

## Water Splitting: Recent Scientific and Technological Advances

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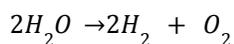
### Abstract:

Hydrogen is a green fuel and has great potential as a sustainable and renewable energy carrier. It can be produced by electrocatalytic, photocatalytic, photoelectrochemical water splitting. It is essential to develop highly effective catalysts for economic and large-scale hydrogen production. Currently, phosphorus-containing catalysts have gained a lot of attention because of their unique properties such as different oxidation states, tunable structure, and exceptional physiochemical properties. In this review paper, the topics discussed are part of numerous research carried out to date in water splitting by phosphorus-containing photocatalysts and electrocatalysts that include phosphorus in elemental form, metal phosphonates, metal phosphates, transition metal phosphides, metal phosphorus trichalcogenides, and phosphorus-doped materials. A detailed mechanism of water splitting and the activity origin of phosphorus-containing catalysts are presented. Lastly, there are some challenges in water splitting listed below that we need to overcome shortly.

**Keywords:** Photocatalytic water splitting, Electrocatalytic water splitting, Photoelectrochemical water splitting, phosphorus-containing catalysts

### 1. Introduction

The chemical reaction in which water splits into oxygen and hydrogen is water splitting.



The speed at which the average global temperature is increasing is alarming. One of the leading causes of ever-increasing global warming is burning fossil fuels. At the time of the industrial revolution, fossil fuels have played a significant role in transforming the world. But the harmful effects of the release of carbon dioxide and other greenhouse gases can no longer be tolerated. So, there is a need to replace fossil fuels with alternative fuels as they have a lesser carbon footprint than fossil fuels. Hydrogen is considered a green fuel. One of the most efficient methods to produce hydrogen fuel is water splitting. To obtain a better hydrogen yield at an economic

level, the optimization of water splitting is the primary experimental factor. The chemical transformation that can decompose water into oxygen and hydrogen can be done by various processes like electrolysis, photocatalytic, photochemical, thermal decomposition, and radiolysis. Hydrogen is potentially one of the most sustainable fuels because of its high gravimetric energy density, high combustion efficiency, and eco-friendly by-products.

For photoelectrochemical, photocatalytic, and electrolytic water splitting, there is a need for a catalyst with high activity to ensure sustainable hydrogen production.

The significant difference between photocatalysis and electrocatalysis is the driving force of electrons<sup>1</sup>. In photocatalytic water splitting, photon energy leads to

the generation and separation of excited electrons and holes, which transfer to surface-active sites and initiate redox reactions. In electrocatalytic water splitting, electricity provides electrons directly for catalytic sites. The combination of photocatalytic water splitting and electrolytic water splitting is called photoelectrochemical water splitting.

Some carbon and metallic compounds with high electrical conductivity exhibit high electrocatalytic performance, while some semiconducting materials exhibit outstanding photocatalytic activities. P-containing compounds show excellent catalytic performance for both electrocatalytic and photocatalytic water splitting<sup>2</sup>. P-containing compounds act as efficient catalysts for electrocatalysis and photocatalysis water splitting because of their unique properties such as fast carrier mobility, high conductivity, and broad light absorption. The stable valencies of phosphorus are -3, 0, +4, and +5. P can exist in elemental form and form various inorganic compounds by combining with metals or non-metals and forming phosphides<sup>3</sup>, metal phosphates<sup>4</sup>, metal phosphorus trichalcogenides, organic hybrid metal phosphonates<sup>5</sup>. They all exhibit superior catalytic properties for electrolytic and photocatalytic water splitting.

Transition metal phosphides are effective catalysts for electrocatalytic water splitting because of their excellent electrical conductivity. They act as a co-catalyst to counter the recombination of holes and electrons during photocatalytic water splitting<sup>6</sup>. High metal content is used to enhance the conductivity of transition metal phosphides, and transition metal phosphides rich in phosphorus have a more significant number of active sites. So, the catalytic

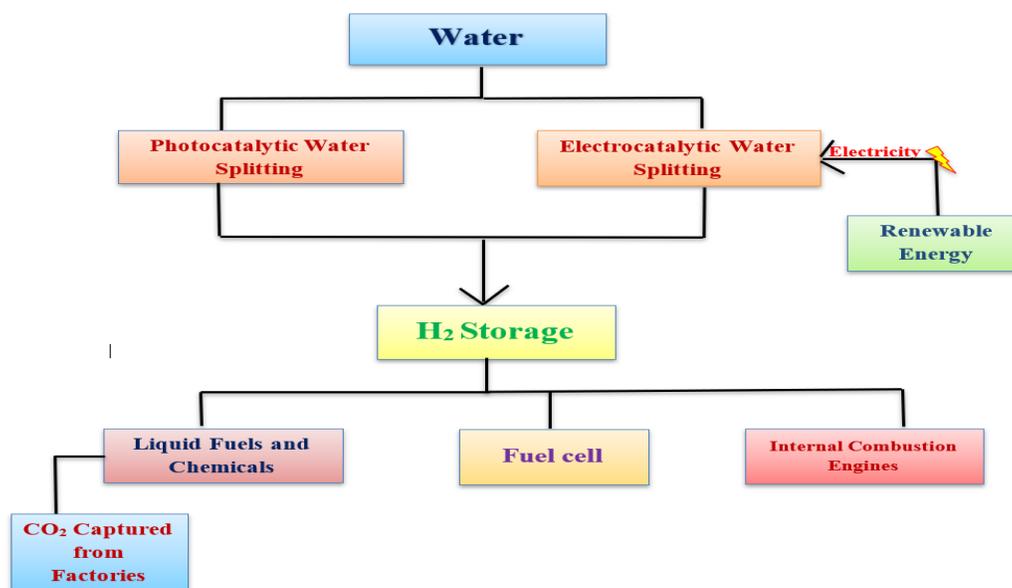
activity of transition metal phosphides is determined by the balance of metal and P content. Metal phosphates have excellent photon conductivity and strong redox ability. Cobalt phosphate electrolyzed water in a neutral solution for the generation of oxygen<sup>7</sup>. Silver phosphate is used under visible light for efficient water splitting because of its carrier generation ability and excellent light absorption<sup>8</sup>. The pore structure of organic hybrid metal phosphonates can speed up the mass transfer, and organic chromophores can increase light absorption, making them excellent photocatalysts and electrocatalysts<sup>9</sup>. P can act as a dopant to be incorporated into non-metals and metals to adjust electronic structure, light absorption capacity, and bandgap.

## **2. Fundamentals of phosphorus-containing catalysts for photocatalytic, photoelectrochemical, and electrocatalytic water splitting.**

### **2.1 Basic Principles of photocatalytic, photoelectrochemical, and electrocatalytic water splitting.**

As shown in Figure 1, we can utilize renewable energy sources to split water and produce hydrogen through electrocatalytic and photocatalytic technology. Hydrogen acts as a medium to convert water and renewable energy into fuel cells and internal combustion engines.

Carbon dioxide captured from factories can react with hydrogen to produce fuels and chemicals, so developing electrolytic and photocatalytic water splitting technology becomes very important.



**Figure 1:** Flowchart of sustainable hydrogen fuel cycle based on electrocatalytic and photocatalytic water splitting

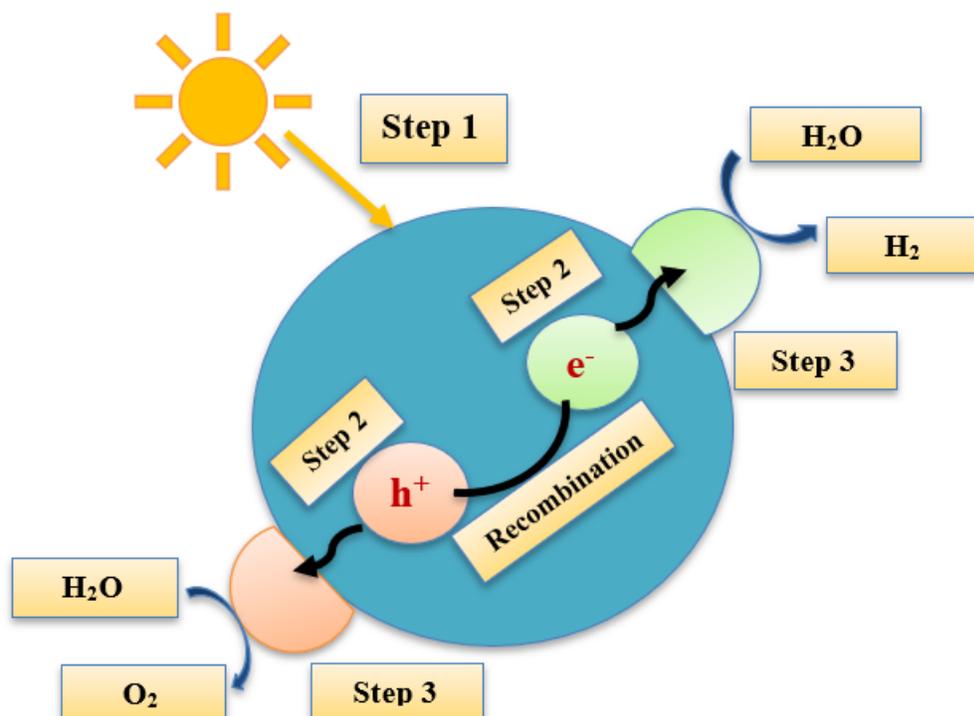
### 2.1.1 Photocatalytic water splitting:

Photocatalytic water splitting, which is also considered artificial photosynthesis, is a severe reaction, and there is an increase in Gibbs free energy<sup>10</sup>. In photocatalytic water splitting, there are three processes: the first one is light-harvesting, the second is charge separation and migration, and the last one is redox reaction taking place at the surface. (Figure 2) First, a catalyst absorbs photons from the irradiated light source at specific wavelengths. The photons having equal or more energy compared to bandgap energy of catalyst excite the electrons from the valence band to conduction band, which results in the formation of excited electrons-hole pair simultaneously. In the second step, electrons & holes are separated, and they move towards active surface sites. In the last step, the photoexcited carriers and surface-active sites induce the redox reaction<sup>11</sup>.

For effective photocatalytic water splitting, a photocatalyst needs to fulfil certain conditions including charge separation, bandgap, and active sites. The electrons in the conduction band reduce the protons to generate hydrogen. Oxygen is produced

via the oxidation of water molecules by the holes in the valence band. This implies that the valence band maximum should be more positive as compared to  $O_2/H_2O$  oxidation potential and the conduction band minimum should be more negative compared to  $H^+/H_2$  reduction potential. During the separation of charges and migration of charges, the photoexcited electron present in the conduction band moves to the valence band where they recombine with holes to decrease the rate of reaction. The defects present in the photocatalyst can act as recombination centres of holes and electrons<sup>12</sup>. Photocatalysts should have minute particle size and high crystalline quality so that there is no recombination of holes and electrons. There should sufficient surface-active sites because they play a vital role in photocatalytic reaction. If there are fewer active sites, then there are chances of recombination of holes and photogenerated electrons transferred to the catalyst's surface.  $Pt$ ,  $P$ ,  $IrO_2$  are some oxygen evolution reactions and hydrogen

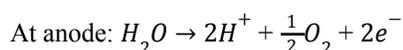
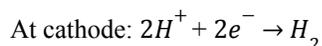
evolution reaction catalysts that can act as co-catalysts for photocatalytic water splitting



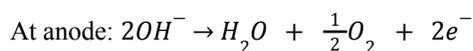
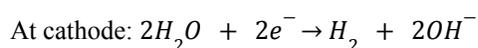
**Figure 2:** Steps followed in photocatalytic water splitting: step 1 is the absorption of light; step 2 is charge separation and migration and, step 3 is redox reaction taking place at the surface

**2.1.2 Electrocatalytic water splitting:** There are two half-reactions in electrocatalytic water splitting. One is the hydrogen evolution reaction at the cathode and another is the oxygen evolution reaction at the anode. The water-splitting reaction has distinct expressions depending on the pH value of electrolytes (Figure 3).

In acidic solution:



In neutral or alkaline solution -:



The hydrogen evolution reaction initiates with the Volmer reaction in which the catalyst absorbs H atoms. Then the H atoms that are adsorbed on active sites react with another proton which diffuses to the surface of the catalyst to generate hydrogen by electrochemical desorption which is known as the Heyrovsky reaction. There is another possibility that the adsorbed H atoms on the active sites combine with the adjacent adsorbed H atoms to produce hydrogen by chemical desorption which is called a Tafel reaction. To determine the kinetics of reaction and mechanism of hydrogen evolution reaction catalyst, we can use Tafel slope.

The mechanism of oxygen evolution reaction has not been explained fully but the most acknowledged

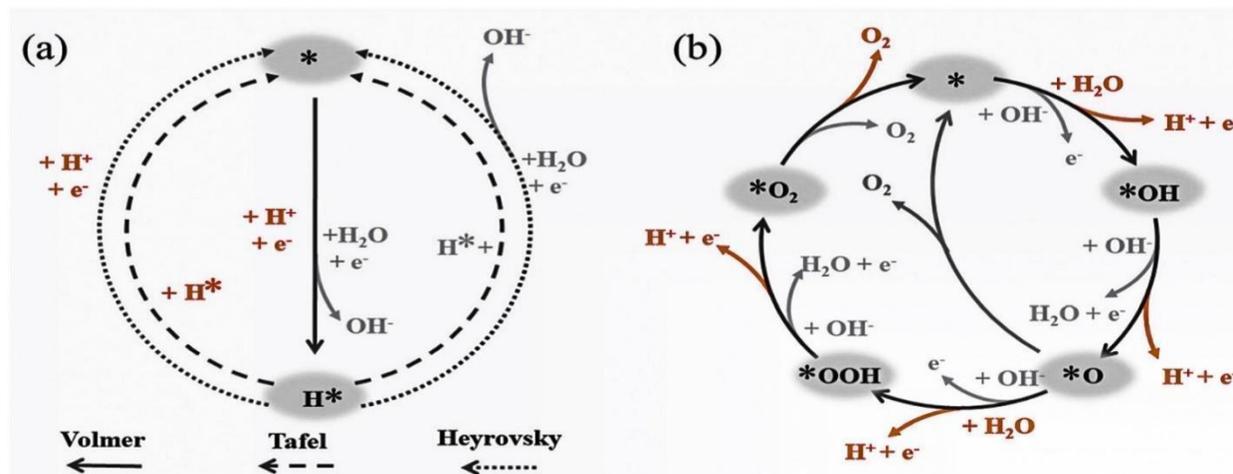
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reaction pathway of oxygen evolution reaction is the combination of two adsorbed oxygen intermediates to produce oxygen<sup>13</sup>. The oxygen evolution reaction is more complex because it involves the adsorption of  $\text{OH}^-$  and desorption of protons and also produces  $\text{*OH}$ ,  $\text{*O}$ ,  $\text{*OOH}$ , and  $\text{*O}_2$  intermediates. In each step, there is an accumulation of potential barriers which results in slow kinetics of oxygen evolution reaction and it will require a high overpotential to overcome the barrier<sup>14</sup>.

An excellent electrocatalytic reaction can be attained on the catalyst surface with moderate bonding energy. If there is a very strong bond present between catalyst surfaces and intermediates then the reaction will become very slow because there will be slow desorption of products which will limit the number of available active sites. If the bonding is very weak then also the reaction will become slow because then

the intermediate will adsorb very slowly. A moderate bonding between the catalyst surfaces and intermediates assisted an ideal balance between the combination of intermediates and removal of intermediates, which helps in easy detachment of hydrogen and oxygen. The Gibbs free adsorption energy ( $\Delta G$ ) is used to reflect adsorption properties.  $\Delta G_{\text{H}^*}$  is equal to or closer to zero for hydrogen evolution reaction and noble metals which can meet the above conditions are Pt and Pd.

The electrocatalytic activity is a function of  $\Delta G_{\text{O}^*} - \Delta G_{\text{OH}^*}$  in oxygen evolution reaction and shows a volcano shape<sup>15</sup>. At the top of the volcano, iridium and ruthenium-based compounds are present and have outstanding oxygen evolution reaction performance.



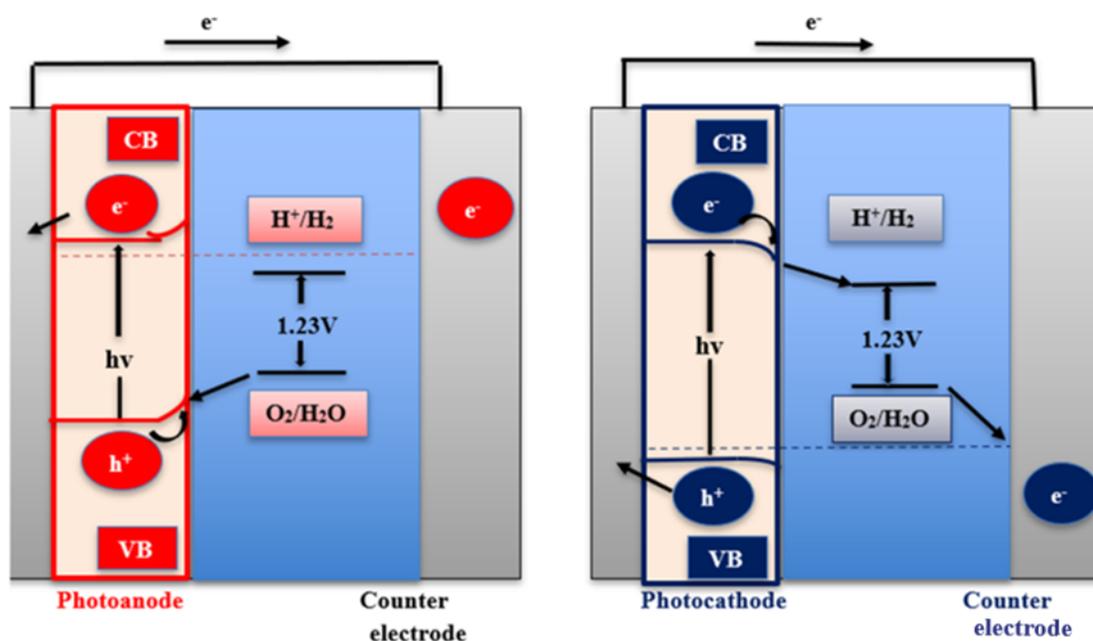
**Figure 3:** Hydrogen evolution reaction mechanism (a) and oxygen evolution reaction mechanism (b) in acidic (brown) solutions and alkaline (grey) solutions (\* refers to the active sites on the catalyst)

**2.1.3 Photoelectrochemical water splitting:** The combination of photocatalytic water splitting and electrolytic water splitting is photoelectrochemical water splitting. In the photoelectrochemical water splitting, the utilization of electrical energy is very less because it can make full use of solar energy. The sunlight and bias provide the required energy to derive photoelectrochemical water splitting. To compensate for the potential gap between the work

function of the counter electrode and the fermi level of the semiconducting electrode, an external bias is applied between the counter electrode and the working electrode<sup>16</sup>. (Figure 4) In the n-type semiconducting photoanode, the photoinduced holes that are accumulated on the surface react with water to produce oxygen and through an external circuit, the electrons migrate to the counter electrode to generate hydrogen. In a p-type semiconducting

photocathode system, oxygen is produced at the counter electrode, and hydrogen is produced at the working electrode. Like photocatalytic water splitting, the selection standard for photoelectrodes for photoelectrochemical water splitting is based on light absorption, active sites, and separation and migration of photogenerated carriers. But the only difference is photoelectrochemical water splitting is performed on two photoelectrodes that are photocathode and photoanode. This helps in easy

separation of the products and also lowers the requirements for semiconductor band gaps. The valence band of the photoanode catalyst should be more positive compared to oxygen evolution potential and the conduction band of the photocathode catalyst should be more negative compared to hydrogen generation potential.



**Figure 4:** Photoelectrochemical water splitting cells

## 2.2 Activity origin of different P-containing compounds

In photocatalytic and electrocatalytic water splitting, P-containing compounds have made notable achievements and they can replace noble metal catalysts. The differences like composition, structure, valency, coordination, etc. in phosphorus-containing compounds lead to differences in their catalytic activity.

### 2.2.1 Elemental Phosphorus

There are three main allotropes of phosphorus and they are white phosphorus, black phosphorus, and red phosphorus, under specific conditions, they can be converted into each other. White phosphorus has a tetrahedral structure and is highly reactive, volatile, poisonous, and ignites easily in air and so it has a limited number of applications whereas black phosphorus and red phosphorus have low toxicity and they are highly stable, have high conductivity, and sufficient band gap, and they are widely used for energy-related applications.

Red phosphorus is the most abundant allotrope and is classified into five different types- amorphous phase, hitorf phase, hexagonal phase, fibrous phase, and metastable phase<sup>17</sup>.

Fibrous and hitorf red phosphorus have similar crystal structures. They have a layered structure which allows them to be exfoliated to a few layers and even to a monolayer. The monolayer Hittorf's phosphorene has enhanced conductivity, bandgap, and band energy compared to bulk Hittorf phosphorus. When many honeycomb monolayers called phosphorene combine through van der Waals forces of interaction form bulk black phosphorus. Each monolayer shows a double-layer structure in the zigzag direction and puckered structure along the armchair direction. In black phosphorus, reducing the number of layers from bulk crystals to monolayer will result in a blue shift in absorption infrared light to U.V., bandgap also increases ranging from 0.3eV to 2.0 eV, and also charge mobility can also be affected by structure direction. As compared to the zigzag direction, the armchair direction has 16 times higher photon diffusion, 14 times greater electron mobility, and 10 times higher absorption coefficient<sup>18</sup>. So, the armchair direction has enormous potential in photocatalytic and electrocatalytic reactions because of its outstanding ability of charge mobility and light absorption.

### 2.2.2 Transition metal Phosphides

For electrocatalytic and photocatalytic water splitting, transition metal phosphides are highly favourable because of their polytropic composition and structures, enhanced electrical conductivity and suitable redox potentials<sup>19</sup>. In transition metal phosphides, the bond between metal and phosphorus is covalent as well as ionic which provides high chemical and thermal stability to transition metal phosphides. Transition metal phosphides with formula  $M_xP_y$  can be categorized into two types- metal-rich phosphides where  $x > y$  and phosphorus-rich phosphides where  $x < y$  depending on the stoichiometric ratios<sup>20</sup>. In metal-rich

phosphides, superconducting characteristics of transition metal phosphides can be achieved by the presence of a metallic bond(M-M). The high chemical and thermal stability of transition metal phosphide is provided by partial electron transfer on the covalent bond  $(M^{\delta+} - M^{\delta-})$ <sup>21</sup>. For example, *GaP* and *InP* are well-known semiconductors, the unique metallic properties are shown by *CoP*, *Fe<sub>2</sub>P*, *TiP* and *Ni<sub>3</sub>P*, *W<sub>3</sub>P* and *Mo<sub>3</sub>P* have superconducting characteristics. In phosphorus-rich phosphides, the high amount of phosphorus encourages the formation of a P-P bond which enhances the reactivity and reduces stability and conductivity. With different Ni/P stoichiometric ratios, nickel phosphides can exist in nine phases. For electrolytic and photocatalytic hydrogen evolution reactions, *Ni<sub>5</sub>P<sub>4</sub>* has displayed excellent activity. For electrocatalytic oxygen evolution reaction, metal-rich nickel phosphides have exhibited superior catalytic activity. *Ni<sub>2</sub>P* with suitable phosphorus content has acted as a bifunctional catalyst towards oxygen evolution reaction as well as hydrogen evolution reaction<sup>22</sup>. So, transition metal phosphides with a proper proportion of phosphorus should be designed to accomplish exemplary catalytic performance.

### 2.2.3 Metal Phosphorus Trichalcogenides

Metal phosphorus trichalcogenides have the formula  $MPX_3$  where M is a metal and X is S or Se. They have a 2D layered structure. They possess important properties like ionic conductance, magnetism, wide bandgaps, intercalation, reduction behaviour etc<sup>23</sup>. The oxidation state of phosphorus is +4 in metal phosphorus trichalcogenides and metal cations have generally a +2 oxidation state. There can be even monovalent and trivalent metals and they can exist as mixed valence to attain charge neutrality. Some examples are  $Mn_{0.5}Ag_1PS_3$  and  $Cr_{0.5}Ag_{0.5}PS_3$ . All metal phosphorus trichalcogenides have  $(P_3S_6)^{4-}$  or  $(P_2Se_6)^{4-}$  anion sublattice that can exist within each

layered crystal. The value of the bandgap is decided by the metal cations. The bandgap of sulphides is more as compared to selenides when metal cations are consistent and it is because S is more electronegative than Se. On comparing with bulk structure, Metal phosphorus trichalcogenides having 2D layered structures have higher strength for light absorption ranging from UV to near-infrared region. For effective electrocatalytic and photocatalytic water splitting, metal phosphorus trichalcogenides are considered as promising candidates because of their exceptional electronic structures, intense light absorption and 2D morphology.

#### 2.2.4 Metal Phosphates/Phosphonates

Metal phosphates and metal phosphonates are flourishing P-based catalysts because they are inexpensive, have ample reserves and have exceptional physicochemical characteristics. For electrocatalytic oxygen evolution reaction, cobalt phosphate is considered to be an outstanding catalyst in a neutral medium. The proton coupling electron transfer process was put forward in which there is a dynamic equilibrium between  $Co^{+3} - HPO_4^{2-}$  and  $Co^{+2} - HPO_4^{2-}$  which assures great stability of cobalt phosphates in the oxidation process and the whole process, proton acceptor  $HPO_4^{2-}$  plays a very important role. In metal phosphates, there is a strong ionic bonding between metal cations and phosphates. The metal species in various oxidation states can increase their redox ability and high protonic conductivity is provided by the phosphate group. Outstanding electrocatalytic oxygen evolution performance is exhibited by some transition metal phosphates (Mn, Fe, Co, Ni, Cu) and noble metal phosphates (Ir and Ag)<sup>24</sup>. Taking the example of cobalt phosphates, phosphates are very useful as they activate the distorted geometric structure of cobalt to encourage the water molecules' adsorption and also act as an acceptor of proton to increase the stability of the catalyst. Metal phosphates with light response capability are used to catalyse the photocatalytic

water splitting and examples include Ti, Fe, Cu, Bi, Zr, Ag phosphates. For photocatalytic hydrogen evolution reactions, cobalt phosphates are used as co-catalysts<sup>25</sup>. Regardless of whether the oxidation of water is driven by electricity or light, silver phosphate is considered to be an excellent catalyst. The body-centered cubic silver phosphate consists of isolated regular phosphate tetrahedral unit cells that lead to exemplary protonic conductivity and also trap holes and reject electrons to encourage the separation of holes and electrons that are induced by light.

Metal phosphonates have manageable porosity and are formed by the coordination between metal atoms and organophosphorus ligands, and they form a very strong bond. They are applicable even in harsh conditions because they have excellent acidic, mechanical, and thermal stability. Metal phosphonates have the capability of light-harvesting and surface functionality which can be altered by changing the organophosphorus ligands or the metal cations. Metal phosphonates have found applications in environmental and energy uses like catalysis, energy storage, and adsorption. For electrocatalytic and photocatalytic water splitting, cobalt and nickel phosphonates have proved to be excellent catalysts<sup>26</sup>. For photocatalytic hydrogen evolution reactions, titanium phosphonates have been explored as efficient catalysts.

#### 2.2.5 P-doped materials

To alter the electronic and chemical properties of photocatalysts and electrocatalysts, phosphorus can be used as a dopant. In the photocatalytic process, the addition of phosphorus can narrow the bandgap and produce charge imbalance which further improves the transfer of electron and obstruct the recombination of photoinduced charge electrocatalysts containing phosphorus exhibit remarkable electronic conductivity and hydrophilic acid surface which leads to enhancement of electrocatalytic performance<sup>27</sup>. phosphorus has the capability of stabilizing nanostructures which can maintain outstanding catalytic activity even in harsh conditions.

Now let us take an example of phosphorus-doped  $TiO_2$  where Ti can be substituted by  $P^{+5}$  cation to form Ti-O-P in an environment which is rich in oxygen while oxygen can be substituted by  $P^{-3}$  anion in an environment that is rich in Ti. This can be recognized by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy and DFT calculation<sup>28</sup>. The advantage of  $P^{+5}$  cation is that it can slow down the growth of crystal grains and stabilize anatase  $TiO_2$  which leads to the magnified specific surface area, improved stability and enhanced catalytic activity<sup>29</sup>. The advantage of  $P^{3-}$  anion is that elevating the valence band can broaden light absorption to the visible light region. In addition, there can be a transformation of Ti-O-P to phosphates by increasing the phosphorus content which can help in the separation of photogenerated carriers because of the conjugated structure of  $O-P=O$ .

By carbonization of carbon precursor and phosphorus-containing compounds, we can synthesize phosphorus-doped carbon compounds<sup>30</sup>. In phosphates, phosphorus exists in the pentavalent tetracoordinate form where some P-O bonds can be substituted by P-C bonds. Two-dimensional  $g-C_3N_4$  is one of the most well-known carbon compounds which are formed by tris-S-triazines joined through tertiary amines where phosphorus can be present in three doping states that are P-N bonds, P-C bonds, and interstitial dopants<sup>31</sup>.

### 3. Conclusion

The generation of hydrogen by photocatalytic and electrocatalytic water splitting are notably green technologies. In photocatalytic and electrocatalytic reactions, phosphorus-containing compounds have proved to be excellent catalysts because of their unique properties. Despite the enormous progress that has been made, there is a lot of research needed to be done on phosphorus-containing photocatalysts and

electrocatalysts and for that, we need to overcome a lot of challenges in the coming future.

There is still a lot of mechanism investigation that has to be made for phosphorus-containing photocatalysts and electrocatalysts. There are chances that under photo-induced oxidation, phosphorus in its elemental state undergo corrosion for which the underlying mechanism has been questionable until now.

During the electrocatalytic process, transition metal phosphides, metal phosphates, and metal phosphonates undergo reconstruction but in elemental phosphorus and metal phosphorus trichalcogenides, such transformation is not observed.

So, the study of catalyst mechanism becomes very important because it will provide proper direction for optimization of electrocatalytic and photocatalytic performance. If there is no authentic data to assess catalytic performance in electrocatalytic and photocatalytic water splitting, then the comparison between different systems becomes insignificant. Temperature, reaction media, source of light, photocatalyst mass, all these parameters can lead to different catalytic activity in photocatalytic water splitting. The parameters like scan rate, reaction solutions, mass loading of catalysts on the electrode can have a significant influence on electrocatalytic performance. There is an overlap observed in oxidation peak of transition metal phosphides with oxygen evolution reaction onset current during the estimation of activity of oxygen evolution reaction done by the help of linear cyclic voltammetry, which can cause the overestimation of the activity.

So, it is imperative to perform benchmark research on electrocatalysts and photocatalysts required to optimize catalytic performance. Towards oxygen evolution reaction and hydrogen evolution reaction, the phosphorus-containing compounds have a single function, and especially for photocatalysis, the overall water splitting is not effective. So, bifunctional phosphorus-containing catalysts are

required to increase the activity of hydrogen evolution reaction and oxygen evolution reaction. The cost of catalysts has been lowered by the use of phosphorus-containing compounds but still, efficient approaches are required for their synthesis to avoid harsh conditions like high pressure and temperature and production of poisonous  $PH_3$  gas. In photochemical water splitting, some concerns require attention like the change in the temperature of the cell

while operating and electrolyte circulation. Renewable energy sources such as wind turbines; photovoltaic modules can be integrated with electrochemical devices to lower the cost by designing corresponding configurations. So, it is predicted that the research that is being carried out in this particular field will surely overcome these issues to design more efficient phosphorus-containing catalysts for the production of green hydrogen.

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