

# A Solar Hydrogen Generation by Using Nanostructured Materials

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## Abstract

A clean and effective method of producing hydrogen using renewable energy sources is one of the key prerequisites for a future hydrogen economy. A promising energy source due to its high energy content and clean combustion is hydrogen. Particularly, photocatalysis and photoelectrolysis, which produce hydrogen from water and solar energy, are examples of sustainable and renewable energy production techniques. Here, along with functional materials, we will discuss the fundamentals of photocatalysis and the PhotoElectroChemical cell (PEC cell) for water splitting. Chemical aspects of the defect will be highlighted. The functional materials' decreasing length scale, which has reached the nanoscale, has received a lot of attention to date. When the photo-generated charge carriers' diffusion lengths are significantly different, the nanostructure is advantageous.

**Keywords:** Hydrogen production, PhotoElectroChemical cell, Nanostructured

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## 1. INTRODUCTION

### 1.1 HYDROGEN PRODUCTION

Hydrogen does not naturally occur as the molecule H<sub>2</sub>, despite the fact that it is an appealing alternative to fossil fuels. Instead, it exists as a chemical compound bound to others, such as water or hydrocarbons, which must undergo chemical transformation to produce H<sub>2</sub>. Diverse

domestic resources, such as fossil fuels like natural gas and coal, nuclear power, hydroelectric power, biomass, and renewable energy sources like wind, solar, and geothermal power, can all be used to produce hydrogen. (R.van de Krol, 2011) Methane in natural gas can be converted to hydrogen using the steam reforming process, which uses hot steam. Similar liquid reforming techniques combine steam and high-temperature reactions with liquid fuels like ethanol to create hydrogen close to the point of use. Water is split into hydrogen and oxygen using the electrolysis process, which uses electricity produced by wind, solar, geothermal, nuclear, or hydroelectric power. In the process of gasification, coal or biomass are broken down into gaseous elements, which are then combined to create synthesis gas, which is then reacted with steam to create hydrogen. In order to fuel chemical reactions that split water into hydrogen and oxygen, thermochemical water splitting uses high temperatures produced by solar concentrators or nuclear reactors. (R. van de Krol, 2011)Hydrogen is produced as a byproduct of the photobiological process, which involves microbes like green algae consuming water while exposed to sunlight. Similar to this, photocatalytic and photoelectrochemical systems generate hydrogen from water splitting with the help of specialised semiconductors and solar energy. These procedures are unquestionably viable options for producing hydrogen over the long term.

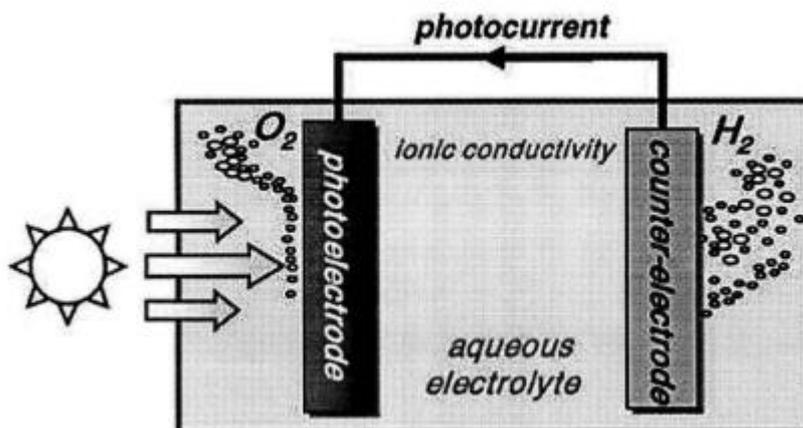
## **1.2 PHOTOELECTROCHEMICAL SPLITTING OF WATER**

One of the "sacred goals" of spotless and sustainable hydrogen creation is photoelectrochemical (PEC) water parting, which utilizes daylight to part water atoms into their part gases of hydrogen and oxygen. Since Fujishima and Honda revealed hydrogen creation in a photoelectrochemical cell with a titanium dioxide cathode enlightened with close to bright light in 1972, it has been a logical and designing goal (O.Khaselev, 2001). In a solitary semiconductor-based gadget, a PEC framework consolidates the electrolysis of water and the catch of sun-oriented energy. Water and daylight consolidate to deliver unadulterated hydrogen and oxygen. Despite the fact that it sounds great, it's not exactly that straightforward. Sun oriented energy can be straightforwardly changed over completely to electrochemical energy for parting the water when a PEC semiconductor gadget is lowered in a water-based arrangement. In any case, this will possibly happen on the off chance that all important circumstances are fulfilled. To part water, a semiconductor material must successfully ingest daylight and produce enough photovoltage, and the semiconductor interface should be helpful for supporting the development of hydrogen and oxygen gases.

The PEC framework should likewise be reasonable for any broad arrangement and keep up with soundness in arrangement.

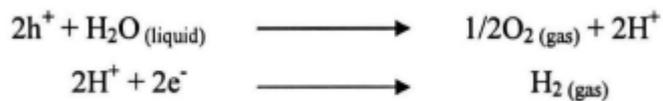
### 1.2.1 PEC WATER-SPLITTING ACTION

PEC framework for water parting with basic two-terminal arrangement. A metallic counter-terminal is wired to a fluid arrangement drenched, light-delicate semiconductor photoelectrode in the sanctioned model. The semiconductor's photogenerated electron opening matches communicate electrochemically with ionic species in arrangement at the strong/fluid connection points when presented to daylight. (R.van de Krol, 2008)The oxygen-advancement response (OER) is driven by photoexcited openings at the anode surface, while the hydrogen-development response (HER) is driven by photoexcited electrons at the cathode surface. In the photoanode framework openings are infused into the semiconductor surface's answer for advance oxygen, while photoexcited electrons are shipped to the counter-cathode to develop hydrogen. Conversely, electrons are brought into an answer in photocathode frameworks, where oxygen is developed at the counter terminal while hydrogen is advanced at the semiconductor surface. PEC photoelectrodes oftentimes capability as minority transporter gadgets, similar as strong state pn-intersection sun powered cells. (A.B.Murphy, 2006) Like the p-n intersection, the semiconductor/fluid intersection allows the progression of minority transporters while discouraging the progression of larger part transporters. Along these lines, photoanodes made of n-type semiconductors that grant minority-transporter opening infusion are desirable over photocathodes made of p-type semiconductors. The response for semiconductor material is composed as follows:



**Fig.1:** The typical two-electrode PEC water splitting setup is displayed in the photoanode configuration with a distinct counter electrode.

Without recombining, these electrons-holes become separated and migrate to the semiconductor's surface (hole) and to the counter-electrode (electron). Water molecules are oxidised by holes at the photoanode (the semiconductor working electrode), creating oxygen gas (equation 1.2). Free electrons interact with water molecules at the cathode (metal counter-electrode), reducing the H<sup>+</sup> and generating hydrogen gas as a result.



The overall process of the photoelectrochemical splitting of water can therefore be expressed as follows:



At the point when the photons consumed by the photo-anode have an energy equivalent to or more noteworthy than  $E_t$ , the limit energy, the water parting response happens:

$$E_t = \frac{\Delta G_{\text{H}_2\text{O}}^0}{2N_A}$$

Where  $N_A$  is Avogadro's number, which approaches  $6.022 \times 10^{23}$  moles, and  $\Delta G_{\text{H}_2\text{O}}^0$  is the standard free enthalpy per mole of condition 1.4, the two of which are equivalent to 237.141 kJ/mol. This outcome

$$E_t = h\nu = 1.2289 \text{ eV}$$

Gibb's free energy at 298 K is in this way 237.141 kJ/mol, or 2.4578 eV per H<sub>2</sub> particle created, for the water parting response. Likewise, as displayed in Figure 1.3, the energy expected to part water is 1.2289 eV per electron (regularly adjusted to 1.23 eV). The whole bright and noticeable segments of the sun powered range ought to hypothetically be accessible for sun oriented water parting on the grounds that a photon with an energy of 1.23 eV has a wavelength of near infrared (1000 nm). In fact, nonetheless, 1.8 eV (or a cut-off

wavelength of around 685 nm) is required. To represent inescapable misfortune systems like cathode over possibilities, more energy has been added.

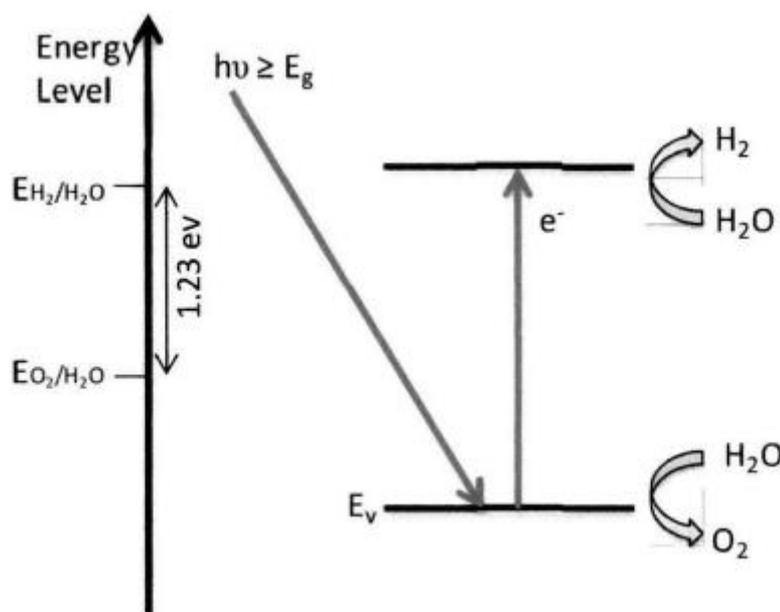


Figure. Hydrogen production via semiconductor photoelectrolysis mechanism

### 1.3 3-Dimensional Nano Structured Materials

The capacity to make 3D NSMs with a controlled design and morphology is exceptionally fascinating. The great many applications for 3D nanostructures in the fields of catalysis, attractive materials, and cathode materials for batteries make them a significant material too. (Brillet, 2010,) Besides, in light of the fact that the nanostructures have a bigger surface region and give sufficient retention destinations to all elaborate particles in a dense space, 3D NSMs have as of late drawn in serious exploration interest. In any case, materials with three-layered porosity, for example, nanoballs (dendritic designs), nanocoils, nanocones, and nanoflowers, could bring about better sub-atomic vehicle.

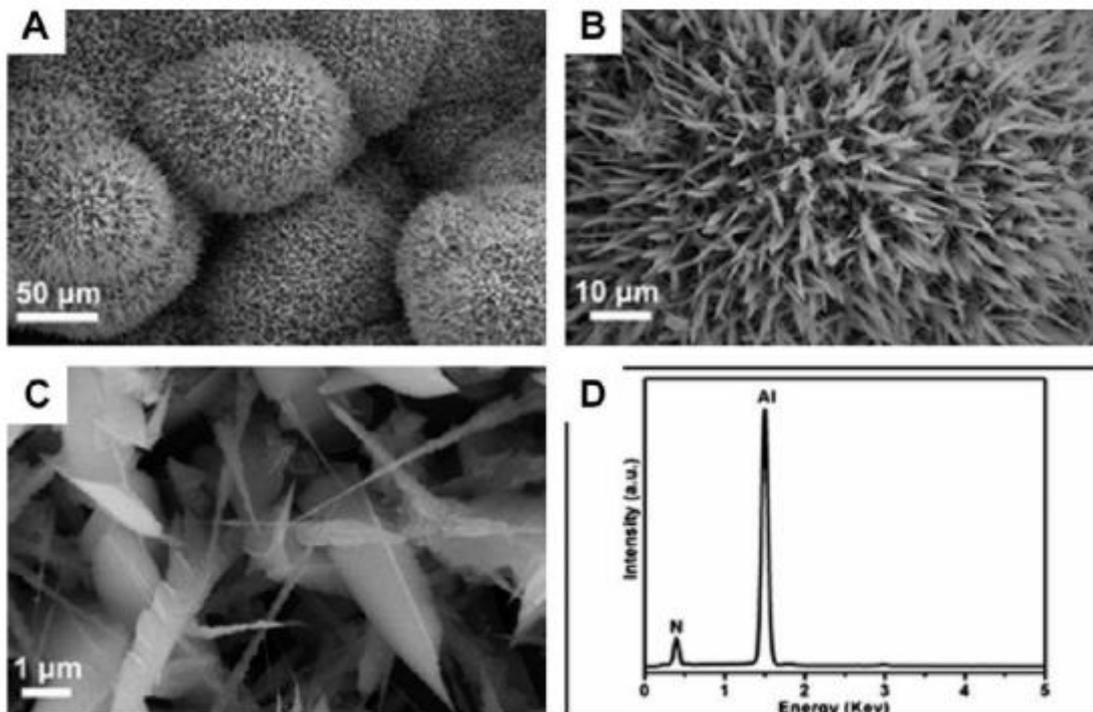


Figure.2: D urchin-like nanostructured AlN

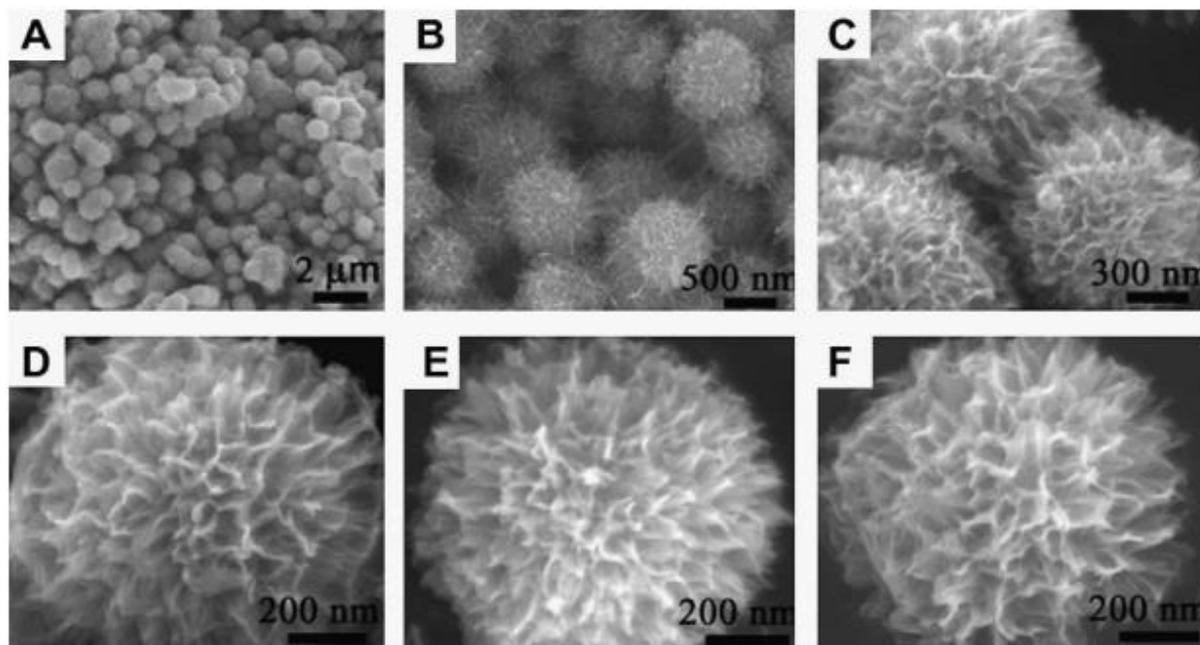


Figure.3: Low-magnification SEM images of 3D crystalline TiO2 nanostructures

## 2. Literature Review

Early studies on the PEC properties of hematite conducted in the 1970s and 1980s focused on polycrystalline hematite as a photoelectrode, specifically prepared as pellets from powder using ceramic technique or thermal oxidation. By Wilhelm et al. in 1979[2], Yeh and Hackerman in 1977[3], and Candea in 1981[4], thermally grown hematite was investigated in PEC generation of hydrogen; however, the long-term stability of the films was questioned due to the excessively thin films. The creation of polycrystalline hematite pellets and the observation of the onset of photocurrent at photon energies greater than 2.1eV were both reported by McGregor et al. in 1979 [5]. They also noted that photo current saturation occurred at higher voltages and that space charge layer states predominated over surface states. Redon et al. presented a comparison of the PEC behaviour of single crystal and amorphous hematite in 1981 and discovered that the single crystal's PEC characteristic was more conducive to hydrogen production [6]. But the amount of photocurrent produced was still quite small, and using a single crystal was quite expensive.

**Kennedy et al., in 1980 and 1981** Si dopant was viewed as more powerful than Ti in improving photoresponse, showing a photocurrent of 120 An at 0.OV/SCE with 400 nm light [17, 15]. In 1982, Shinar and Kennedy arranged different hematite tests that were doped with Zr, Hf, Ce, V, Nb, W, Al and C and found that dopants have numerous capabilities. In their investigation of the strong dissolvability of Ge, Si, and Mg in hematite, Sanchez et al. (1982) found that examples with Ge doping had further developed PEC reaction.

**Gratzel et al. (1985)** hematite powder might encounter apparent light-actuated photograph separation or consumption in an acidic medium, especially when chloride particles are available [18]. Houlihan et al. performed substitutional doping of hematite with Si, Ca, Nb, Cu, Ru, Mg, and Zr in 1985 [19]. These doped examples were sintered in air for 20 hours at 1350°C, diminished in hydrogen air for 30 minutes at 300°C, and afterward momentarily reoxidized at 700-900°C. Subsequently, tests were created with resistivities going from 0.01 to 5000  $\Omega$ -cm. These examples were found to have unrivaled PEC attributes.

**Parent et al. [20] in 1987** Under plasma flash, Mg and Si doped hematite was ready, and Fe<sub>3</sub>O<sub>4</sub> was found in the examples. They reached the resolution that the presence of Fe<sub>3</sub>O<sub>4</sub> significantly upgraded the photoresponse in hematite. By substance fume testimony, Sanchez et al. (1988) created a solitary hematite gem that was doped with Nb [21]. They saw that

doping produces sub band hole energy levels, yet the low photoresponse was credited to the lower transporter versatility and slow charge move across semiconductor intersection.

**Aroutiounian et al. in 2002, 2006, and 2007** The presentation of hematite arranged utilizing customary clay strategies and doped with an assortment of dopants at different doping focuses has been entirely considered [22, 23, 24].  $\text{AFe}_2\text{O}_3$  turned into a n-type semiconductor when pentavalent ( $\text{Ta}^{5+}$ ,  $\text{Nb}^{5+}$ ) or quadrivalent ( $\text{Sn}^{4+}$ ) particles were added. The photoelectrodes containing 0.5at% Ta were the most dynamic and shown photocurrent - 0.64mA/cm<sup>2</sup> at 0.7V/SCE, as indicated by the photoelectrolysis current for  $\text{Ta}^{5+}$  doped  $\text{aFe}_2\text{O}_3$  [22] at different doping fixations from 0.1 to 2.0at%. The PEC reaction to  $\text{Sn}^{4+}$  doping in iron oxide [24] showed an irrelevant improvement, which was associated with the recombination of photogenerated charge transporters. IPCE reliance on the Nb focus was seen in semiconductor photoelectrodes produced using strong arrangements of  $\text{Fe}_2\text{O}_3$ - $\text{Nb}_2\text{O}_5$  [23], with a lot more grounded impact at more limited wavelengths than at longer wavelengths.

**Sayama et al. (1990)** It was found that nickel-stacked  $\text{Rb}_4\text{Nb}_6\text{O}_{17}$ , which has a similar layered construction of niobium oxide sheets with interlayers as that of  $\text{Kb}_4\text{Nb}_6\text{O}_{17}$ , shows a high movement for photocatalytic water parting to frame hydrogen and oxygen under band hole light. This was finished by contemplating photocatalytic deterioration of water over a Ni stacked  $\text{Rb}_4\text{Nb}_6\text{O}_{17}$  impetus. For over 10 hours, they recalcined the impetus powder in air at a temperature somewhere in the range of 1153 and 1173 K. The response was completed in refined water with a pH of 9.7 and a quantum productivity at 330 nm of 10% at the underlying phase of the response more than  $\text{NiO}$ (0.1 wt%)-  $\text{Rb}_4\text{Nb}_6\text{O}_{17}$  to accomplish the most noteworthy movement.

### 3. The photo-electrode

The selection of semiconductor electrodes is very important. Strong absorption of visible light, high chemical stability in both dark and light, valence electron ( $E_v$ ) and conduction band edge ( $E_c$ ) locations allowing oxidation and reduction of water, photogeneration in semiconductors Efficient transport of electrons and holes, low overvoltage electrode reactions and low cost are requirements for suitable materials [5]. The spectral range in which a semiconductor absorbs light is determined by the photobandgap. The theoretical energy

required to split the anode water (1.23 eV), the thermodynamic loss of about 0.4 eV, and the overvoltage (0.3–0.4 eV) required to speed up the electrode reaction rate are all , contributes to the minimum bandgap. Therefore, the bandgap energy should be at least 2.0 eV. The bandgap should also be as small as possible to ensure as much overlap as possible between the absorption of the material and the solar spectrum.

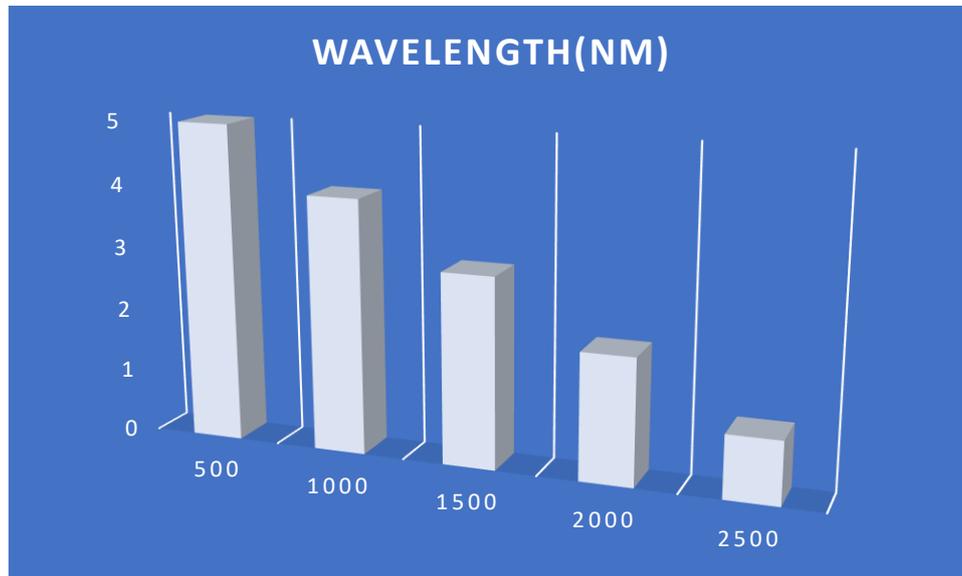


Figure.1: The ratio of the photon flux of solar radiation to wavelength

#### 4. . Water splitting efficiencies

The wavelength underneath which the material starts to assimilate light can be connected with the ideal bandgap energy ( $E_g$ ) for photograph electrolysis (the cut-off wavelength),

$$E = \frac{hc}{\lambda}$$

Here,  $E$  is the energy,  $\lambda$  is the wavelength (m),  $h$  is the Planck constant ( $6.62610 \cdot 10^{-34}$  J.s), and  $c$  is the speed of light ( $3108$  m/s) (J). Eq. (1) can be composed all the more basically as follows:

$$E \text{ (in eV)} = \frac{1240}{\lambda \text{ (in nm)}}$$

The Maximum hypothetical transformation effectiveness can be determined from the material's bandgap energy and related cut-off frequency. This is finished under the reason that all photons with frequencies beneath the end esteem are ingested and that all consumed

photons are switched over completely to electron-opening matches that add to the photocurrent,  $j_{photo}$ , and thusly to the water parting response. Coming up next is the equation for the supposed applied predisposition photonto-current productivity, or ABPE:

$$ABPE = \frac{j_{photo} (V_{redox} - V_{bias})}{P_{light}}$$

Here,  $P_{light}$  is the episode light power (around 100 mW/cm<sup>2</sup> for AM1.5 daylight),  $V_{bias}$  is the remotely applied predisposition potential that is as often as possible expected to accomplish sensible photocurrents, and  $V_{redox}$  is the redox potential for water parting (1.23 V). This articulation yields the real sun based to-hydrogen transformation productivity, or STH, for a two-cathode estimation without inclination:

$$\eta_{STH} = \frac{j_{photo} V_{redox}}{P_{light}}$$

Table.1: Several popular semiconducting metal oxide photo-electrode materials include maximum water splitting efficiencies are possible.

Material	Bandgap (eV)	$\eta_{STH}$ (%)
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	2.2	16.1
WO <sub>3</sub>	2.3	7.4
TaON	2.5	9.6
Cu <sub>2</sub> O (p-type)	2.1	9.6
TiO <sub>2</sub> (anatase)	3.32	18.2
TiO <sub>2</sub> (rutile)	3.12	2.2

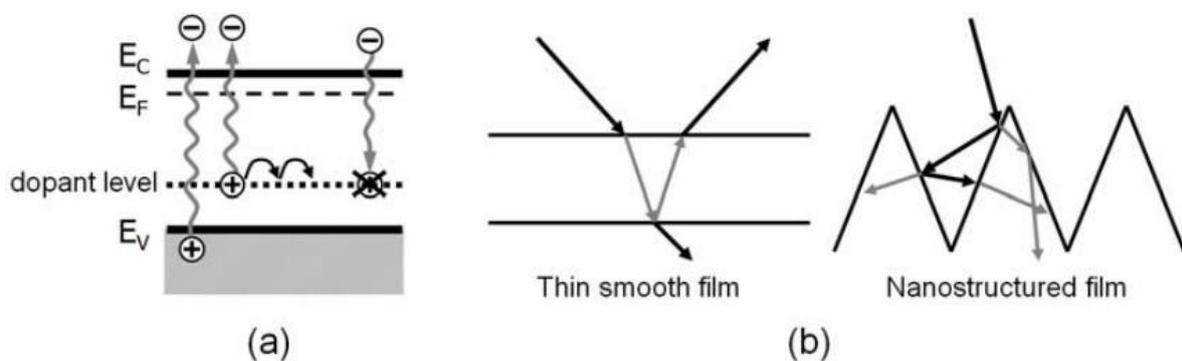
For a number of extensively researched photo-electrode materials, the maximum solar-to-hydrogen efficiencies were calculated using Eq. (4), where  $j_{photo}$  was determined by integrating the AM1.5 spectrum up to the cut-off wavelength.

### 5. Photo-anode materials: Doping's role

In the fluid electrolytes of PEC cells, the traditional sun oriented cell materials, like silicon (Si), gallium arsenide (GaAs), and cadmium telluride (CdTe), are not steady under

brightening. To stop electron opening vehicle to the semiconductor/fluid electrolyte interface, they either disintegrate or a flimsy oxide film structure. Additionally, these materials (Si, GaAs) are either too expensive or undesirable from an environmental standpoint for use in photovoltaic solar cells (CdTe). For these reasons, metal oxides are the category of photo-anode materials that has been the subject of the most research. With a few notable exceptions, wide-bandgap metal oxide semiconductors generally exhibit photo-corrosion stability. TiO<sub>2</sub>, -Fe<sub>2</sub>O<sub>3</sub> (hematite), and WO<sub>3</sub> polymorphs in their anatase and rutile forms are excellent examples (Table 1).

The restricted assimilation of apparent light is the primary downside of utilizing wide-bandgap materials. For example, TiO<sub>2</sub> has a huge bandgap energy of 3.2 eV and just ingests close to UV light. A great deal of exploration has been finished with an end goal to coordinate optical retention towards the noticeable range of the sun. Doping with cations and anions has been broadly investigated so far. The change metal particles, like Cr and Fe, stand out enough to be noticed as far as cation doping. These particles possess Ti-destinations in TiO<sub>2</sub> and bring limited imperfection energy levels into the bandgap. Consequently, noticeable light is utilized to energize electrons from these confined deformity energy levels. Be that as it may, contrasted with the valence band electron openings' portability, the photograph created electron openings should bounce starting with one energy level then onto the next. Thus, the probability of charge catching and recombination is expanded by the restricted imperfection energy levels. Because of the restricted solvency of dopants, their focuses are likewise low, and thus, their ingestion coefficients are normally exceptionally low. Regardless of some achievement, the cation-doping approach doesn't raise the general viability of photograph terminals.



Asahi et al. distributed a paper on anion doping of TiO<sub>2</sub> a decade prior. The wave elements of the anion N and C dopants fundamentally cross-over with the wave elements of the oxygen

valence band, as per their quantum synthetic estimations. Thus, the sub-bandgap imperfection energy levels are less restricted than for the cation dopants. This would essentially bring down recombination, and it has been shown that doping TiO<sub>2</sub> with N and C improved photocatalytic exercises. Splash pyrolysis of TiO<sub>2</sub> in a carbon dioxide air or a high-temperature treatment in a hexane-containing climate have both been utilized to concentrate on the statement of nitrogen-or carbon-doped dainty film TiO<sub>2</sub> photograph anodes. The dopant focuses, notwithstanding, were inadequate to adjust the ingestion range altogether. The grouping of the anion dopants N and C can be raised through different techniques, which have been examined. It has been recommended that oxidative strengthening of TiC films is a promising methodology.

## 6. CONCLUSION

In this brief outline, we have talked about the basics of direct photoelectrochemical water parting as well as probably the main prerequisites put on photoelectrode material properties. Metal oxide semiconductors are magnificent contender for this application because of their security and moderateness. The essential trouble is conquering a portion of the intrinsic requirements that this class of materials presents, like poor noticeable light retention, obliged charge transporter dissemination lengths, and pitiful water oxidation synergist movement. Most of these problems can be solved using nanostructured morphologies, if not all of them. It is necessary to develop novel fabrication techniques in order to convert multicomponent designs with nanostructures into useful, affordable photo-electrodes and solar energy conversion devices in order to advance this exciting field.

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