photocatalyst react with separated charge carriers, adsorbed H_2O, and CH_3OH are oxidised by holes with the formation of OH- and various fragments including CH_3O-, CH_2O-, CHO-, HCOO-, and HCOOH; as formed HCOOH is further oxidised to CO_2.
- A large quantity of protons formed from the last steps and are reduced by the electrons either on the Conduction Band
- (CB) of TiO_2 or Au to form Hydrogen (H_2)

CH_3CH_2OH-> (hv) $CH_3CHO + H_2$
$CH_3COO\ 3H_2O$-> (hv) $2CO_2 + 5H_2$
$CH_3CHO + H_2O$-> (hv) $CH_3COOH + H_2$
$CH_3COOH + 2H_2O$-> (hv) $4CO_2 + 4H_2$

For the Photocatalytic Reforming of Methanol using Au/ TIO_2 semiconductor photocatalyst, the photo activity was very low for pure TiO_2. Owing to the multiphase TiO_2 materials demonstrate higher performance with respect to the corresponding monophasic systems in many photocatalytic processes. The crystal structure of TiO_2 plays an important role in the catalytic activity. There are three types of Crystalline structures. Anatase, Rutile and Brookite. The Brookite is unstable due to its weak interaction with the alence bonds. The anatase-structure lattice of TiO_2 contains more defects and vacancies, which results in more oxygen vacancies to capture electrons. Rutile TiO_2 is a very stable Crystalline structure and has mere defects which makes the electron holes recombine thus making the exhibited composite evolve higher photocatalytic activity of Methanol Reforming. In photocatalysis, a semiconductor is irradiated with photons with energy equal to or greater than the band gap energy, resulting in the excitation of electrons from the valence band (VB) to the conduction band (CB).

The photo-excited electron leaves a positively charged hole in the VB. These charge carriers are referred to as an electron–hole pairs. The charge carriers can recombine in the semiconductor bulk dissipating energy as heat or light or they can migrate to the surface of the semiconductor. At the surface, they can undergo charge transfer processes driving redox reactions with chemical species which are adsorbed at the surface of the photocatalyst.

Photocatalysis has been widely studied for the degradation of organic pollutants. The organic pollutants can either undergo direct oxidation by holes, indirect oxidation by reactive oxygen species including hydroxyl radicals, or they may be transformed by a reductive route involving CB electrons. The most common electron acceptor in a photocatalytic oxidation reaction is molecular oxygen since it is abundant in the air and is reasonably soluble in aqueous solutions. The oxygen is reduced by the CB electrons to form the superoxide radical anion (O_2•.-). The ability of a semiconductor to perform the desired redox reactions depends on the band gap energy and the band edge potentials for the VB and the CB. For the reactions to be thermodynamically possible, the CB edge potential should be more negative than the desired reaction reduction potential and the VB edge potential should be more positive than the desired reaction oxidation potential. In the water splitting reaction, the CB should be more negative than the hydrogen evolution reaction (HER) potential (0 V vs NHE at pH 0), and the VB should be more positive than the oxygen evolution potential (+1.23 V vs NHE at pH 0).For the oxidation of wastewater pollutants, the CB needs to be more positive than the oxidation potential of the pollutants. These potentials are more negative than the potential for water oxidation, requiring less energy for the overall reaction.

The ideal semiconductor material for photocatalytic hydrogen production from wastewater compounds would have the following general requirements: suitable band edges position,

good light absorption, efficient charge transport, chemical and photochemical stability, low over potentials for the desired reduction and oxidation reactions, low cost and abundant. It is important to consider that almost half of the incident solar Energy on the earth's surface is in the visible region (400 nm < λ < 800 nm), and therefore, for solar applications the photocatalyst should be able to utilise both the UV and visible photons.

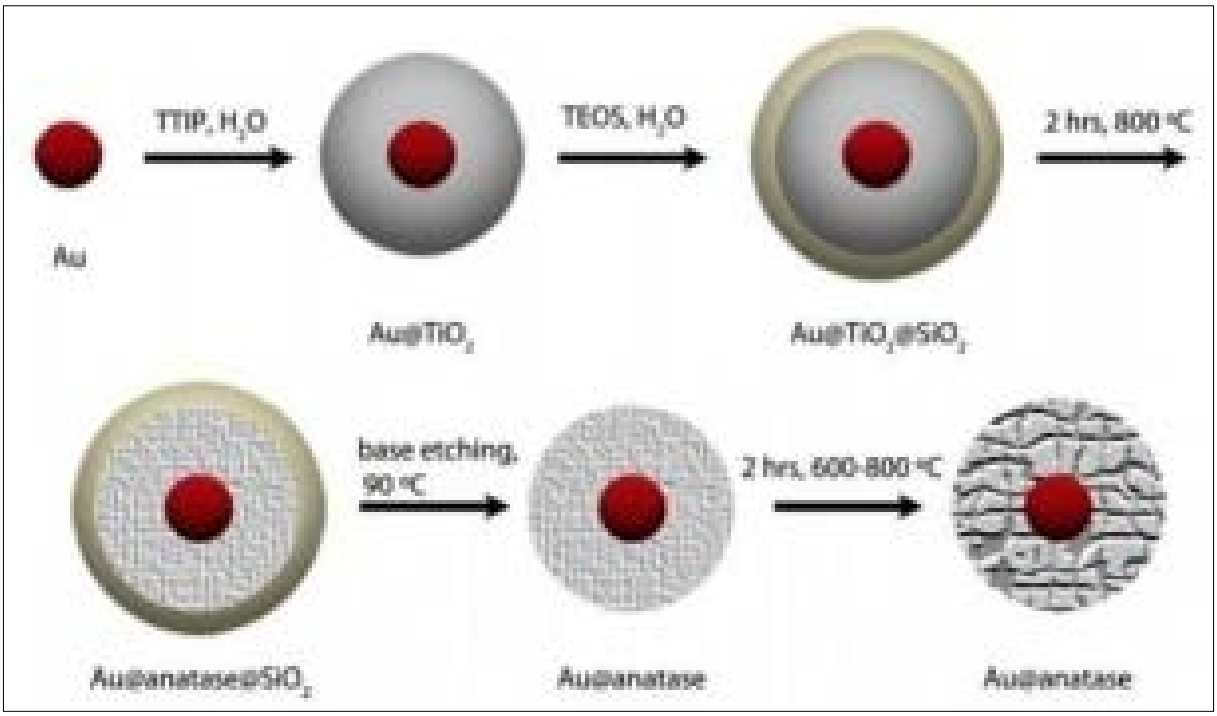


Fig 16: Au- TiO_2 Over-Shell Nanocomposite Formation

Use of Modified Nano composite TiO_2 for Photo catalytic Hydrogen Production

TiO_2 nanostructures such as nanorods nanosheets, mesoporous spheres and hollow spheres have been demonstrated to be excellent candidates for photocatalysis due to their chemical inertness, photostability, inexpensive material consumption, and simple technological process. Specifically, TiO_2 mesoporous nanospheres (MS) with large specific surface areas and strong light scattering as a catalyst have been synthesised, which possess fast response time, low dark current, and high sensitivity. Thus, the general photocatalytic activity of TiO 2 is very limited, especially under visible light irradiation. This is due to its wide bandgap (3.2 eV) (TiO_2) presents excellent physicochemical properties, has crystalline phases with gap energies between 3.2 eV and 3.05 eV and are n-type conductors, leading to a small UV light range absorption, resulting in low solar energy utilisation efficiency. As one of the photocatalysts, TiO_2 has been widely applied in the photocatalytic degradation of organic pollutants, photocatalytic reduction of carbon dioxide, CO_2. Meanwhile, it was applied in renewable hydrocarbon solar fuels, sensors, battery electrodes and supercapacitors. Photocatalytic water-splitting technology by using nano-sized TiO_2 can produce low cost and environment- friendly hydrogen using renewable resource such as solar energy, which can fulfil the future requirements of energy. Nano-sized TiO_2 is highly efficient as a semiconductor photocatalyst possessing high surface area. The significant drawbacks of utilising TiO_2 as photocatalysts are reduced absorption capacity of visible radiation and fast recombination of photoexcited electron/hole (e−/h+) pair. Its activity is restricted to UV light, which is only ~3–5% of the solar spectrum. This present review elucidates various aspects and the recent researches related to TiO_2 nano photocatalysis for the effective solar hydrogen generation via photocatalytic water splitting technology.

It has been previously characterised, that Pt/ TiO_2 nano-composites, exhibited photocatalytic activity in Reforming. The effect of crystals on photocatalytic hydrogen production. It was found that compared with Pt/ P25, the finely adjusted anatase- rutile Pt/ TiO_2 photocatalysts improved the overall efficiency of the photocatalytic activity 3 to 5 times, and greatly reduced the CO concentration in the hydrogen production, which can meet the fuel application requirements for the battery technology, since this result can be attributed to the adjustment of the semiconductor Crystalline form in favour of light- induced charge separation, as well as the adjustment of the acidity and basicity of the interface surface.

Also, Later, some other ligand free modified nanocomposites were investigated. Pt, Rh, Cu, Ni, Ir and Au nanoparticles modified by TiO_2 were materialised for photo-electro catalytic Reforming of glucose ($C_6H_{12}O_6$) for hydrogen production. It was found that the supported metals exhibited the property of trapping electrons at the Schottky Barrier of metal in contact with the TiO_2 surface, which greatly improved the hydrogen evolution rate and also reduced the CO selectivity concentration. The specific impact depends on the type of metal, the generation rate of H_2 on these metal modified TiO_2 followed the Order Ir< Ru< Au< Ni≈ Cu≈Pt< Rh. It can be found that Pt-based catalysts are the best fits for modification with TiO_2 and Au could be applied as the next alternative Nanocatalyst for Hydrogen production.

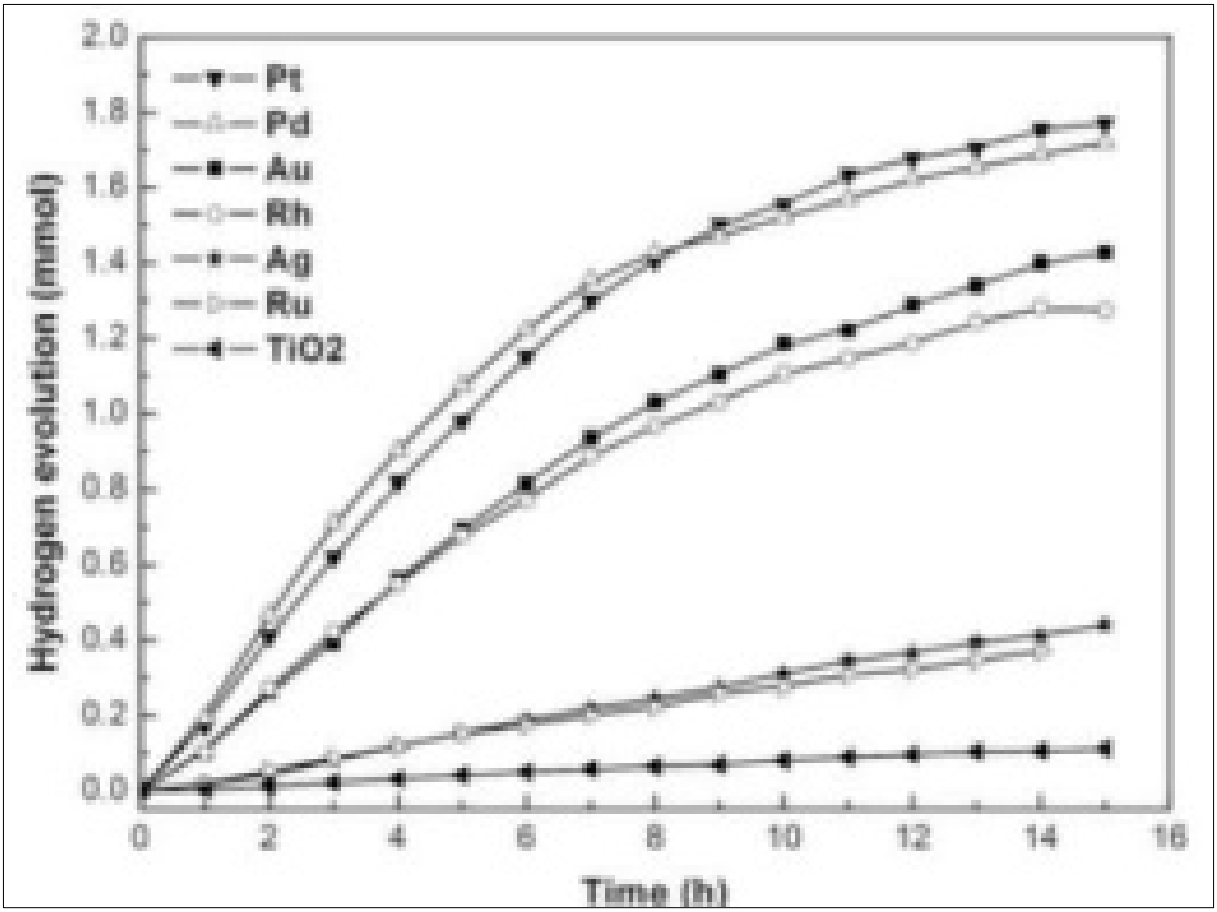


Fig 17: Effects of Noble metals- loaded TiO_2 in the hydrogen evolution

TiO_2 Nanostructures and Properties

TiO_2 probably plays the most important role in the photoelectrocatalytic degradation of water due to its excellent physicochemical properties. In 1972, demonstration of photocatalytic water splitting of water on a TiO_2 electrode was demonstrated by two Japanese scientists, Fujishima and Honda. However the quality of band gap of TiO_2 corresponds to the Ultraviolet (UV) light region, which shows inactive behaviour under visible light irradiation. At present, TiO_2 has become activated in the visible range of light spectrum irradiation region by metal and non-metal doping and also the fabrication of nanocomposites. TiO_2 has been widely obtained in many morphological studies such as ultrathin nanosheets, nanotubes, and hollow nanospheres due to its characteristics of larger surface area and more durably exposed surface active sites. Nano-TiO_2 applications can also be efficiently used for environmental photocatalytic degradation for hydrogen production, dye degradation, CO_2 absorption and Nitrogen fixation. It also promotes the ligands free semiconductor photocatalysis widely, used in the field of environment and energy sources. The size of the Nano TiO_2 particles is smaller than 100nm I at least one dimension photocatalyst.

For TiO_2 as the particle size decreases, it's photocatalytic activity will increase to a certain extent showing a specific size effect. There are possible size effects of nano TiO_2 photocatalytic materials.

Quantum Size Effect - Since TiO_2 is an n type semiconductor, when it's particle size is less than 50.5 mm, it will have different properties from the single crystal semiconductors which is called the " quantum size effect". When the particle size decreases to a certain value. The electron energy level widens to a larger gap near the Fermi level from a quasi continuous phase to a discrete energy level. At this time, the potential of the Conduction Band decreases to more negative energy and the potential of the valence Band becomes more positively charged thereby increasing the specific energy value of the Photogenerated electron holes enhancing the redox capability of the semiconductor photocatalyst nanocomposite and improving its photovoltaic activity.

Surface Area Effect- As the particle size decreases to nanometers, the specific surface area of the photocatalyst will greatly increase as well ad the number of surface ligands/ atoms, so that the light absorption efficiency will be improved and the surface photocurrent density and photo electron carrier concentration will increase accordingly so that the surface redox reaction efficiency can be improved. Also, with the decrease in particle size, the specific surface area increases and the bondinv state as well as electronic state of the semiconductor surface becomes different from the inside. The unsaturated coordination of the surface atoms leads to an increase in surface active sites. Therefore, as compared with powders of large particle sizes, their number of surface active sites are higher, so the adsorption capacity of the substrate is enhanced, at a higher potential and the reaction activity is increased. In addition, the number of hydroxyl groups on the surface of the catalyst directly affects the catalytic activity during the photocatalytic reaction. When TiO_2 powder is immersed in the aqueous solution, the surface undergoes a hydroxylation process. Therefore, as the size decreases, the specific surface area increases, and the number of surface hydroxyl groups also increases, thereby improving the reaction efficiency.

Carrier Diffusion Effect- The grain size nanoparticles also has a great influence on the environmental recombination rate of the Photogenerated carrier electrons. The smaller the particle,

the shorter the time for the Photogenerated electrons for Diffusion from the crystal to the surface and the lower the probability of electron holes recombination in the particles improves the photoelectrocatalytic degradation efficiency of the overall process. Also by doping metal and non metal ions, introducing vacancy and fabrication of nanocomposites with other semiconductors, the band gap of TiO_2 is adjusted to make it have better and efficient photocatalytic activity for hydrogen production.

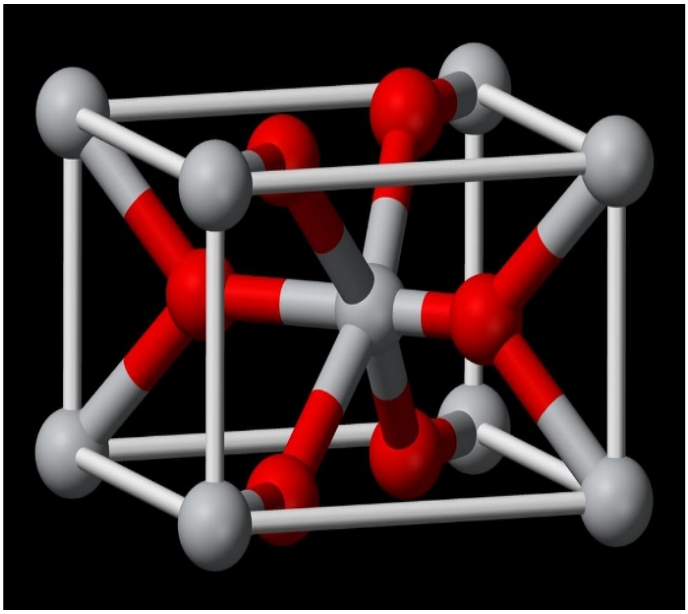


Fig 18: Nanostructure of TiO_2

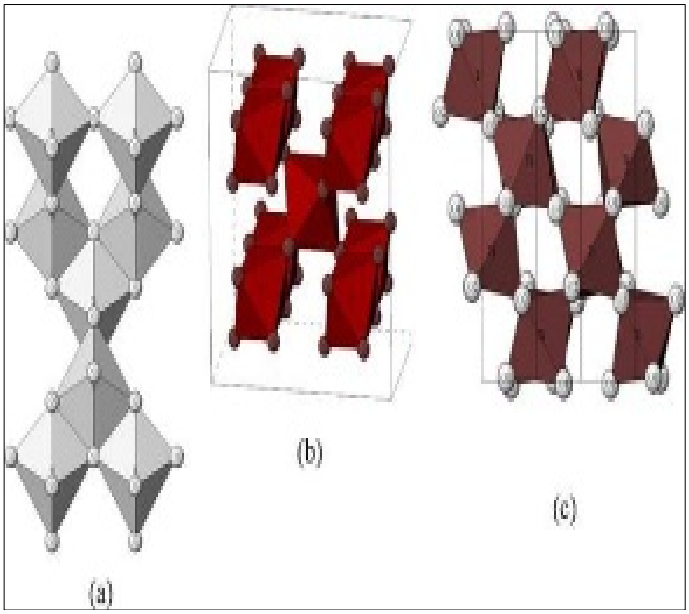


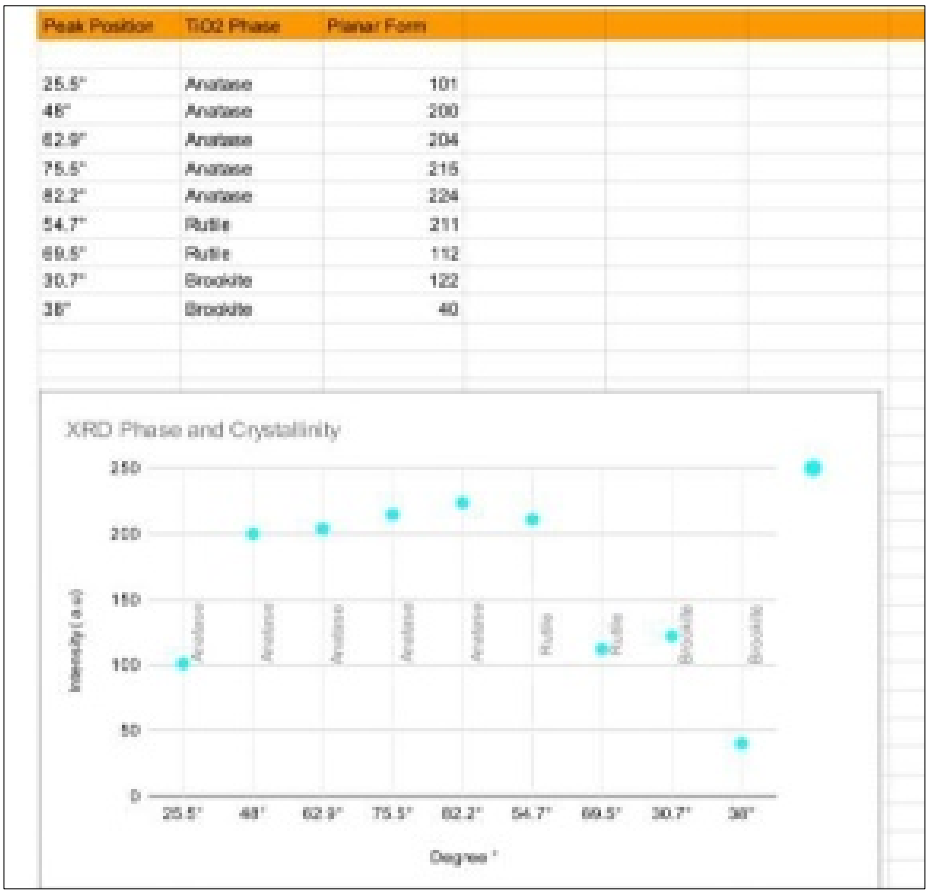
Fig 19: Crystalline structures of Titanium dioxide (TIO_2)-Anatase, Rutile and Brookite

Naturally, TiO_2 usually has three different Crystalline phases: Anatase, Rutile and Brookite. Additionally, there are also several metastable crystal nanostructures of TiO_2 such as TiO_2 (H) and TiO_2 II. These metastable crystal structures can be obtained by artificial synthesis. Among the three phases, Rutile is the most abundant and stable Crystalline form of TiO_2. When the particle size decreases to the nanometric level, Rutile is still the most stable TiO_2 nanomaterial. Anatase and Brookite can be transformed into rutile at high temperatures. The synthesis of Anatase TiO_2 nanomaterials usually requires solution synthesis or Los temperature chemical vapour deposition. But the synthesis of rutile TiO_2 nanomaterials requires high temperature deposition or heating reaction. Rutile TiO_2 has a tetragonal structure and the crystal facets have the lowest energy. Thus it is thermodynamically stable and morphologically truncated octahedron. Anatase has a tetragonal structure and its c axis is longer than the a axis.

Example of the anatase-structure: Tetraethoxysilane. Anatase TiO_2 also has a lower energy crystal planer form which is the same as rutile, thus it can show as a truncated octahedron. The Brookite belongs to an orthorhombic structure, and its structural unit is relatively larger which is composed of eight TiO_2 units. Anatase is an indirect band gap semiconductor and rutile and Brookite both belong to the direct band gap semiconductor. Thus this leads to the longevity of lifetime of Photogenerated electrons and holes for Anatase than those for Rutile and Brookite. The valence bands of TiO_2 in Anatase, Rutile and Brookite are mainly composed of second order O 2p and mixed with a few Ti 3d 3rd order. Above the Fermi level, the Conduction Band is composed of Ti 3d mixed with a small amount of O 2p and Ti 3p. The smaller the effective mass of the Photogenerated electron holes, the easier it is for their migration thereby improving the efficiency of photo-electrocatalytic activity. Among the three phases, Anatase has a smaller effective mass and a longer lifetime of Photogenerated electron holes and a higher photocatalytic activity.

Zero dimensional TiO nanomaterials has an isotropic structure and can expose all crystal planes Even with higher energy levels which is highly Conductive to photocatalytic reactions. If the surface of the plane can be properly modified, the recombination efficiency of the electron hole pairs can be greatly reduced which will help to develop the photocatalytic performance of zero dimensional TiO_2 nanomaterials. This improved method could be also used in semiconductor carbon dots, CdS, CdSe and Graphene-based Quantum dots. One dimensional structure of TiO_2 such as nanorods, nanowires and nanotubes possess very fast charge transfer rate in unidirectional way and the electron hole pair has a relatively low recombination efficiency, making it effective for photo-electrocatalytic activity. Two dimensional TiO_2 nanosheets are very thin with large specific surface area and effective absorption area having a high charge carrier and fast charge transfer thus having a higher photocatalytic activity rate.

XRD Phase and Crystallinity



Peak Position	TiO2 Phase	Planar Form
25.5°	Anatase	101
48°	Anatase	200
62.9°	Anatase	204
75.5°	Anatase	215
82.2°	Anatase	224
54.7°	Rutile	211
69.5°	Rutile	112
30.7°	Brookite	122
38°	Brookite	40

Fig 20: No iron or Iron compound peaks (Fe) or Ce were found which can be attributed to much lower quantum of Fe used in the synthesis. The trends also confirm that Fe/ Ce ions are properly incorrect and modified by TiO_2 lattice.

Metal Doping with TiO_2

Doping deals with the replacement of an anion or cation within the surface of a substrate with some other elements with similar charge and radius. The doping technique affects the band structures and decreases the band gap by introducing a new forbidden level in the band.

Recombination can occur on a surface as a whole, and the introduction of impurities or crystal defects can affect recombination. It has been reported that doping ions heterojunction coupling and nanometer crystals can promote electron-hole pair separation and reduce recombination, thus increasing photocatalytic activity. The absorption of visible light by wide-band gap semiconductor was originally realized by doping metal elements. According to the semiconductor band theory, due to the difference in the valence state between doped metal elements and metal elements in the semiconductor, the doped metal elements can generate donor or acceptor levels in the band gap of the semiconductor. The donor (or acceptor) energy level has two states, deep or shallow, due to the strength of the energy level binding to the electron. Metal doping can indeed reduce the impurity levels into the wideband gap semiconductor band, and these impurity levels can also induce the absorption of visible light, thereby improving the photocatalytic efficiency under visible light.

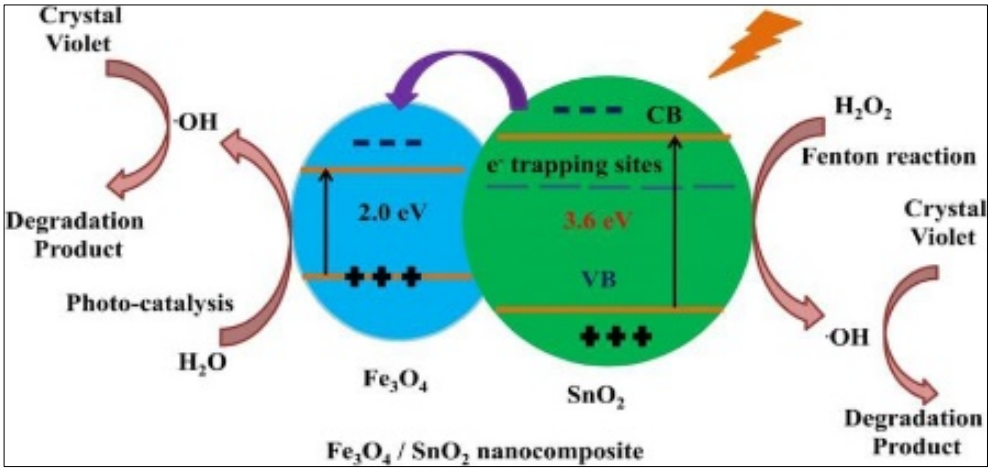


Fig 21: Schematic Illustration of photocatalytic water splitting

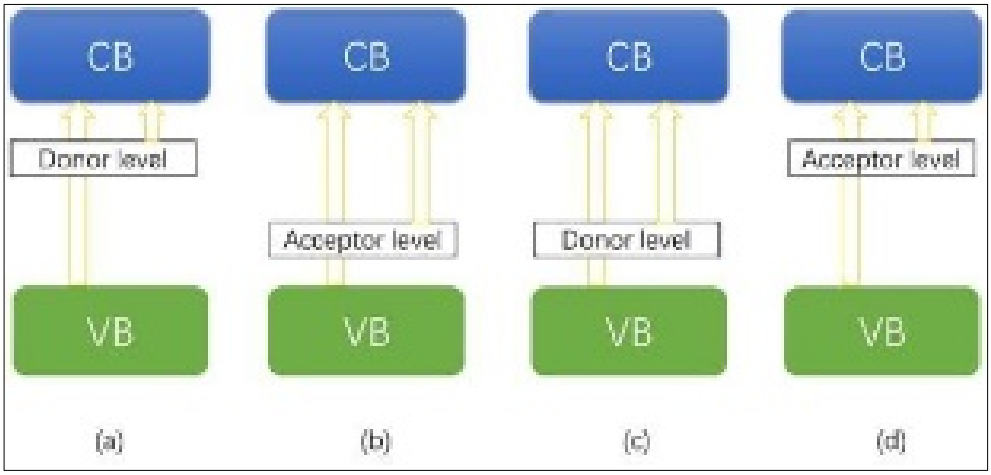


Fig 22: Effects of metal doping on band structure of semiconductors: (a) shallow donor level, (b) shallow acceptor level, (c) deep donor level, and (d) deep acceptor level formed by metal doping

The shallow donor level exists below the semiconductor conduction band and the shallow acceptor level exists above the semiconductor valence band while the deep donor level is close to the valence band in the semiconductor band and the deep acceptor level is close to the conduction band in the semiconductor band Electrons will jump between the donor level (or valence band) and the conduction band (or acceptor level), where the transition from the shallow donor level to the conduction band (or from the valence band to the shallow acceptor level) is a shallow transition, and the transition from the deep donor level to the conduction band (or from the valence band to the deep acceptor level) is a deep transition. Since the energy barrier to be crossed for shallow or deep transitions is smaller than the intrinsic band gap of the semiconductor, visible light can excite shallow transitions and, in most cases, deep transitions.

ElementalDoping withDoubleElement-Au/TiO_2

- **Catalyst:** Au
- **Morphology:** Nanosheets / Nano-composite
- **Synthesis:** Thermolysis, Sol- Gel, Solid - State Reaction
- **Source of irradiation:** Xe / Hg lamp of 300 W, Visible Light irradiation
- **H_2 generation rate:** 6755 µmol/h/g

TiO_2 Modification by Gold (Au) for photo-electrocatalytic hydrogen production

Au nanoparticles modified branched TiO_2

(Au/B-TiO_2) arrays were synthesised and the crystallization and morphology of the branches could be well controlled by simply altering the reaction rate and times. The B- TiO_2 array is composed of ultra thin nanorods within a minimum thickness of ~5 nm that showed enhanced quality photoelectrochemical performances compared to TiO_2 nanocomposite array due to decreased resistance and increased quantum charge carrier transfer efficiency. Thereafter the modification of Au nanoparticles, the photocurrent density was found to be ~ 3 mA/ cm^2at 1.24V vs WHSV (RHE) which was much higher than that of B- TiO_2 array and TiO_2 nanorods array due to enhanced light harvesting ability, enhanced carrier density that resulted from the synergistic effect of branched structure of TiO_2 and Surface Plasmon Resonance (SPR) effect of Au Nanoparticles. Structure and composition regulation of photoanode can increase the exposure of active sites, facilitate carriers transport property and thus, improve the PEC water splitting performance. The elemental Doping such as Ti-doped TiO_2 can decrease the bandwidth of TiO_2 and enhance visible- light responses. Hierarchical TiO_2, array has enlarged surface area, enlarged fast charge transfer and thus exhibited enhanced solar conversion efficiency. Synthesised hierarchical Rutile/Anatase TiO_2heterogeneousfilm and synthesis of heterostructured TiO_2 nanorod arrays. The hierarchical structure endows them with high light harvesting properties, higher charge carrier separation and higher photoelectrocatalytic degradation efficiency, enhanced performance when applied to Photo electrochemical (PEC) water splitting. In order to enhance the PEC performances of photoanode for solar water splitting, quantum dots sensitization on TiO_2 photoanode expanded visible light response range and also enhanced light harvesting ability and also increased the surface kinetics. Heterojunction photoanode such as Au/ B- TiO_2 can form an internal electrical field which is favourable for carrier transfer and separation that increases the PEC Performance of TiO_2 photoanode to a certain extent. Incorporation of AuNPs can simultaneously enhance the visible light irradiation and charge transfer due to local field enhancement, hot electron injection effects resulting from the Surface Plasmon Resonance (SPR) effect of Au Nanoparticles. The decoration of Au nanoparticles modified by branched TiO_2 nano-composite array structures also enhance the stability of photoanode due to its chemical stability and exhibited higher PEC performance due to its increased light absorption and decreased charge transfer resistance caused by plasmonic effects of Au nanoparticles consisting of higher electromagnetic radiation of wavelengths and nature of thr dielectric- metal- interface between the medium and the particles.

Gold ion-doped TiO_2 and gold-deposited TiO_2 is generally carried out by measuring the photo-activity, X-ray diffraction (XRD) spectra, photoluminescence (PL) spectra, and X-ray photo-electron spectra (XPS) of gold, oxygen and titanium. The anatase phase was the main component and that the electronic structure and interfacial electron transfer are significantly influenced by the presence of either gold ion or gold. The photo-activity is quantified in terms of methylene blue (MB) photo-degradation. As a result, the presence of gold ions in TiO_2 lattices or gold on TiO_2 surface greatly enhanced their photo-activity.

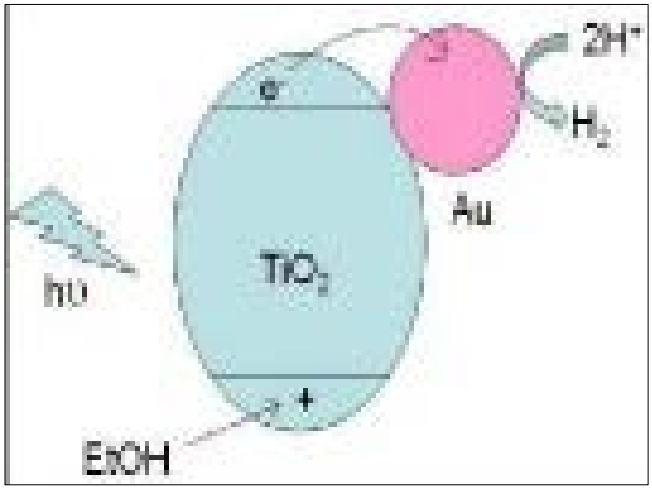


Fig 23: Photocatalytic water splitting on Au/ TiO_2 nano-composite structures. (Image Adapted from Reference)

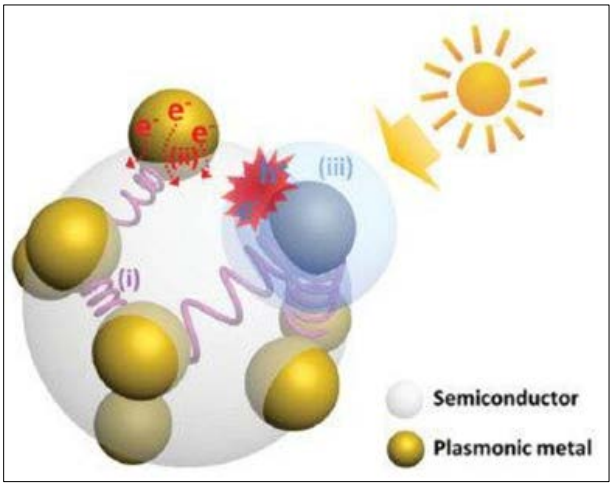


Fig 24: Schematic illustration of three generally accepted mechanisms for plasmonic enhancement: (i) light scattering, (ii) HEI, (iii) PIRET. (Image Adapted from Reference)

Fig 25: Schematic Illustration of proposed mechanism for the pjptocatalysis by Au/ TiO_2 nanorods under a UV and visible light irradiation. (Image Adapted from Reference)

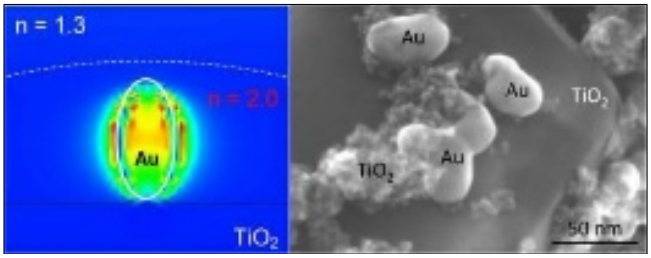


Fig 26: Four types of Au/TiO_2 samples have been studied, i.e., with the lowest and the highest photocatalytic activity under vis irradiation containing fine (ca. 9-nm and 21-nm crystallites) and large (ca. 47 and 60 nm) gold, AuNPs on fine anatase (ca. 11 and 25 nm) and large rutile. (Image Adapted from Reference)

Thus the results obtained showed that a Au/ B-TiO_2 nanocomposite of Au nanoparticles modified branched TiO_2 array was fabricated by the hydrothermal decomposition and followed by photo deposition method that exhibited higher photocatalytic activity and photocurrent density in a PEC cell. It is also expected that this photoanode possess potential applications in renewable energy storage mediums.

Advancement in Photocatalyst Development

The requirements for the photocatalyst to be viable on large scale Industrial usage involves high quantum yield and being inexpensive. In the case of electrochemical degradation, the electrode material should be stable enough during the process and also form highly reactive radicals and oxidant species resulting in high efficiency of pollutant treatment. The process used for the overall industrial wastewater treatment by Electrolysis abd the evolution of hydrogen is Photoelectrocatalytic degradation. Reactive radicals and highly oxidative stability of the species formed on both the cathode and anode can react with pollutants present in the wastewater. The photoelectrocatalytic degradation of pollutants present in wastewater takes advantage of heterogeneous photocatalysis with simultaneous electrocatalysis with the proper selection of semiconductors by using a biassed potential or heavy current at a photodiode that results in an increase in the pollutant removal efficiency and accelerates photoelectrochemical process.

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

Advantages of TiO_2

- Photocatalytic and hydrophilic properties of TiO_2 makes it close to ideal catalyst and when doped with AuNPs increases all its catalytic efficiency.
- High reactivity and reduced toxicity, chemical stability and lower cost.
- Also it has the ability to break down the organic pollutants and even achieve complete mineralization of the wastewater.
- TiO_2 is strongly recommended as a photodiode material for hydrogen production from wastewater compounds.
- TiO_2 has been regarded as an excellent candidate for photo anode in Photo electrochemical (PEC) water splitting cells due to its low cost, non toxicity, high stability and efficient Photoelectron catalysis performance.

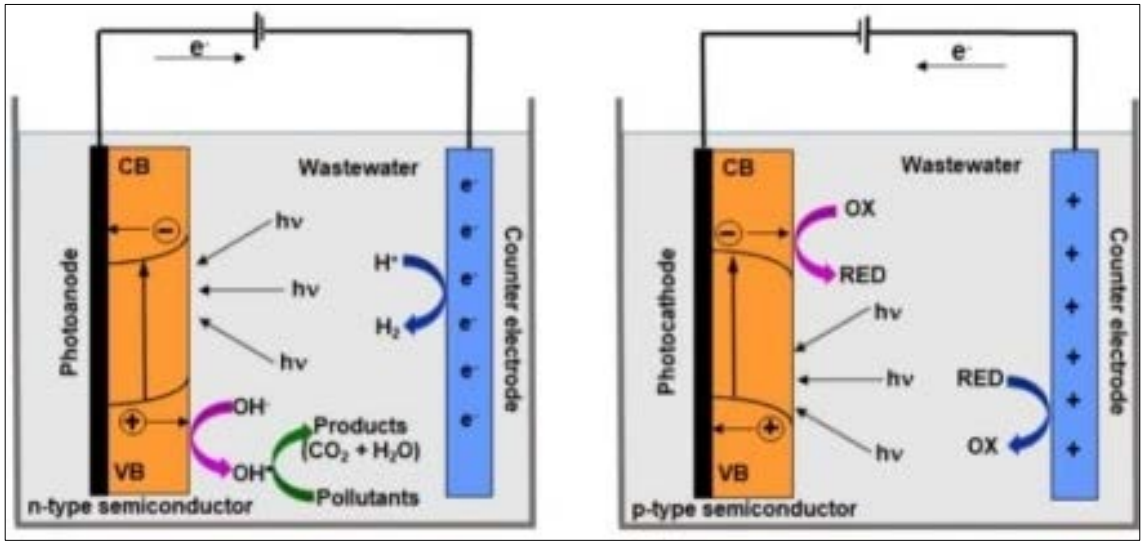


Fig 27: Overall Schematic mechanism of the photoelectrocatalytic degradation of pollutants in wastewater with the application of n- type and p-type semiconductor electrodes

DecolonizationofMethylOrangeSolutionbyfirstorderkineticsofPhotocatalytic Action on TiO_2

Methyl orange (MO) dimethylaminoazobenzene sulfonate is a common and typical azo anionic dye. This water-soluble organic synthetic dye has very high colorability and presents a bright orange colour when dissolved in water. Methyl Orange, also abbreviated as MO, is an azo dye used as a pH indicator in titration. This is because, at different pH values, it gives clear and distinct colour variance. The Eco friendly approach towards the photoelectrocatalytic degradation of Methyl Orange in TiO_2 suspension was carried out using sources of irradiation of ecofriendly Mercury (Hg) vapour lamp with four different concentrations of very dilute aqueous Methyl Orange mixed with Hg vapour lamp at constant PH = 4. The photocatalytic processes were influenced by the concentrations of Methyl Orange dye solution. The % amount of degradation from orange to pale colour very high at PH-4& TiO_2 = 30mg/ 50ml with approximately 120 minutes (irradiation time) that is irreversible and colour degradation rate of the Methyl Orange followed the pseudo-binary phase first order kinetics. This technique is carried out by using Shimadzu UV Visible 1601 Spectrometry and the Photo reactor- cylindrical cell with optical windows with 160 watt vapour lamp at medium atmospheric pressure. The photocatalytic activity of the catalysts (TiO_2) was examined using the UV Visible spectrophotometer.

Ligand-free Semiconductor nano-composite of TiO_2 being a very good photocatalyst for the removal of impurities from wastewater and air due to its low cost and Chemical strength, detoxification property and high photo-electrocatalytic reactivity and incompletely soluble in nature. TiO_2 suspension with photo energy greater than the band energy gap if the semiconductor, conduction band (CB),electrons and Valence band (VB) holes are developed that act as powerful oxidising reagents which can simply attack any organic pollutants and adsorbed on, or placed close to the surface catalyst, thus leading to their entire degradation into slight inorganic substances.The Combination of the Anatase and Rutile Phase of TiO_2 acts as a major degradation and dye decomposition reagent for the purification and treatment of wastewater pollutants.

TiO_2 +hv = e-(cb) (TiO_2) + h+(vb)(TiO_2) OH-+ h+(vb) ->.OH O_2+ e-(cb) ->.O_2- 2-+ H+ ->.HO_2 2.HO_2 -> O_2+ H_2O_2 H_2O_2+.I2- -> OH- +O_2

The Decolonization Formula for calculation (%): (C^o - C)/C^o ×100

- **Mechanism of the Photocatalysis**

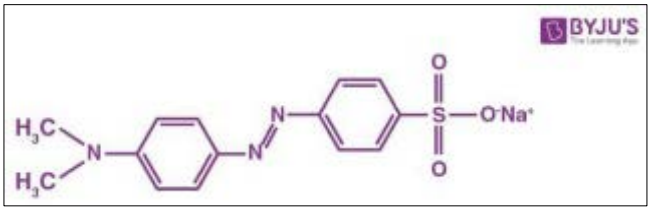
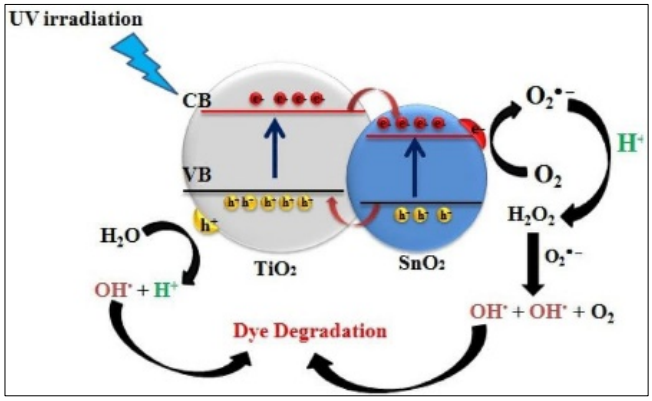


Fig 28: Structure of Methyl Orange (MO)

For The Photocatalytic degradation (TiO/ hv) for colour removal from the acid- base indicator solution and methyl Orange dyes, Mercury Hg lamps were used as irradiation sources for the colour removal. Utilisation of the visible daylight/ sunlight radiation provides energy supply as dependency of dye oxidation rate on the consequent parameters such as initial dye concentration, irradiation time, irradiation intensity and so on. The dye absorbs the visible range of light and not by semiconductor TiO_2 is mixed with Methyl Orange dye solution and magnetically stirred under the visible light irradiation in the range of Amax = 420 nm. The TiO_2 nanoparticles are separated from the solution and the dissimilarities in the absorbance progress of Methyl Orange dye is monitored spectrometrically. The rate constant for the kinetics degradation is assessed for.

Effect of dye concentration % of degradation is evaluated

At the end, Methyl Orange, the colour started fading speedily when the light radiation was passed Continuously for a longer time period of 120 minutes and when the adsorption-desorption equilibrium rate constant of the adsorbed dye onto TiO_2 surface is reached in the first order reaction kinetics at all dye concentration. The rate expression is given by: dCdt= k1t.



** Thus, Decolonization of Methyl Orange Solution occurs after 2 days of keeping the solution in visible light irradiation with each time of 30 minutes at 32 °C and 2 atm pressure

Fig 29: Schematic mechanism of the photocatalytic dye degradation of Methyl Orange by TiO_2

Semiconductor nanostructured photo catalysts for Wastewater treatment

Hydrogen has attained a lot of attention as the new source of sustainable energy. It can be used to directly generate power in fuel cells and to produce liquid fuels such as Methanol. Water Splitting is an ideal clean way of producing H_2 because it uses water and sunlight, two renewable resources.

Semiconductor Nano-composite materials demonstrate promising potential for the purification and treatment of wastewater due to their photo-electrocatalytic properties, which can be controlled on the basis of bandgap structures design. The Photogenerated electron holes in semiconductor materials provide efficient oxidation/ reduction performance for the degradation of pollutants, either directly or indirectly, through the generation of reactive species. Photocatalytic degradation has been utilised to treat contaminants ranging from chemical precursors, dyes and pharmaceutical organic / inorganic compound wastes. The advances in wider light absorption ranges and extended charge carrier through recombination or doping of heteroatoms or formation of heterojunctions. nanostructures and particularly nanostructured heterojunctions for photo-electrocatalytic hydrogen generation have been synthesised by four different systems. Perfluorinated compounds have also contributed to improving the efficiency of these nanomaterials in real water matrices in the presence of multi-component interfering ions.

CdSe nanowires (NWs) (II) Cdse/Cds core shell NWs (III) CdSe NWs decorated with Au or Pt NPs. (IV) CdSe/ Cds NWs decorated with Au or Pt nanoparticles. This is motivated by

1. CdSe NWs absorb visible light irradiation from the UV to the near infrared.
2. The NWs morphology simultaneously enables us to explore the role of nanoscale dimensionality in photocatalytic processes.
3. A CdS coating can enhance Photogenerated carrier and Metal nanoparticles are photocatalytically active and can also enhance charge separation efficiencies.

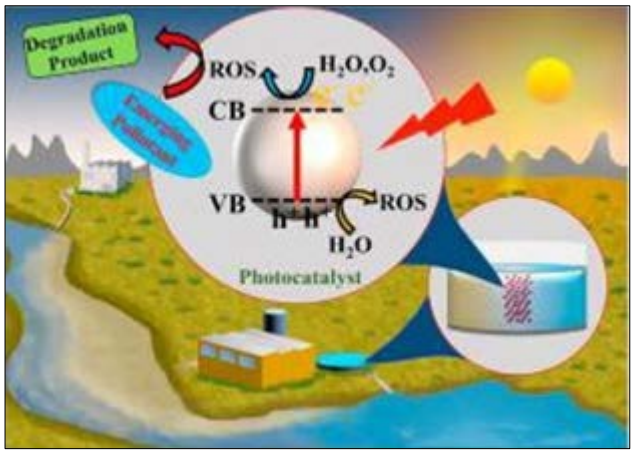


Fig 30: CdSe nanowires (NWs) (II) Cdse/Cds core shell NWs (III) CdSe NWs decorated with Au or Pt NPs. (IV) CdSe/ Cds NWs decorated with Au or Pt nanoparticles

Charge Separation and charge transfer across interfaces are the major aspects in the design of efficient photocatalysts for solar energy conversion. The Transient Differential Absorption (TDA) Spectroscopy has been used as a tool to show how semiconductor/ metal and semiconductor/ semiconductor heterojunctions affect the charge separation and amplification of hydrogen generation efficiencies of these hybrid photocatalysts. The use of this technique helps in hydrogen evolution and also reveal CDs and CdSe NWs and metal NP interact within metal NP decorated CdSe and CdSe/ Cds NWs during photocatalytic hydrogen production reactions. Electron transfer event's across both the heterojunctions with semiconductors are followed to identify where H_2 is evolved and determining a system's overall role. When TiO_2 is used HER- Hydrogen Evolution Reaction, usually metal co catalysts are added. The work function of the noble metals is typically larger than TIO_2, thus the Photogenerated electrons transfer from the semiconductor Conduction Band (CB), to the metal. Platinum (Pt) has been widely applied co catalysts for HER since it has the highest work function among the noble metals, creating a stronger electron trapping ability and has a low activation energy for proton reduction. Pt Cocatalyst ability strongly depends in its particular size and loading.Also Cds/CdSe NWs absorb visible light irradiation and is a good visible light photocatalyst. It helps in hydrogen production, Carbon Capture. CO_2 reduction to hydrocarbons or pollutants degradation. Cds is characterised by a narrow band gap of 2.4eV. Which enables the absorption of light until 520 nm. It exhibits a good photochemical properties and quantum efficiency thus to increase the photo oxidation stability and industrial application for Hydrogen Evolution under certain conditions. The photocatalytic performance can. Be evaluated using quantum efficiency. The quantum efficiency or yield is defined as the useful photo conversion events per absorbed photons at a determined wavelength

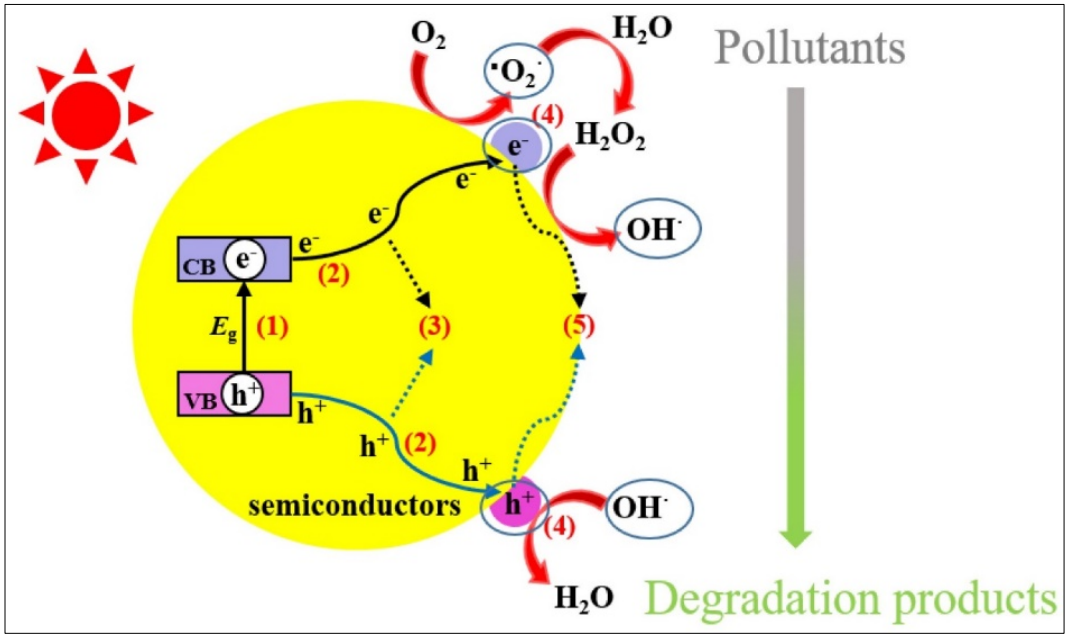


Fig 31: Semiconductor photocatalyst for detoxification of wastewater

Photo electrochemical cells

An approach to enhance improvement and efficiency of photocatalysis is thd use of the electrochemically assisted photocatalysts in a PEC- (Photoelectrochemical cells). The oxidation and reduction reactions are performed by the two different combined electrode materials that are connected through an external circuit which drives the oxidation by the holes in the photo anode, while the electrons travel from the photo anode through the external circuit to the photocathode, where the reduction reactions take place. This process is below represented schematically. When a PEC is utilised to produce hydrogen fuel from Solar energy, it is referred as a photosynthetic cell. Similarly when the PEC is employed to produce electricity from the photodegradation of substances, it can be defined as photo fuel cell. In the systems where wastewater compounds are being oxidised in a PEC to generate Hydrogen, depending on the Thermodynamics of reaction, the system can also produce electricity and therefore being a combination of both cells, Hydrogen is produced by a flow of current, could also be considered as a photo fuel cell. PECs can be used with different configurations, I.e- semiconductor nanostructured photoanode with metallic cathode, semiconductor photocathode with metallic anode or photoanode with photocathode (photodiode). These cells are driven by the potential difference between the Fermi levels of the two electrodes. For a typical n- type semiconductor photoanode, the Fermi Level is close to the Valence band (VB). The ability of a semiconductor to perform the desired redox reactions depends on the band gap energy and the band edge potentials for the VB and the CB. Thus with electrochemically assisted photocatalysis, an external voltage or electrical bias can be applied to drive the reactions with more positive CB potential for more H/ H+ production.

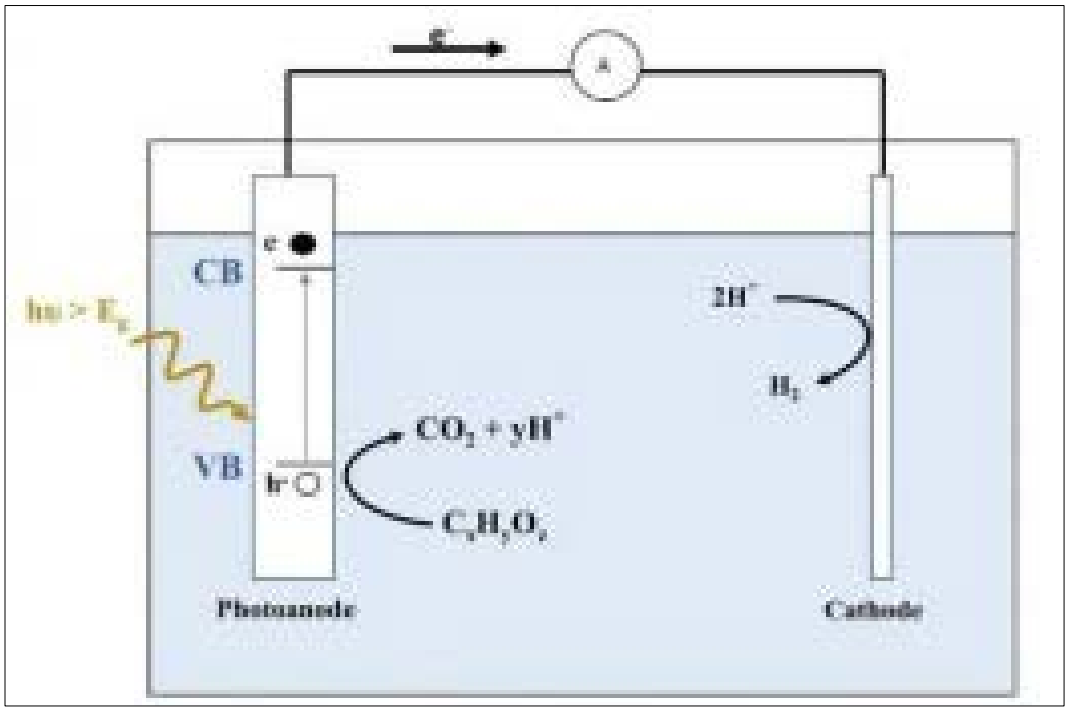


Fig 32: Schematic flowchart of PEC and photocathode and photoanode used in the photoelectrochemical Reaction

Synthesis of the Nanocatalysts

The Bottom up Lithography involves the joining a molecule by a molecule,atom by atom and clusters by cluster. In this method, single molecules are explored to form a complex structure of nanoscale dimensions.

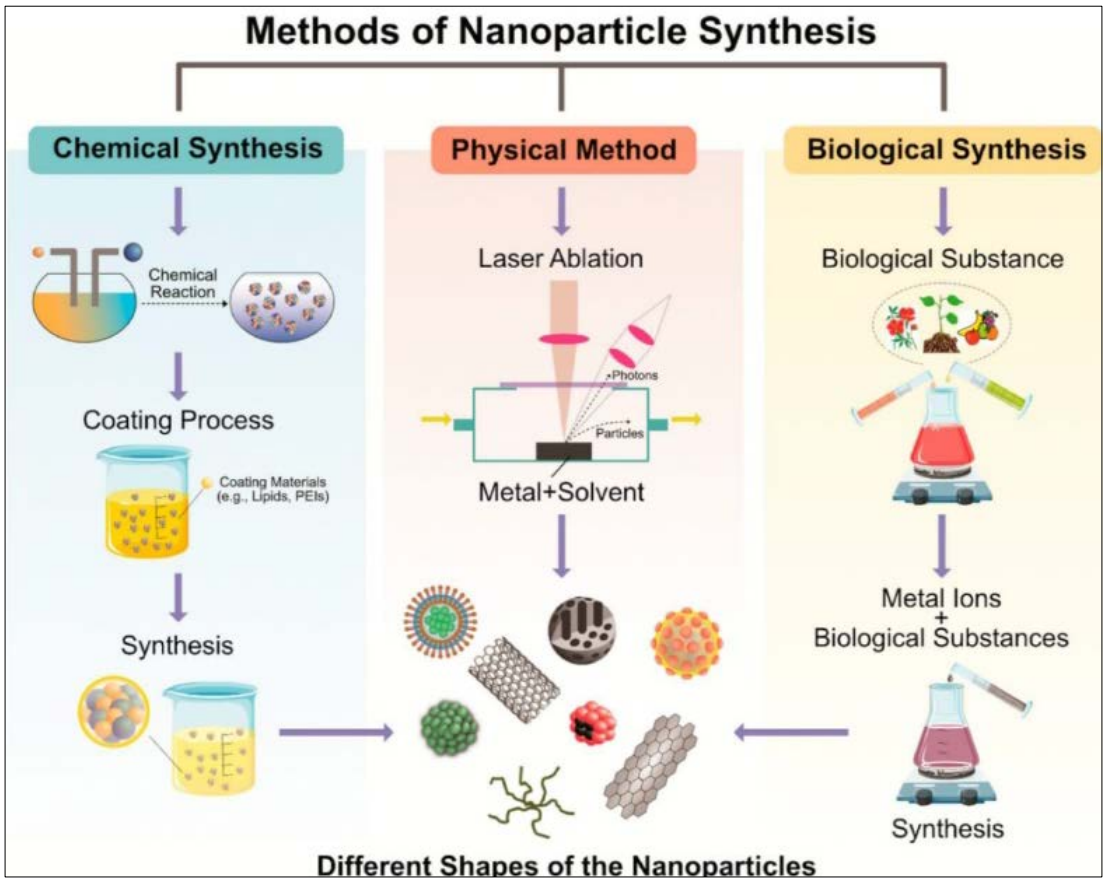


Fig 33: Nanoparticles Synthesis

Catalyst stability is investigated using the FTIR spectrum and XRD Analysis after recovering and regeneration of the catalysts. The initial broad peak observed at around 500 cm^{-1} which is attributed to high metal oxygen vibration that is seen in the catalyst after usage. It is also observed that peaks are almost in the same position for the Ce- TiO_2 (US) Catalyst before and after sonophotocatalytic activity.

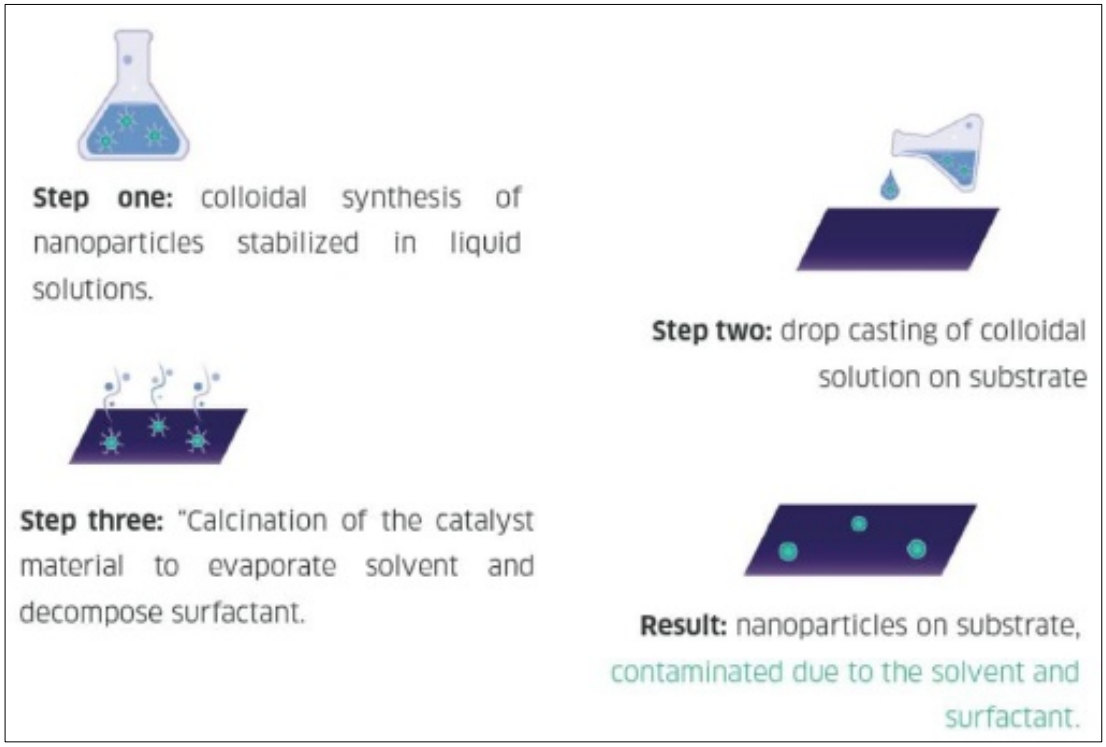


Fig 34: Method of Nanocatalysts Synthesis

- It can be concluded that, there is no change in the structure of the catalyst before and after application of sonophotocatalytic process.
- Ti content in the solution is 102.9 ppb and Ce content of the solution is found to be 46.2 ppb which are almost negligible from the leaching test by the CP- MS.
- The results can be attributed to the faster kinetics for US-assisted synthesis methods, which does not allow enough time for the particle growth reducing the overall particle size.
- In the case of Ce- TiO_2, it is evident that higher percentage of particles with larger surface diameter exists in conventionally synthesis catalysts higher percentage of particles with smaller diameter exists in sonochemically synthesis catalysts.

Samples	Specific surface area (m²/ g)	Pore Diameter (nm)	Total Pore Volume (cc/g)
Ce- TiO2 (C)	67.27	24.02	0.4039
Ce- TiO2 (US)	211.39	7.81	0.4133
Fe- TiO2 (C)	185.65	7.68	0.3566
Fe- TiO2 (US)	173.79	7.85	0.3411

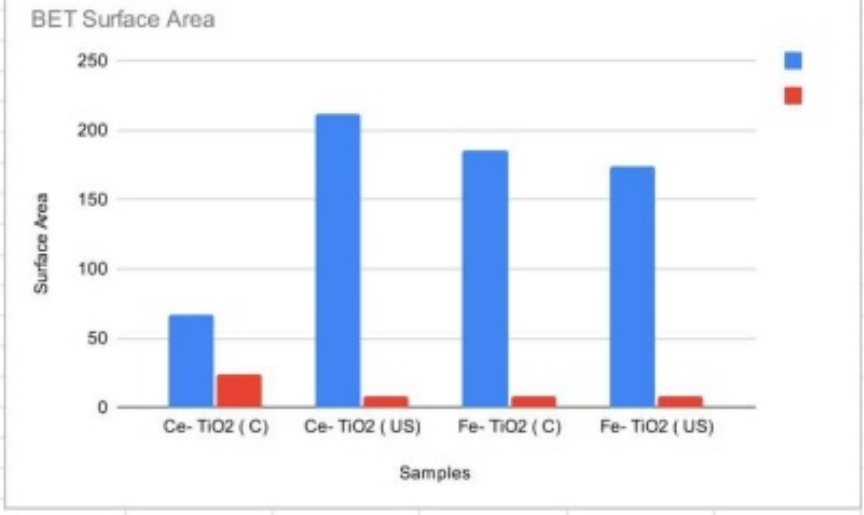


Fig 35: BET Surface Area Curve for Various TiO_2 doped Nanocatalysts

SynthesisandCharacterizationof TiO_2dopedAu

There are mainly two types of synthesis methods used for synthesising TiO_2 doped with AuNPs. Hydrothermal approach, sol-gel method, rapid breakdown anodization will show different shapes of TiO_2 and its photocatalytic properties.

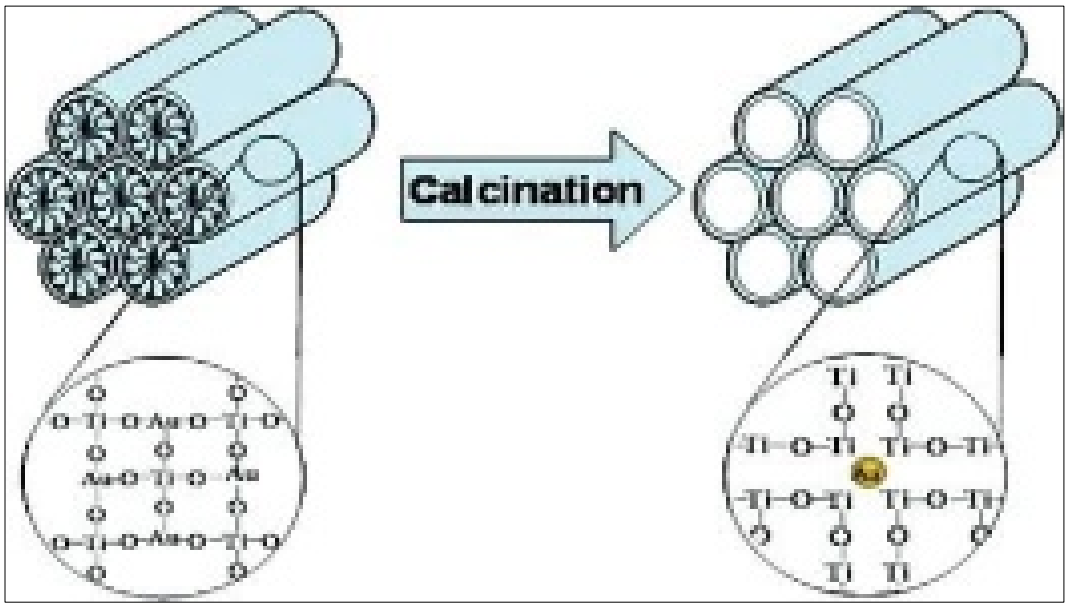


Fig 36: Au- TiO_2 Doping

Hydrothermal Synthesis of ultrathin mesoporous TiO_2 Nano sheets

Ultrathin mesoporous nanosheets with high Crystallinity have been obtained through a facile hydrothermal approach with the assistance of chlorine ions, which is not only beneficial for obtaining stable mesoporous TiO_2 samples with high Crystallinity, enlarging the surface area from 152.938 m^2/ g to 178.496 m^2/ g and pore volume from 0.162 cm^3/ g to 0.201 cm^3/ g. It can be demonstrated that the facile Cl ions assisted method could lead to obtaining stable Anatase TiO_2 nanoparticles with high Crystallinity while retaining or even enlarging surface area. Ti^{3+} atomic defects in the ultra thin mesoporous TiO_2 play a crucial role in suppressing the recombination of electron hole pairs and enhancing the photocatalytic activity in H_2 production rate. The photocatalytic activity of the mesoporous TiO_2 towards photocatalytic water splitting under simulated solar UV Visible light irradiation without filter.

Thermal Decomposition- In general, Metal Alkoxide is dissolved in the organic solvents to form homogeneous solution with the addition of chelating agents. Inorganic thin films are prepared by coating on the substrate, followed by drying, thermal decomposition and annealing approach. Gold ion-doped being a hardcore metal combined with nanoparticle oxides can readily be synthetically prepared by the Thermolysis or Thermal Decomposition method. The synthesis as well as chemical and physical characteristics of metals and semiconductor nanoparticles (NPs) and nanocomposites are presently of considerable interest due to their potential applications in materials science, including molecular electronics, Obtaining polymeric materials containing nanoparticles. The surface of nanoparticles are covered by stabiliser screening interactions between the metal and the polymer. Ot oz also difficult to obtain a uniform dispersion of NPs in the matrix. The decomposition of organometallic precursors directly in the polymer film should lead to a Cleaner metal surface (no strongly bound stabiliser layer between the metal and polymers) and good dispersion without using additional stabilisers. The preparation of Gold nanoparticles by thermal decomposition of an organometallic precursor dispersed in solid polymer films or as microcrystalline. The organometallic complex, u^3- oxo[tris (triphenylphosphine) gold] (+1) tetrafluoroborate (-1) ($Au(PPh_3)$)3] [BF4] was chosen as the Au atom precursor, because it has been reported to be a good source of Au for NP synthesis in the solution, well soluble in many organic solvents and sufficiently stable to handle in an ambient atmosphere [O($Au(PPh_3)$)3] [BF4], was synthesised according to the starting materials used to obtain nanocomposites with gold nanoparticles were polymer films with a dispersed organometallic complex. Poly (methyl methacrylate) (PMMA) (Tg= 115 °C) was used as the stabilizing matrix. The films were prepared by casting toluene (for PMMA) solutions and slowly evaporating the solvent. Initial solutions (4% of the polymer with respect to the solvent) contained the precursor (0.25- q5wt. % of the precursor with respect to the polymer). Two kinds of films were studied:- Standard free-standing films cast on glass plates(ca.20 um thick, which were used for UV-Vis and XRD measurements and thin films (below 200 nm) were prepared by placing a drop of the solution directly on a TEM copper support grid covered with a carbon layer that can act as a highly effective antibacterial agent. The decompositions of precursor crystals or thin layers obtained from solution, without the polymer, on TEM grids or on a solid support were also carried out. Samples for SEM were prepared by depositing a drop of the precursor solution or gold NPs in a suitable solvent on a freshly cleaved mica or Silica support covered with a 100 nm SiO_2 layer. Thermal decompositions of the gold precursor were performed in air at 130°C. The initially transparent film turns red during the reaction due to absorption by surface plasmons.

The below figures shows the TEM images of the gold NPs obtained by the thermal decomposition of [O ($Au(PPh_3)$)3] [BF4] in a thin PMMA film for various concentrations of 1- 2 wt. %, the obtained NPs are small (ca.5nm) and uniformly distributed. For higher concentrations, the average size increases and the size distribution is much broader that is probably caused by the coalescence of the small NPs rather than by their continuous growth. At high concentrations, NPs have some tendency to agglomerate in the film and their distribution is not so uniformly spread. The formation of gold nanoparticles gives rise to surface Plasmon absorption in the visible light range.

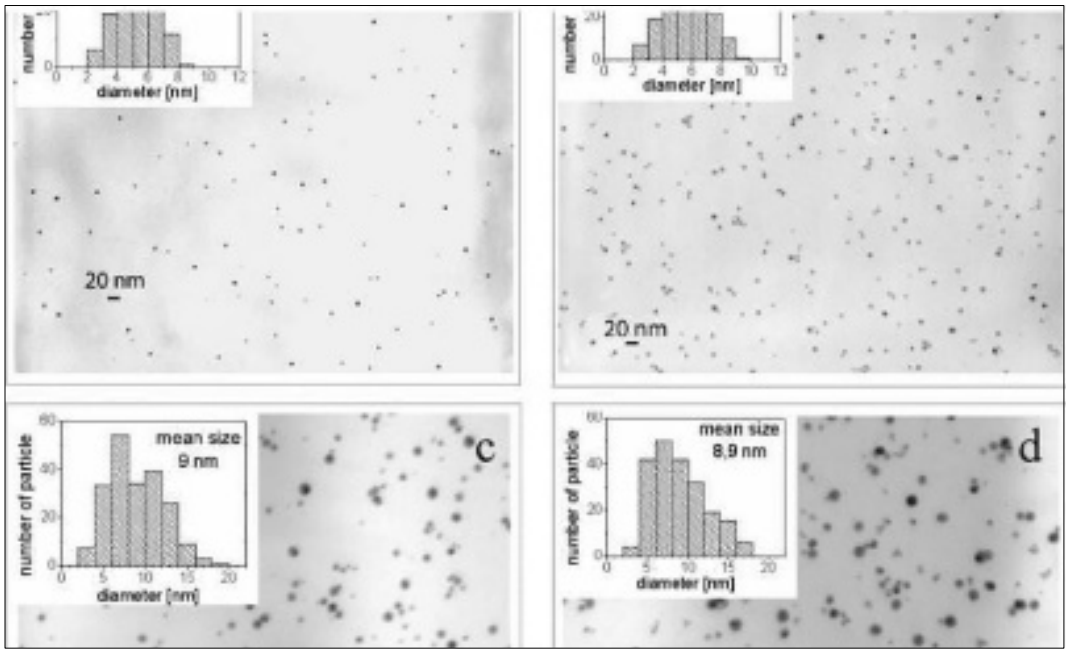


Fig 37: TEM images of AuNPs Synthesis (Adapted from Reference)

Sol- Gel Method for Synthesis of Gold (Au) Nanoparticles

The sol- gel process is a more wet chemical method also known as chemical solution decomposition, used for the synthesis of various nanostructures, especially metal oxide nanoparticles. In this method, the molecular precursor (usually metal alkoxide) is dissolved in water or alcohol and converted to gel by heating and stirring by hydrolysis/ alcoholysis. Metal alkoxide is dissolved in organic solvents to form homogeneous solutions with the addition of chelating agents. Inorganic thin films are prepared by coating over the substrate, followed by drying, thermal decomposition and annealing. Ultra - thin Titanium dioxide (TIO_2) nanorod films show good photocatalytic and electrochemical characteristics for the photocatalysts applications. The textural properties of TiO_2 such as thickness, surface roughness, grain size and particle size, pore size distribution and porosity of the semiconductor TiO_2 films influence greatly on the photocatalytic activity. The sol- gel process involves several steps in the following chronological order: - hydrolysis and polycondensation, gelation, ageing, drying, densification and crystallisation. High purity and the achievability of uniform nanostructures at low temperatures were the main benefits of sol- gel processing technology. By capping the particles with appropriate ligands, the dispersion can be stabilised in this liquid phase synthesis. Presence of ethanol leads to the high quality, clear and distinct uniformly synthesising particles with desirable spherical morphology and larger particles of surface upto 170 nm in constant temperatures. The sol- gel (SG) method has been the most widely applied because of the low cost of the required equipment, the mild reaction conditions and also because, usually TiO_2 is of high homogeneity and purity is obtained. Since the gel obtained from the hydrolysis process is wet or damp, it should be dried using appropriate methods depending on the desired properties and applications of the gel. After the drying stage, the produced gels are powdered and then calcined. The sol-gel Method is a cist effective method and due to the low reaction temperature, there is good control over the chemical composition of the semiconductors. The sol- gel Method can also be used in the process of making ceramics as a moulding material and also can be used as an intermediate between the thin films of metal oxides in various applications. This method also helps in formation of chromatographic homogeneous sol from the precursors and its conversion into a gel. The solvent in the gel is then removed from the gel structure and the remaining gel is dried making it significantly useful for surface coating, building insulation and in the industries. This process is known as “solvent removing method" and is able to achieve nanoparticles from it.

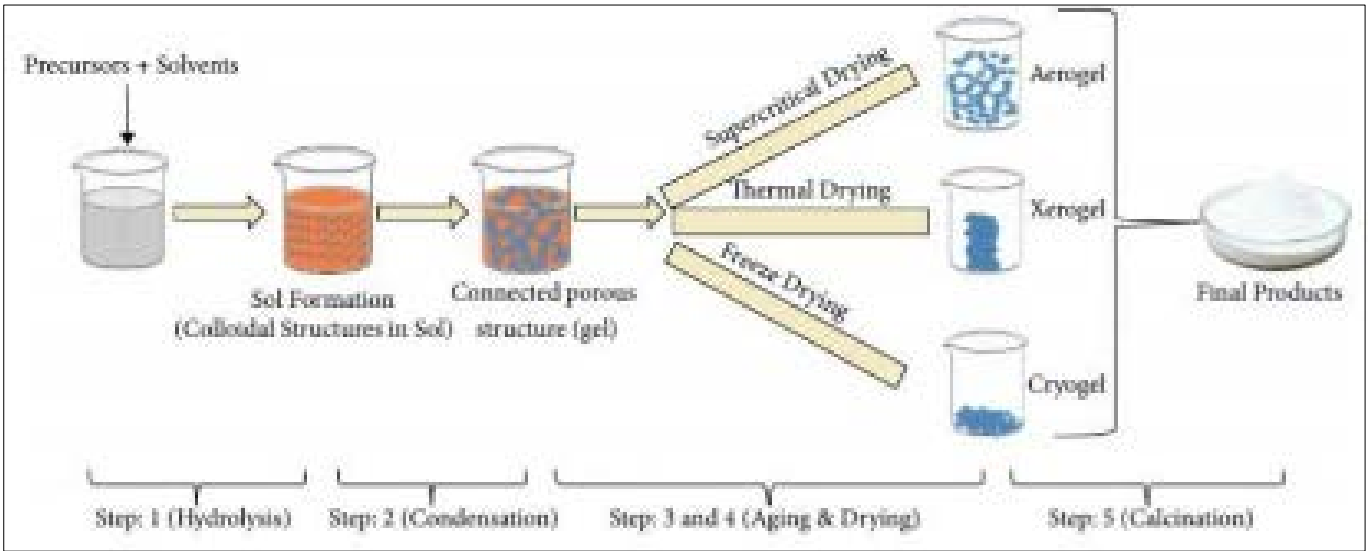


Fig 38: Schematic Illustration of the Sol- Gel Method

Rapid Breakdown Anodization Methods

The TiO powdered nanotubes are prepared by the rapid breakdown anodization sensitised with Pt-based catalysts, and mainly Pd and Ni nanoparticles (NPs) for the photocatalytic activity of water splitting for Photogeneration of Hydrogen. It was reported that the samples sensitised with the Pt Nps loadings were more active and superior to the Pd and Ni sensitised TiO_2 NTs powders. Noticeably, tge smaller the quantity of the NPs loaded over the TiO_2 NTs, it produces better Photogeneration of the Hydrogen molecules. The evolution of hydrogen is larger with the addition of metal NPs and moreover lower quantity deposits produced better results. It is also reported that the Pt NPs addition was better anong the pre mentioned Pd and Ni in terms of Hydrogen Generation over the other metals of the same group. The Pt/ TiO_2, NTs with 5% metal sensitization, generated hydrogen with a specific release rate of 242 umol $g^{-1}min^{-1}$. The degeneration and deactivation of the Pt catalysts thereby formation of coke and charcoal and also higher costing Pt I'd replaced with AuNPs (Gold Nanoparticles) as a better alternative. Gold being a solid hard bimetallic nanometal it produces better synthetic fibres after synthesis that help remove the impurities from the wastewater and thereby improves the capability of hydrogen production.

Experimental Data of TiO_2/ Audoped semiconductor photo catalyst Nano composite materials from XRD

SL No.	Sample	Weight Fraction B:A:R	XRD Peaks Relative Intensity IB: IA	Average Crystalline Size (D)
1	NRT- 1.0	51:30:19	01:11:50	15.39
2	NRT- 2.5	52:29:19	01:11:00	14.7
3	NRT- 4.0	52:28:20	01:07:50	12.35
4	MST- 5.5	53:27:20	01:08:40	11.67
5	MST- 7.0	53:25:15	01:07:40	10.65
6	NRT- 8.5	54:26:25	01:06:00	10.45

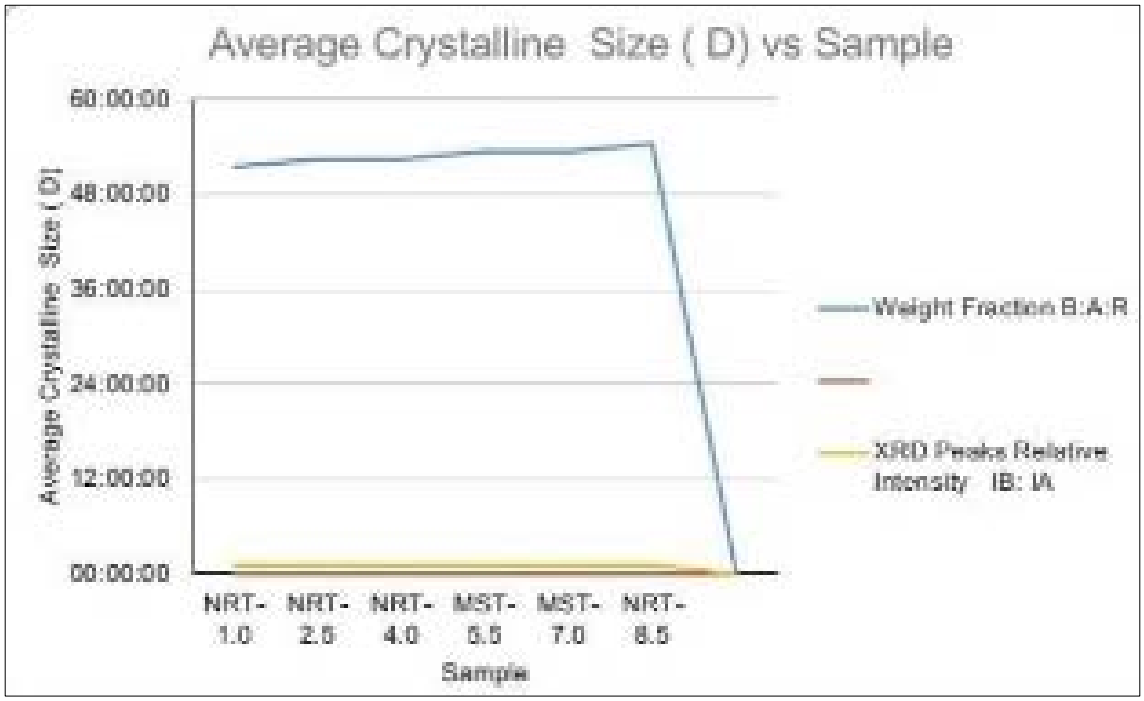


Fig 39: Average Crystalline Size of the TiO_2 nanoparticles Vs the Weight Fractions of the various samples tested [1]

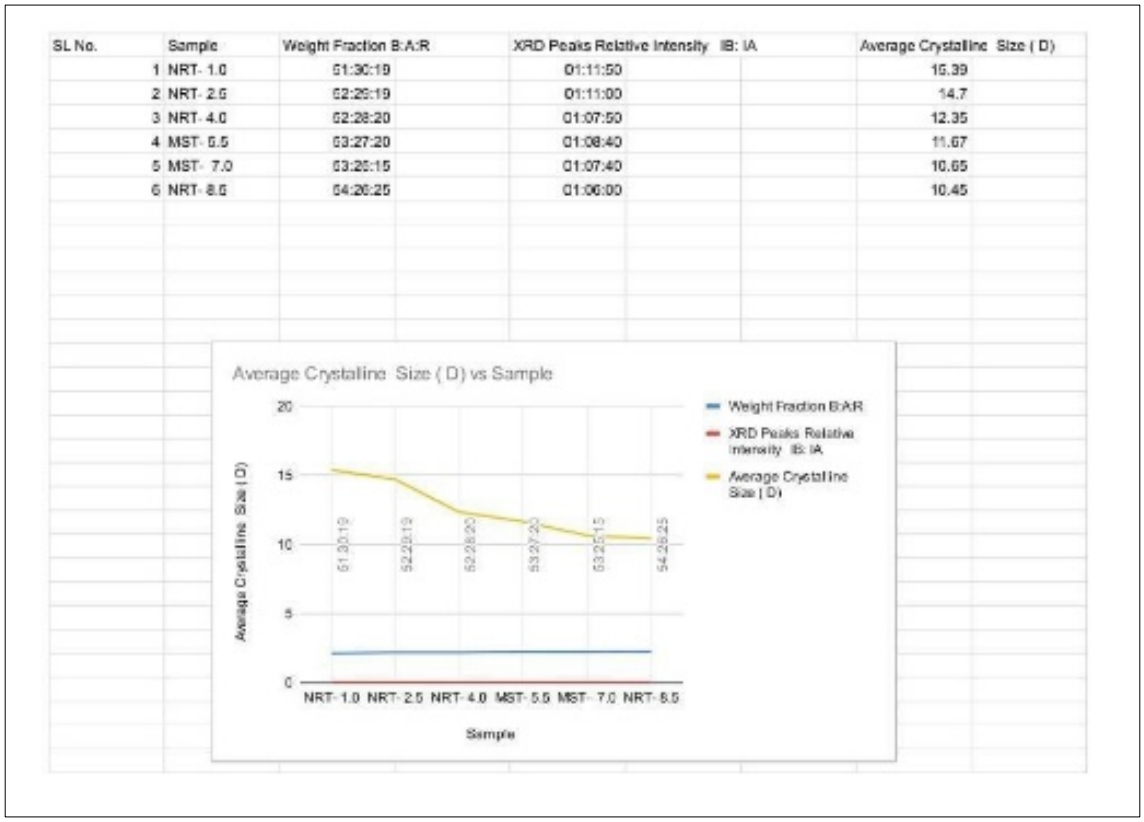
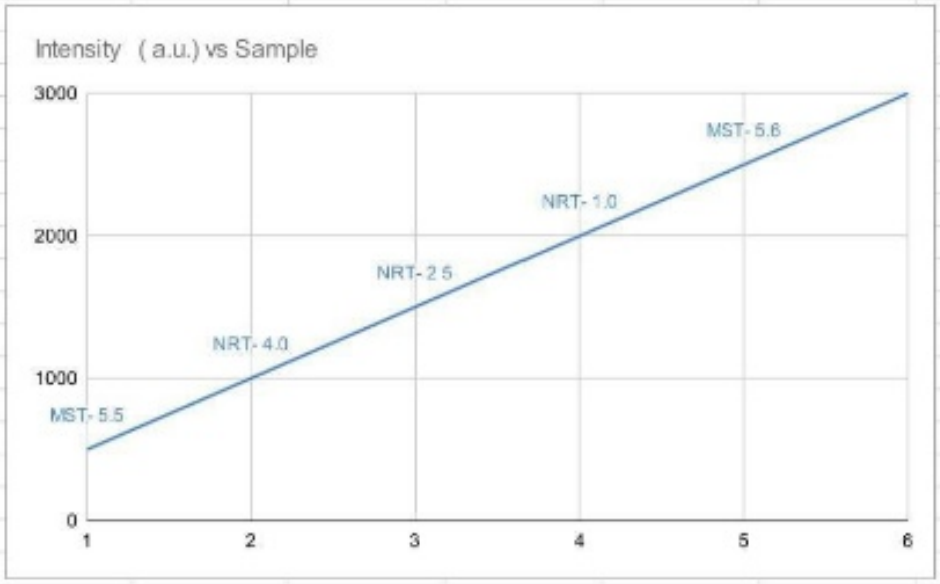


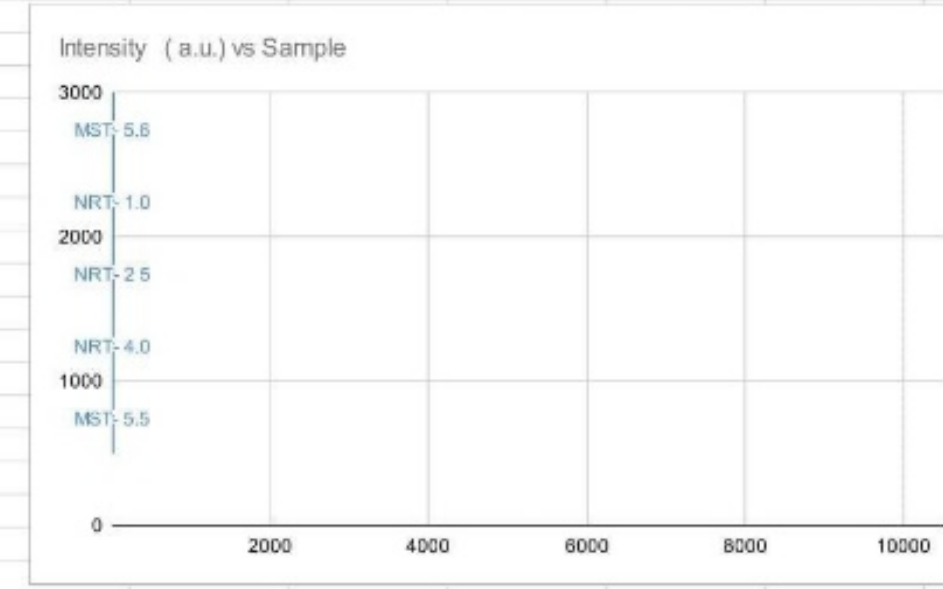
Fig 40: Weight fractions and average Crystalline size of the prepared TiO_2 nanoparticles (estimated from XRD Analysis) [2]

Sl No	Intensity (a.u.)	Sample	ICSD FILE NO.S
1	500	MST- 5.5	01- 086- 1156
2	1000	NRT- 4.0	01- 076- 1938
3	1500	NRT- 2 5	01- 076- 1934
4	2000	NRT- 1.0	01- 076- 1845
5	2500	MST- 5.6	01- 077- 1246
6	3000	NRT- 3.2	01- 078- 1358



a)

Sl No	Intensity (a.u.)	Sample	ICSD FILE NO.S
1	500	MST- 5.5	01- 086- 1156
2	1000	NRT- 4.0	01- 076- 1938
3	1500	NRT- 2 5	01- 076- 1934
4	2000	NRT- 1.0	01- 076- 1845
5	2500	MST- 5.6	01- 077- 1246
6	3000	NRT- 3.2	01- 078- 1358
10521			



b)

Fig 41: Material Characterization- XRD patterns of the synthesised mesoporous TiO_2 samples [1, 2]

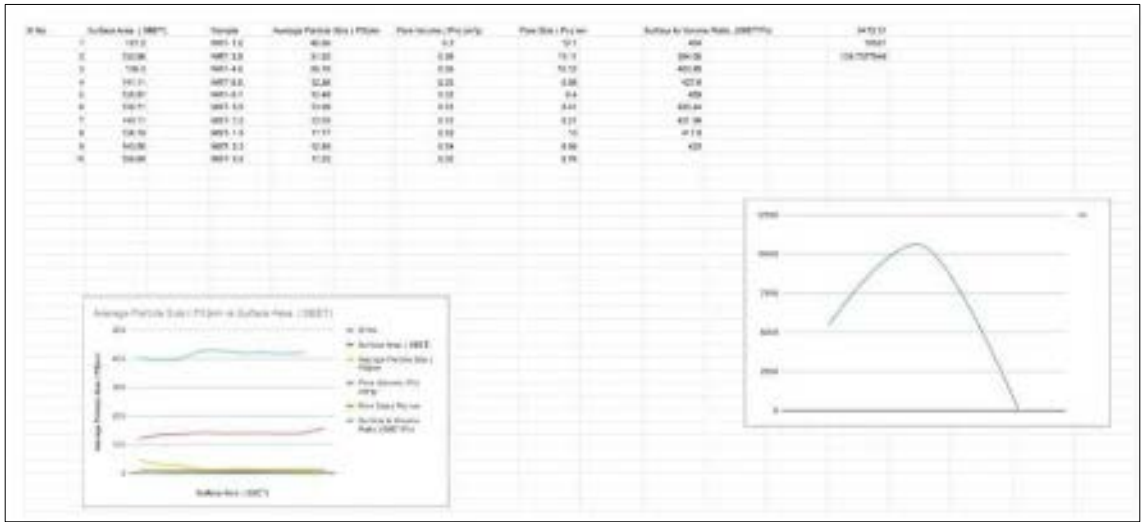


Fig 42: Surface Area, Avg Particle Size, Pore Volume, Pore Size, Surface to Volume Ratio of the synthesised TiO_2 NPs

Photocatalytic Water Splitting

In order to prevent the rapid breakdown of charge carrier recombination, and to isolate the redox potential sites on the catalytic surface separately. It is essential to spatially separate the electron holes in different compartments which can be accomplished by hetero-coupling two or more semiconductors. Recently heterojunctions formed between two solid materials have attracted more attention, including semiconductor- semiconductor (S- S), semiconductor- metal (S- M) doping and semiconductor- carbon nanotube heterojunctions), eg:- Graphene nanotubes.

Au- TiO_2 doping has gained attention in the photocatalytic degradation of water due to its high visibility towards the UV-visible light irradiation and green synthesis patterns by sol-gel and hydrothermal approaches, low - cost effectiveness and superior quality Surface Plasmon Resonance (SPR) effect with increased surface area, high selectivity and lower HC band - gap energy level towards hydrogen production.

The Photogenerated electrons and holes can recombine in a bulk or in vacuum surface of the semiconductor within a very short period of time, releasing energy in the form of heat or photons. Electrons and holes that migrate to the surface of the semiconductor without recombination can, respectively, reduce and oxidise the reactants absorbed by the semiconductor. The reduction and oxidation reactions are the basic mechanisms of the photocatalytic hydrogen production. Nature itself demonstrates an efficient strategy to utilise solar irradiation near unity quantum yield by spatially separating electrons and holes in wireless photosynthesis reactions. The process of water splitting can be envisaged as two half reactions:- water oxidation and secondly, protons reduction yo hydrogen fuel. Thermodynamically, water spitting reaction is an uphill process. It is an Endothermic reaction requiring a minimum energy of 1.23 eV because the Gibbs Free energy changes for the reaction is $\Delta G = °= 237.2kJ\ mol^{-1}$ or 2.46 eV per molecule of H_2O and $G= \Delta H – T(\Delta S)$, $T(\Delta S)$ is positive, so ΔS is positive, thus requires overpotentials. For Hydrogen Production, the CB level should be more negative than the hydrogen production level (EH_2/ H_2O), while The VB band should be more positive than the water oxidation level (EO_2/ H_2O) for efficient oxygen production from wastewater by photocatalysis. In case of photo-electrocatalytic water splitting, a catalyst absorbs photons energy and consequently, electrons are transferred from its valence band (VB) to its conduction band (CB). If its band gap is large enough, above that needed dor water splitting (1.23eV), and its band edges meet the Thermodynamic requirement for the charge transfer to occur, then in principle, excited electrons can reduce hydrogen ions and holes can oxidise oxygen anions.

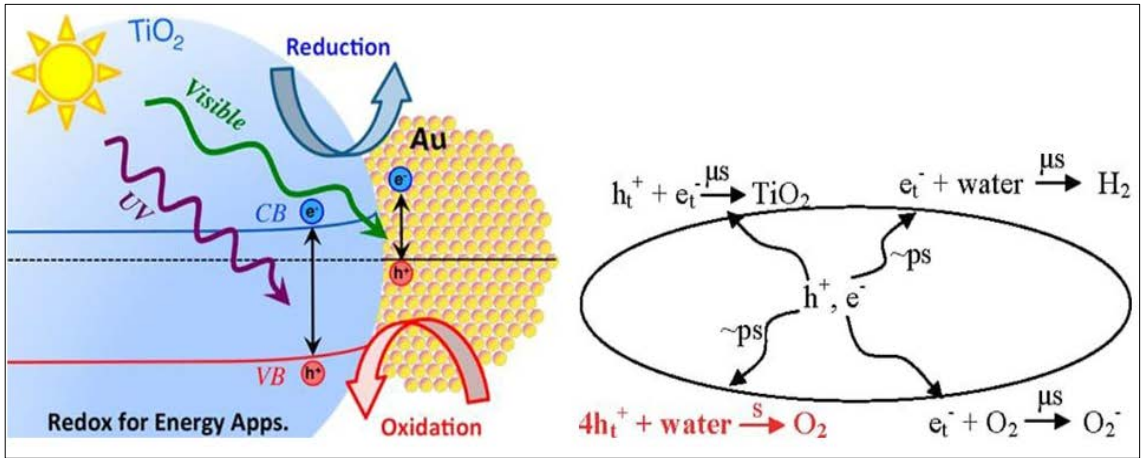


Fig 43: Photocatalytic activity of TiO_2 in water splitting.

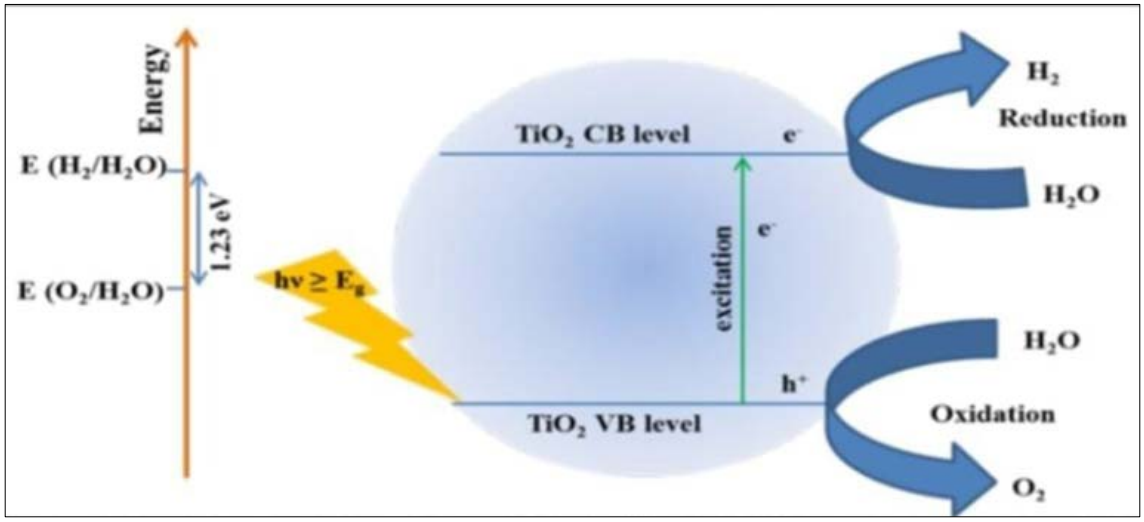


Fig 44: Mechanism of TiO_2 for Photocatalytic Water splitting for hydrogen production

According to the proposed mechanism, when metal nanoparticles (NPs) are used for sensitising TiO_2 upon exposure to UV light of 366 nm. The TiO_2 NPs form electrons and holes. The electrons first move to the CB of the TiO_2 and from there it interacts with the metal NPs. It is the interaction of these electrons with the metal NPs that decide the photoelectrocatalytic route to be taken for hydrogen production.

Conclusion

Photocatalytic water splitting and hydrogen production as a clean and renewable way of energy can contribute to replacing fossil fuels and reduce greenhouse gas emissions. It has been studied different methods of synthesis of photo-electrocatalytic materials based on TiO_2 especially Ligand-free Semiconductor Gold (Au) Nano-composites assisted for photocatalytic water splitting for green hydrogen production and also offer possibilities of preparation of molecular electronic materials. Thus.this review paper has shown that there are advances and achievements in the development of new photocatalysts for water splitting but, in future more research is required for scaling up the process for the generation of Biohydrogen and making it the main source of fuel in the current world's industrial as well as domestically economical solution and other large scale applications with the use and novel approach of TiO_2 nano photocatalysts (.doped nano TiO_2 or nanocomposites of TiO_2).

Conflict of Interest

There are no conflicts of interest.

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