



Splitting of Water by Artificial Photosynthesis

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The energy requirement of the growing humanity as well as increased industrialisation is causing an energy crisis in the world. To overcome this crisis, it is crucial for us to develop clean, low cost and renewable sources of energy. Mimicking the natural photosynthesis in the form of photocatalytic water splitting to generate hydrogen is a viable option. Hydrogen can be used as a clean fuel to solve the energy crisis. Photocatalytic splitting of water utilises the sunlight to split water into hydrogen and oxygen, and we examine important aspects of photocatalytic water splitting in this article.

1. Introduction

The rate of depletion of fossil fuels and the environmental concerns caused by them has made it mandatory for researchers to search for a clean, renewable and inexpensive form of energy. In this regard, an inexhaustible energy source available to humanity is solar energy reaching earth's surface. There have been several attempts to utilise solar energy in the form of solar cells [1], photocatalytic water splitting [2], CO₂ reduction [3] and so on. Photocatalytic water splitting is a promising approach to solve the energy crisis as it produces hydrogen. Hydrogen is a good fuel for future purposes as it is the cleanest source of energy producing only water on burning and with the highest energy density per unit weight. In nature, plants convert solar energy to chemical energy in the process of photosynthesis. To mimic the process in nature, we have to first understand the process of natural photosynthesis and arrive at a strategy to make suitable catalysts for the efficient photocatalytic splitting of water.

2. Natural and Artificial Photosynthesis

Photosynthesis in plants occurs at reaction centres which are transmembrane proteins. The two reaction centres, PSII and PSI, are used in series in the so-called Z-scheme (Fig 1a)[4]. The reaction centres contain antenna pigments which capture high energy photons as excitons and then funnelling them to the reaction centres leading to charge separation [5]. PSII utilises the visible light to carry out four-electron oxidation of two water molecules to oxygen. PSII (or P680) absorbs a photon and transfers an electron to pheophytin forming P680⁺. The electron is transferred to PSI along a chain of molecules in order to reduce charge recombination. P680⁺ subsequently takes an electron from water, oxidising it to oxygen, in a reaction catalysed by a water oxidising centre which is a cubic Mn₄O₅Ca cluster (Fig 1b)[6]. The H⁺ formed as a by-product of this reaction is reduced in the PSI. PSI (or P700) absorbs light and transfers an electron to reduce the H⁺ converting NADP⁺ to NADPH and generating P700⁺. The electron from PSII is taken up by P700⁺ returning it to its resting state thereby completing one cycle of photosynthesis.

Following the processes in natural photosynthesis, similar systems can be designed to carry out the process in the laboratory. Artificial photosynthesis consists of a light-harvesting unit, a catalytic centre and an electron-hole transfer pathway, suitably coupled with the two. It can be carried out in a single or a two-step process. The single step process involves a single photon absorber directly attached to an electron donor and an electron acceptor (Fig 2a). The excitation site can be a dye molecule or a semiconductor. The absorption of light depends on the band gap of the semiconductor or the HOMO-LUMO gap of the dye molecule. The electron donor and electron acceptor should meet some principal requirements. The energy level of the electron donor must be more negative than the excited state reduction potential of the semiconductor or the dye and more positive than the water oxidation potential. Similarly, for the electron acceptor, its potential energy levels must be between those of the semiconductor or dye excited state oxidation potential and the reduction potential of water.

Analogous to the Z-scheme in natural photosynthesis the two-step process of artificial photosynthesis involves two-photon absorbers connected to each other by an electron-transfer relay material. It utilises two photons to generate one electron-hole pair. The two-step process can utilise lower energy sunlight, as low as infrared, to carry out the overall water splitting (Fig 2b). The single-step process is simpler in comparison to the Z-scheme but has several drawbacks such as the choice of the chromophore is limited due to the constraint on the potential energy of the excited state reduction and oxidation. Moreover, only a fraction of sunlight can be utilised in this process. The two-step process although utilising lower energy sunlight faces difficulty in maintaining the kinetics of the full electron-transfer process with minimal energy loss by charge carrier recombination.

3. Photocatalytic splitting of water

Several efforts have been made to mimic natural photosynthesis, involving splitting of water to produce hydrogen and oxygen via two redox reactions:

Reduction: $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$ (0V vs. SHE)

Oxidation: $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$ (1.23V vs. SHE)

From the above chemical equations, it is evident that the water-splitting reaction requires a minimum of 1.23 eV, hence is an uphill process with a Gibbs free energy change of 237.2 kJ mol⁻¹. The oxidation half of the water splitting reaction has been shown to be the rate determining step in the overall reaction. In a study by Tang *et al.* it was shown that O₂ production takes ~1 s and the quantum yield peaks at 4 photons/particle [7, 8]. The first example of the overall splitting of water was reported by Fujishima and Honda in 1972 with TiO₂ photoelectrodes under UV illumination [9]. The mechanism of natural or artificial photosynthesis broadly involves three aspects or steps: (i) absorption of light, (ii) generation and separation of charge carriers and (iii) redox reactions (Fig 3).

Photocatalytic splitting of water can be carried out via two types of processes as mentioned above: one-step and a two-step process. The one-step process involves splitting of water into hydrogen and oxygen by a single photocatalyst. This photocatalyst must have thermodynamic potential suitable for water oxidation and reduction. The second approach, the two-step process, inspired by the natural Z-scheme uses two different photocatalysts (Fig 4)[10].

The overall photocatalytic splitting of water employing a single photocatalyst is a challenging task, but one can preferentially carry out either water reduction (hydrogen evolution) or water oxidation (oxygen evolution) by the use of suitable sacrificial agents (electron or hole scavengers). Splitting of water has been carried out by employing various types of catalysts broadly semiconductors based catalysts and dye-sensitised catalysts.

3.1 Semiconductor Catalysts

Semiconductors absorb photons of energy greater than its bandgap, generating an electron-hole pair. The electrons and holes subsequently migrate to the surface to carry out the redox reactions. Charge carrier recombination competes with the separation of charges and redox reactions. The position of the valence and conduction bands of the semiconductor determines the feasibility of the redox reactions.

After the excitation of the electron, the electron in the conduction band reduces the proton to hydrogen while the hole in the valence band oxidises water to oxygen. The potential of the electron and hole should be high enough to carry out the reduction and oxidation reactions, respectively. Thus, the conduction band minima must be more negative than the reduction of H⁺/H₂ (0V vs SHE) and the valence band maxima must be more positive than the O₂/H₂O (1.23V vs SHE). This puts a theoretical limit on the minimum band gap of the semiconductor as 1.23 eV (Fig 5). For a semiconductor to be a suitable catalyst for the splitting of water must fulfil this condition. Fig 6 shows various semiconductors and their comparison with water reduction and oxidation potential.

Use of a sacrificial agent in the system provides a control over the products obtained. A hole scavenger, which is a strong reducing agent such as an alcohol or sulphide, gets oxidised by the hole in the VB (instead of water) suppressing the oxidation of water. Similarly, an electron scavenger gets reduced by the electron in the CB whereby suppressing the reduction of water. The use of a hole scavenger leads to only the hydrogen evolution reaction (HER) while the use of an electron scavenger leads only to the oxygen evolution reaction (OER).

3.2 Dye-sensitized Catalysis

Semiconductor photocatalysts suffer from the problem of a large band gap and inefficient utilisation of solar spectrum. These problems can be solved by sensitization of semiconductor with dyes, where it acts as a visible light responsive component. On absorbing a photon an excited electron is generated in the dye and if the excited state oxidation potential of the dye is more negative than the CB of the semiconductor, the electron is transferred to the CB of semiconductor, eventually causing a reduction a reaction [11, 12] (Fig 7). The dye can be replenished by a sacrificial electron donor or redox shuttle such as I³/I⁻. A variety of materials in combination with dyes have been studied for the splitting of water [13, 14].

4. Reduction of Water

The simplest hydrogen evolution catalysts are semiconductor-based photocatalysts where the semiconductor acts as both the photon absorber and catalyst. Semiconductors such as CdS, CdSe, TaON, Y₂Ta₂O₅N₂, ZnO, etc. have been studied extensively in this regard [15]. An ideal oxide semiconductor photocatalyst for the hydrogen evolution reaction (HER) must have a sufficiently negative conduction band for H₂ generation and a narrow band gap for visible light absorption, but it is difficult to develop such an oxide semiconductor.

Few semiconductors possess the desirable VB and CB positions for overall water splitting and various means have been employed to synthesize the semiconductor photocatalysts with desirable features. Modification of the electronic structure by doping of cations and anions, for example, doping of nitrogen in large band gap semiconductors like TiO₂, ZnO decreases their band gap, making them photocatalytically active in the visible spectrum. Doping of oxides with only N induces defects and charge imbalance leading to recombination of charge carriers. Aliovalent anion substitution of F with N overcomes all these problems. Co-doping of N and F in ZnO has been shown to decrease the band gap considerably, rendering ZnO active in the visible spectrum and making it more active towards the reduction of water [16, 17].

Redox reactions of water splitting happen on a microsecond timescale whereas the charge carrier recombination occurs on a nanosecond timescale. This implies that most of the e⁻-h⁺ pairs recombine before going to the surface for the redox reactions. Physical separation of water reduction and oxidation sites by using NiO-NaTaO₃ heterostructure has been demonstrated by Kato *et al.* [18] as an efficient method to overcome the fast charge carrier recombination. Various researchers have since explored various types of semiconductor heterostructures such as ZnO/CdS [19], TiO₂/SrTiO₃ [20], etc. ZnO/CdS exhibit lifetimes up to 220 ns, whereas individual ZnO and CdS have a decay lifetime of only 60 ns [19]. A Pt-tipped CdS nanorod with embedded CdSe has been developed by Alivisatos and co-workers which has tunable properties [21]. Heterostructures of these types have a type II band alignment which ensures enhanced charge separation (Fig 8). The charge separation and water splitting activity can be further enhanced by the use of co-catalyst such as RuO₂ and Pt which provides active sites for surface redox reactions.

Heterostructures of the type ZnO/Pt/CdS, ZnO/Pt/Cd_{1-x}Zn_xS and ZnO/Pt/CdS_{1-x}Se_x have been recently employed for water splitting under UV-visible and visible irradiation in our group (Fig 8) [22]. It has been shown that by substitution of the anion and the cation in CdS modifies the optoelectronic properties of the ZnO/Pt/CdS heterostructures. A hydrogen evolution rate of 31.2 mmol h⁻¹ g⁻¹ with an apparent quantum yield (AQY) of 23.1% was obtained for ZnO/Pt/Cd_{0.8}Zn_{0.2}S under UV visible irradiation in the presence of Na₂S-Na₂SO₃ as hole scavengers. This study was further extended by using doped ZnO in the heterostructures. Heterostructures of the type ZnO_{1-x}(N, F)_x/Pt/CdS are indeed more active than the un-doped ZnO heterostructures exhibiting a hydrogen evolution rate of 43 mmol h⁻¹ g⁻¹ and AQY of 44% under visible light irradiation in the presence of benzyl alcohol-acetic acid as hole scavengers [23].

Another interesting hydrogen evolution catalyst is MoS₂, which is found to be useful both for electrochemical and photochemical hydrogen evolution reaction. The edge structure of MoS₂ bears a close resemblance to the active site of nitrogenase (hydrogen-producing enzyme), and it was shown theoretically as well experimentally that edges of MoS₂ are catalytically active, while the basal planes are inert [24, 25]. Bulk MoS₂ has an indirect band gap of 1.29 eV and on sensitisation with [Ru(bpy)₃]²⁺ shows photocatalytic HER activity. MoS₂ crystallites supported on a conducting but otherwise inert substrate are good materials for HER. Enhanced HER has been reported for MoS₂ supported on graphene [26] or carbon nanotubes [27]. A composite of MoS₂ with heavily nitrogenated RGO shows excellent HER activity, where incorporation of N in graphene enhances the electron donating ability of graphene. Single layers of the metallic 1T polytype of MoS₂ was synthesized by Li intercalation followed by exfoliation which shows extraordinary HER activity of 30 mmol h⁻¹ g⁻¹ with a high turn-over frequency (TOF) of 6.25 h⁻¹ [13]. It is to be noted that the electrons used in the reduction of water are not photocatalytically generated on MoS₂ but transferred from the photosensitizer Eosin Y (EY). The photosensitization of EY generates highly reductive species EY[#] which subsequently donates an electron to MoS₂ [28] (Fig 9). The 1T polytype of MoSe₂ is even more active than the 1T MoS₂ with a HER activity of 62 mmol h⁻¹ g⁻¹ and TOF of 15.5 h⁻¹ [29]. A recent study from this laboratory shows a strategy to covalently cross-link C₃N₄ with sheets of MoS₂ as well as NRGO by carbodimide method. The study demonstrates beneficial effects of covalent bonding in C₃N₄-MoS₂ and C₃N₄-NRGO [30]. The cross-linked composites were shown to be more active than the C₃N₄ and MoS₂ separately. The enhanced HER activity is attributed to the increased planarity, enhanced charge transfer and higher surface area of the cross-linked composites (Fig 10). DFT calculations show that the charge transfer occurs between cross-linked layers simultaneously through bonds as well as space [30]. The above phenomenon is also confirmed by MoS₂-BCN composites which also show higher HER activity than the constituent compounds themselves.

5. Oxidation of Water

The oxygen evolution reaction (OER) which is an uphill reaction involving a four electron transfer process, is kinetically the key step in photocatalytic water splitting. RuO₂ and IrO₂ have been used widely as oxygen evolution catalysts [31-34]. The water oxidation catalyst in natural photosynthesis consists of cubane type Mn₄O₅Ca unit in PSII having [Mn₄O₄] core. Similar to the WOC in natural photosynthesis, Mn and Co oxides with cubane-type units such as [Mn₄O₄] and [Co₄O₄] [35-37], Marokite-type oxides, CaMn₂O₄ and CaMn₂O₄·xH₂O have been shown as water oxidation catalysts [38, 39]. Nanoparticles of β -MnO₂ obtained by delithiation of LiMn₂O₄ shows a much higher OER activity attributed to the extra flexibility of the [Mn₄O₄]

cubic unit (Fig 11) [40, 41]. Similarly, [Co₄O₄] cubic structural unit was demonstrated as the necessary criterion for catalytic activity of nanoparticles of Li₂Co₂O₄ [42]. A study from our group on Mn and Co oxides of spinel and perovskite structures shows that trivalency and the electronic configuration of the B-site metal cation is an important factor in determining OER activity. The cations with d⁴ and d⁶ configurations with a single electron in eg orbital show high activity irrespective of the crystal structure. Thus, Mn₂O₃, LaMnO₃ and MgMn₂O₄ with Mn in the +3 state with electronic configuration of t_{2g}³ eg¹ show good catalytic activity (Fig 12). Similarly, compounds with Co³⁺ in the intermediate spin state (t_{2g}⁵ eg¹), such as LaCoO₃ and Li₂Co₂O₄ also show high catalytic activity. The singly occupied eg orbital yields the appropriate strength for the interaction between oxygen and the catalyst required for OER activity. The eg orbital forms π -bonds with anion adsorbates and aids in the binding of oxygen-related intermediate species to the catalyst [43, 44].

6. Conclusions

There is need for concerted effort to solve the energy problem by discovering alternate sources. Water splitting to generate hydrogen using solar radiation is a viable option and there is considerable scope for innovation in this area. This article should serve to demonstrate the success and viability of photocatalytic splitting of water to produce hydrogen and oxygen, employing the strategy that nature adopts in photosynthesis.

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