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Review Article

# Nanomaterials for photoelectrochemical water splitting – review

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ABSTRACT

Photoelectrochemical (PEC) water splitting using nanomaterials is one of the promising techniques to generate hydrogen in an easier, cheaper and sustainable way. By modifying a photocatalyst with a suitable band width material can improve the overall solar-to-hydrogen (STH) energy conversion efficiency. Nanomaterials can tune their band width by controlling its size and morphology. In many studies, the importance of nanostructured materials, their morphological and crystalline effects in water splitting is highlighted. Charge separation and transportation is the major concern in PEC water splitting. Nanomaterials are having high surface to volume ratio which facilitates charge separation and suppress electron-hole pair recombination. This review focuses on the recent developments in water splitting techniques using PEC based nanomaterials as well as different strategies to improve hydrogen evolution.


## Contents



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## Introduction

The greatest challenge in the near future of scientific era to be addressed is the huge energy requirements. Researchers are emphasizing their efforts more on investigating clean, safe and sustainable energy resources to cure out the expected shortage of non-renewable energies and to control the pollution. Hydrogen is one such fuel with no emission of pollutants when burned in oxygen. It is a very promising renewable fuel, used in vehicles, spacecraft propulsion, aircraft and electric devices. Hydrogen is locked up in water, hydrocarbons, and other organic matter. Techniques are introduced for the separation of hydrogen from these compounds.

One of the exciting ways to extract hydrogen is water splitting process. Water splitting is the process of separation of water into oxygen and hydrogen. Various methods for water splitting have been issued like photoelectrochemical (PEC) [1], photocatalytic [2], radiolysis [3], photobiological [4] and thermal decomposition [5]. Radiolysis produces nuclear waste as a by-product [3]. Photobiological water splitting is with the aid of algae bioreactor, switches from oxygen production (normal photosynthesis) yielding low-$H_2$ production rates [4]. The major drawbacks in thermal decomposition are its low yield of hydrogen and high temperature requirement. Simplest, efficient, cheap and clean methods for the production of hydrogen are photoelectrochemical and photocatalytic water splitting.

### *Basic mechanism involved in PEC water splitting*

Fujishima and Honda introduced the photoelectrochemical water splitting with high efficiency and low cost using a semiconducting material [6]. The basic principle behind PEC water splitting is the conversion of solar energy to hydrogen by applying an external bias on to the photovoltaic materials immersed in an electrolyte which contains redox couple, of which one is made of semiconductor, exposed to light and is able to absorb light. The electricity is then used for water electrolysis. Semiconductors are having a uniqueness to function as a photocatalysts. So, it plays a vital role in activating the chemical reduction and oxidation process in the presence of light. These photocatalyst electrodes are capable of capturing the light, which provides energy for the reactions and the additional voltage required to carry out the reaction is provided by an externally applied electric/chemical bias. This externally applied bias overcomes the slow kinetics and provides sufficient voltage for the PEC cell to drive the reaction at a desired rate/current density. The photoelectrode with the absorption of photon, electrons are excited and electron-hole pairs are generated via redox reaction. Thus formed holes can oxidize the molecule and the electron can reduce $H^+$ to $H_2$ [7–9].

The energy level where the probability of finding electron is half (Fermi Energy ($E_f$)) is important when the reference electrode is used to make measurements; it compares $E_f$ of semiconductor with its own unchanging Femi level. In an intrinsic semiconductor $E_f$ will be exactly at the centre band gap i.e. between $E_c$ and $E_{v.}$ Depending upon the type of dopant $E_f$ shifts towards or away from $E_c$ as depicted in Fig. 1. Equilibration takes place at the interface by shifting the Fermi Level of the semiconductor to match with the redox couple of the electrolyte. This will result in the formation of a thin region of space charge layer close to the surface of the semiconductor leading to band bending upwards or downwards, depending on the type of semiconductor (n-type/p-type) as shown in Fig. 2 [6].

From Figs. 1 and 2 we can summarize that, there is a strong dependency on the electronic properties of the photoelectrode to improve the water splitting efficiency. To optimize all the processes in a single component is proven impossible to achieve. Many efforts have been devoted to improve the efficiency and to absorb a wide range of light spectrum. One of the efforts is the construction of heterostructure photocatalysts (n-n/n-p/p-p junctions). This helps in the migration and separation of charge carriers. The recombination of photogenerated carriers can be reduced using heterojunction structure [10–12].

PEC water splitting can be achieved through two step process known to as Z-scheme, which a kind of mimicking the natural photosynthesis. In this system two different

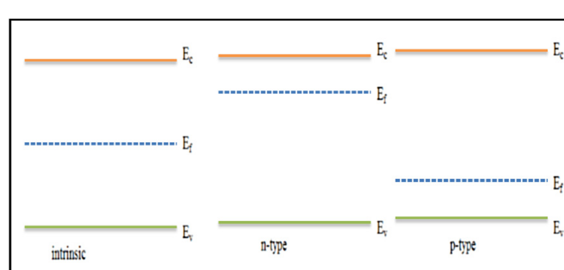


**Fig. 1 – Schematics on $E_f$ shift for extrinsic semiconductor.**