In the development of new energy sources, hydrogen is one of the most attractive fuels for the 21st century. Hydrogen has considerable potential as an alternative fuel, especially if it can be generated inexpensively from an abundant raw material such as water. However, the efficient photocatalytic splitting of water to generate hydrogen using sunlight remains an as yet unachieved goal from a technological standpoint. A number of modification techniques and chemical additives have been developed in recent years to improve photocatalytic activity of TiO₂ under visible light irradiation. The development of better catalysts, tailoring of electronic structure and the reactivity as well as synthetic methods can be employed for controlling the morphology of catalysts. It is also going to benefited from recent progress in nano science. In this section we evaluate the efficiency of our modified catalyst and compare it with the unmodified titania for production of hydrogen through water splitting reaction.
6.1 Introduction

The modern society has been searching for a new form of energy that is clean renewable, cheap and a viable alternative to fossil fuel due to the drastic depletion of fossil fuels by their effective consumption and the serious environmental problems accompanying their combustion. Sunlight in the near IR, visible and UV region radiates a tremendous amount of energy and intensity to the earth so that harnessing this solar energy would contribute significantly to our electrical and chemical needs. Sustainable hydrogen production is a key target for the development of alternative future energy systems that will provide a clean and affordable energy supply. Moreover, it is carbon-free, facilitates use of more efficient power generation systems (e.g. fuel cells) and can be used to chemically reduce carbon oxides (CO, CO₂) to chemical fuels. But presently, 95% commercial hydrogen is produced from the non-renewal sources such as fossil fuels and the rest are obtained from other sources. Among them the major one is water splitting. Renewable hydrogen production is not popular yet because the cost is still high. Solar and wind are the two major sources of renewable energy and they are also the promising sources for renewable hydrogen production. The shifting to hydrogen based economy is based on various fundamental and organizational factors, mainly concerning production, storage and distribution. Among these, the production has received considerable attention. Hydrogen is also a versatile energy carrier that is currently produced from a variety of primary sources, such as fossil fuel, natural gas, naphtha, heavy oil, methanol, biomass, wastes, coal, solar energy, wind, nuclear power, water etc. There are various methods and technologies that have been developed for the production of hydrogen from these materials and few of them have already been practiced. These technologies can be broadly classified as (1-11).

a) Thermo-chemical routes
b) Electrolytic
c) Photolytic

d) Biochemical pathway

e) Chemical (steam reforming of hydrocarbon)

Each of these technologies can be coupled with one another and one can generate further production methods. Among them photo-electrochemical and photo-micro biological methods have been receiving considerable attention in the last few decades. The term “photo electrochemical” refers to a scheme wherein light is used to introduce an electrochemical process which includes, Photoelectrolysis, Photocatalysis’ and Photo assisted splitting. The term photoelectrolysis is correctly applied to a case involving semiconductor photo electrode(s) in an electrochemical cell. Photocatalysis has been generally applied to the case of semiconductor suspensions. Photo assisted splitting’ is recommended for cases wherein the excitation light energy only partially furnishes the voltage needed for the electrolysis process, the rest being accommodated by an applied external bias (12).

Among the various materials for the hydrogen production, water gets prominent role due to its large availability, easy to handle etc. Starting from water as the materials for the hydrogen production, the approaches include electrolysis, thermochemical water splitting, photoelectrolysis and photocatalyzed water splitting. Among these methods, photocatalytic production of hydrogen from water is the most attractive and rewarding work because water is abundant and renewable. And the process can occur at ambient conditions using only sunlight and a semiconductor photocatalyst (3).

Photocatalytic reactions are classified into two categories: uphill (Gibbs free energy being positive) and downhill (negative). Water splitting into H₂ and O₂ is accompanied by a large positive change in the Gibbs free energy i.e., it is an uphill reaction. In this reaction, photon energy is converted into
chemical energy, as seen in photosynthesis by green plants. Therefore, this reaction is termed as artificial photosynthesis. On the other hand, degradation reactions such as the photo-oxidation of organic compounds using oxygen molecules are generally downhill reactions. The reaction proceeds irreversibly. This type of reaction is regarded as a photo induced reaction and has been extensively studied using titanium dioxide photocatalysts (1,2,13).

There are two types of configuration adapted to a photo catalyst that can be used for photochemical water splitting: (i) photoelectrochemical cells (ii) particulate photo-catalytic systems. The photoelectrochemical cell for water decomposition involves two electrodes immersed in an aqueous electrolyte, one of which is a photocatalyst exposed to light. In particulate photocatalytic systems, the photocatalysts are in the form of particles or powders suspended in aqueous solution, in which each particle acts as micro photoelectrode that performs both the oxidation and reduction reactions of water on its surface. The particulate photocatalytic systems have the advantage of being much simpler and less expensive than photo electrochemical cell. But it has got some difficulty for the separation of stoichiometric products of hydrogen and oxygen due to the possibility of reverse reaction (2).

Historically the discovery of photo electrolysis of water directly into oxygen at a titania electrode and hydrogen at a Pt electrode by the illumination of light with energy greater than the band gap of titania is attributed to Fujishima and Honda through photocatalysis by titania. From this date, extensive work has been carried out to produce hydrogen from water by this novel oxidation reduction reaction using a variety of semiconductors (5, 14-17).

The water splitting process for H₂ generation has two major advantages namely the raw material is abundant and cheap and the combustion of H₂ in air produces water. This makes the whole process cyclic and non-polluting. From the
view point of large-scale hydrogen production, particulate photo catalyst systems are considered to be advantageous over more complex multilayer or tandem structure devices and have a wider range of potential applications (18-20).

6.2 Mechanism

The schematic representation of water splitting reaction by photocatalytic materials is shown in Fig. 6.1.

![Schematic representation of photocatalytic water splitting reaction over a semiconductor material.](image)

**Fig. 6.1.** Schematic representation of photocatalytic water splitting reaction over a semiconductor material.

Irradiation of light with energy greater than or equivalent to the band gap of semiconductor photo catalyst can generate electrons and holes in conduction band and valence band of photocatalyst. It causes reduction and oxidation of adsorbed species on semiconducting material. To achieve better overall water splitting, the bottom of the conduction band must be located at a more negative potential than the reduction potential of $\text{H}^+$ to $\text{H}_2$ (0 V at pH 0), while the top of the valence bands must be positioned more positively than the oxidation potential of $\text{H}_2\text{O}$ to $\text{O}_2$ (1.23 V at pH 0). Therefore, the minimum photon energy thermodynamically required to drive the reaction is 1.23 eV (6, 21).
In the last three decades, a large number of semiconductor materials have been investigated for photoelectrochemical process. The semiconductor system which is efficient solar energy converter, should have optimized band gap so as to make maximum utilization of solar radiation, and should also have sufficient chemical stability against photo or other corrosion processes.

Many types of semiconductors with over 130 materials including oxides, nitrides, sulphides, carbides, and phosphides, have been reported to act as efficient photocatalyst for hydrogen evolution via water splitting with varying degree of both positive and negative results. A few of them are semiconductors containing elements such as Ga or In, compounds such as GaAs, CdTe and CdSe, metal oxides such as ZnO, TiO$_2$, ZrO$_2$, SnO$_2$, WO$_3$, Fe$_2$O$_3$, RuO$_2$, sulphide such as CdS, ZnS, GaS, metal (oxy)sulfide, metal (oxy)nitride, tantalates, niobates, Indates, Tungsten based materials, metal oxides with d$^0$ and d$^{10}$ electronic configuration, Perovskite type materils, Inorganic complexes etc (12, 22-39).

Among these titania become a prominent one because of its favourable band gap, high chemical and photochemical stability, biological inertness, low cost, ease of method of preparation etc. A lot of studies with its modified forms are still in progress. One of the main drawbacks of titania material is its wide band gap energy which permits only its activity suitable by UV irradiation.

\[
\begin{align*}
\text{TiO}_2 & \xrightarrow{\text{hv}} h^+ + e^- \\
\text{Oxidation:} & \quad \text{H}_2\text{O} + 2 \text{h}^+ \rightarrow 2\text{H}^+ + 1/2 \text{O}_2 \\
\text{Reduction:} & \quad 2\text{H}^+ + 2 e^- \rightarrow \text{H}_2 \\
\text{Over all:} & \quad \text{H}_2\text{O} \xrightarrow{\text{TiO}_2/\text{hv}} \text{H}_2 + 1/2 \text{O}_2
\end{align*}
\]
Although there has been extensive research during the last decades on titania photo catalyst. An efficient photo catalyst active in visible region with high quantum efficiency is still a dream today. Various methods for improving the efficiency includes: dye sensitization, doping with metals and non metals, coupled with other semiconductors etc (40-47). Among these the non-metal doping predominates over others due to its strong visible absorption by reducing the band gap by mixing their orbital with valence band of titania.

Titania exists mainly in two phases- anatase (band gap 3.2 eV) and rutile (3.0 eV). In most investigation it has been found that anatase is more active than rutile and this can be explained by considering its electronic band structure. The location of valence band of these two phases is almost same but their conduction bands are slightly different. The conduction band potential of rutile coincides almost with the NHE potential, whereas that of anatase is shifted cathodically by almost 0.2 V. Hence the driving force for water reduction is very small for rutile while the reduction takes place more easily in the anatase form. When comparing rutile and anatase, the poor light absorption capability of rutile causes lower mobility for photogenerated carriers which decrease photocatalytic activity for water splitting (3).

Water decomposition is a very difficult and complex reaction. The various intermediate chemical steps present a kinetic limitation that decreases the efficiency of the reaction. One possible way to overcome this problem is the use of sacrificial electron donors or acceptors. The introductions of sacrificial agent (electron donor or proton acceptor) increases the efficiency of hydrogen production through suppressing the recombination of electrons and holes by reaction irreversibly with photo induced species or by reverse reaction between O₂ and H₂ (48-53).
Organic compounds, such as alcohols (methanol, ethanol, isopropanol, etc.), acids (formic acid, acetic acid, etc.), and aldehydes (formaldehyde, acetaldehyde, etc.) have all been used as electron donors for photocatalytic hydrogen generation. Among them, methanol was most widely used for the hydrogen generation process. The suggested mechanic routes as follows (54, 55)

\[
\begin{align*}
\text{h}^+ + \text{H}_2\text{O} & \rightarrow \cdot \text{OH} + \cdot \text{H} \\
\text{CH}_3\text{OH} + \cdot \text{OH} & \rightarrow \cdot \text{CH}_2\text{OH} + \text{H}_2\text{O} \\
\cdot \text{CH}_2\text{OH} & \rightarrow \text{HCHO} + \cdot \text{H} + \cdot \text{e}^- \\
2\text{H}_2\text{O} + \cdot \text{e}^- & \rightarrow \text{H}_2 + 2\cdot \text{OH}
\end{align*}
\]

Overall rean. \( \text{CH}_3\text{OH} \xrightarrow{\text{Catalyst} / \text{h}_\nu} \text{HCHO} + \text{H}_2 \)

The product, formaldehyde (HCHO), could be further oxidized to methanoic acid (HCOOH) and subsequently to \( \text{CO}_2 \) together with hydrogen generation.

\[
\begin{align*}
\text{HCHO} + \text{H}_2\text{O} \xrightarrow{\text{Catalyst} / \text{h}_\nu} \text{HCOOH} + \text{H}_2 \\
\text{HCOOH} \xrightarrow{\text{Catalyst} / \text{h}_\nu} \text{CO}_2 + \text{H}_2
\end{align*}
\]

In metal doping process, most time the doping species itself act as recombination centre and reduce the photocatalytic efficiency. Whereas the presence of noble metals on titania surface results in the formation of a Schottky barrier at the metal/semiconductor interface, which leads to a decrease in electron-hole recombination rate. Decreasing the over potential for hydrogen evolution owing to a large over potential for the evolution of \( \text{H}_2 \) on the surface of \( \text{TiO}_2 \), the material alone becomes inactive. Usually, this problem can be solved by loading \( \text{TiO}_2 \) with co-catalysts of noble metals, such as Pt,
Pd, Au, Rh, and Ag. Loading these metals, which have a low over potential for hydrogen, can make it easier to generate hydrogen (1, 3).

The crystallite defects largely contribute to the efficiency of the photocatalyst. The defects themselves promote as trapping and recombination centers between photogenerated electrons and holes, resulting in a decrease in the photocatalytic activity. The higher the crystalline quality, the smaller is the amount of defects. Therefore, a high degree of crystallinity, rather than a high surface area, is required for a photocatalyst, especially for an uphill reaction like water splitting (1,13).

The objective of the present study is to investigate the effect of N doped and N S co-doped titania for the production of hydrogen through water splitting reaction in visible region. The studies involve the effect of catalyst amount, effect of time and also a comparison of modified catalysts with pure titania prepared in laboratory and a commercial one.

6.3 Experimental section

The photoactivity of all the samples were evaluated under a medium-pressure mercury lamp (Hg, Ace Glass Inc., 450W) irradiation in a closed rectangular quartz cell equipped with a sampling and evacuation ports. The samples were irradiated in an outer irradiation–type quartz cell where lamp was surrounded with water circulation jacket to absorb IR irradiation. The lamp exhibits broad range emission spectra with maxima at both UV and the visible range. The lamp radiates 16% of the radiation in UV and remaining in visible region. The catalytic activity experiments were conducted in static mode for water in methanol (2:1 v/v %) mixtures, in the presence of well dispersed catalyst. The reaction products were analysed over a period upto 6 h with an interval of 2h. A gas chromatograph (Netel (Michro-1100), India) equipped with a thermal conductivity detector (TCD), molecular sieve
column (4m length) with Ar as carrier was employed in the isothermal temperature mode at 50°C oven temperature. The number of photons falling on the reaction cell or flux of the light determined by light flux meter was observed to be $19 \times 10^4$ lux or 278.2 watts/m$^2$ in horizontal geometry irradiation of UV-visible photoirradiator.

6.4 Activity

a. Effect of catalyst amount

Studies involve a 10:5 by volume ratio of water to methanol solution and add catalyst amount of 0.05g, 0.1g and 0.15g respectively. After a four hour irradiation of visible light the sample was collected and analyzed using gas chromatography.

![Graph showing yield of hydrogen against amount of catalyst](image)

**Fig. 6.2.** Yield of hydrogen produced against amount of catalyst
Irradiation time: 4 hour; Water to methanol ratio 10:5

Fig. 6.2 shows the result of hydrogen obtained against the amount of catalyst. It is clear from the figure that the yield of hydrogen increases with increase catalyst amount. The active surface for the generation of photo excited species increases with increase of amount of catalyst. But above an optimized range there is no more higher activity.
b. Comparison study

In this study all the catalyst were used for evaluated for their activity in visible light for the water splitting reaction. Studies involve a 10:5 volume ratio of water to methanol with a catalyst amount of 0.1g. Sample was collected and analyzed at an interval of 2 hours up to 6 hours.

![Graph showing hydrogen yield over time for different catalysts.](image)

**Fig. 6.3.** Yield of hydrogen produced with time against different catalyst
Amount of catalyst: 1.0g; Water to methanol ratio 10:5

The comparison of results of the all the catalyst for the hydrogen production is shown in Fig. 6.3. The results showed that the yield of hydrogen increases with increase of time for all the catalyst except the commercial titania (A-TiO₂), which has a very low activity. It is also observed from the result that NS co-doped titania gives better result than others and this is due to the strong absorption band created by the dopants in visible region by mixing with the valence band of pure titania. Moreover other factors such crystallite nature, anatase phase, surface area, small particle size etc. also contribute to their higher activity.
References


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