Review

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Supported polyoxometalates as emerging nanohybrid materials for photochemical and photoelectrochemical water splitting

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Abstract: Sunlight and water are among the most plentiful and sustainable resources of energy. Natural photosystem II in the plants uses these resources in ecofriendly manner for the production of atmospheric oxygen and energy. Inspired by this natural process, the development of artificial catalytic system to facilitate the solar-induced water splitting for the continuous production of hydrogen is the holy grail of the chemist and energy experts to meet the future energy demand at minimal environmental cost. Despite considerable research efforts dedicated to this area in the last decade, the development of highly efficient, stable and economic photocatalysts remain a challenging task for the large scale H₂ production from water. Polyoxometalates (POMs)-based materials are emerging photo/photoelectrocatalysts in this quest owing to their multi-electron redox potential and fast reversible charge transfer properties, which are the essential requirements of photo-assisted water splitting catalysis. They are generally soluble in aqueous medium and thus their inherent catalytic/co-catalytic properties can be better exploited by

incorporating/immobilizing them over suitable support materials. Therefore, exploration of discrete POM units over the support materials possessing high surface area, functionalizable architecture, flexible pore size and good light harvesting ability is an attractive area of research that has resulted in the generation of a strong library of heterocatalysts. The underlying support not only offers stability and recyclability attributes to the POM units but also provides decent dispersion, easy/maximum accessibility to the active sites, enhanced absorption capability, and synergistically enhances the activity by transfer of electrons and efficient charge/carriers separation by creating POM-support junctions. This mini-review emphasizes on the strategies for the incorporation of POMs on various porous supports like metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), oxide-based semiconductors, carbonaceous materials, etc., and their applications as effective photo/photoelectrocatalysts for water splitting. In addition, the mechanistic study, comparative analysis and the future potential of these novel nanoscale materials is also highlighted. We believe that this review article will provide a new direction and scientific interest at the boundary of materials engineering, and solar-driven chemistry for the sustainable energy conversion/storage processes.

Keywords: hydrogen production; photocatalysis; polyoxometalates; water splitting.

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1 Introduction

An exponential increase in the world population and consequently the depletion of fossil fuels and their negative impact on the environment is posing a serious threat to the humanity. Therefore, harnessing energy from sustainable resources at an affordable cost is much needed than ever to ensure a sustainable and clean future [1]. The development of artificial systems mimicking natural photosynthesis has brought the technological vision of meeting the energy requirements and hence, is considered

as the most dynamic and contemporary research area to meet energy demand and global security [2, 3]. Being a renewable source of energy, photo/photoelectrocatalytic water splitting is a promising strategy for the production of H_2 as a green fuel of future, which can be used in a similar manner as fossil fuels [4, 5]. However, both thermodynamic ($\Delta G = 237 \text{ kJ mol}^{-1}$) and kinetic barriers are the associated challenges for the slow conversion of photon to chemical energy in water splitting module. Therefore, the utilization of effective light harvesting catalytic materials at molecular levels (both homo- and heterogeneous) are worth considering to make this process practically viable [6]. Photo/photoelectrocatalytic water splitting comprises of oxidation (O_2 production) and reduction (H_2 production) processes taking place at the valance band and conduction band of the semiconducting/light harvesting materials, respectively [7]. The efficiency and ability of the catalytic system generally depends upon the position of their redox bands and their compatibility with the respective thermodynamic redox potential of water splitting redox processes [8]. In this regard, several homogenous and heterogeneous catalysts have been developed for photocatalytic water splitting including metal-oxides (i.e., RuO_2 , IrO_2 , $CoOx$, CeO_2 , TiO_2 , etc.), carbon nitride, metal chalcogenides, and the combination of various heterostructured organometallic compounds and molecular complexes [9]. However, the associated problems that limit the large scale application of photocatalytic materials include their low absorption capacity, structural deterioration due to photocorrosion, fast charge (e^-/h^+) recombination and inappropriate band gap and band edge positions [10]. To address these challenges, development of new materials with perfect redox potentials, broad range light harvesting ability, appropriate photochemical stability, and reversibility under mild experimental conditions is highly desired [11]. The development of an effective photocatalytic system with desired properties is on high demand in order to ensure high photon to hydrogen conversion efficiency and extend the existing choices of photocatalytic water splitting redox mechanisms [12, 13].

Polyoxometalates (POMs) are the emerging class of molecular metal-oxo clusters having an ordered and discrete structures at the nanoscale length [14, 15]. POMs are formed by the polycondensation of MO_n polyhedra, where “M” is generally the early transition metal ion (known as addenda atom) in their highest oxidation state such as Mo^{VI} , W^{VI} , V^V , Nb^V and Ta^V and is linked to each other by corner, edge or in rare cases face sharing oxo ligands. The polyanions may or may not contain heteroatoms to form hetero- or isopolyanions, respectively. Keggin ion $[X_{12}O_{40}]^{n-}$ and Lindqvist ion $[M_6O_{19}]^{n-}$ are the

common examples of heteropolyanions and isopolyanions, respectively.

Though the structural chemistry of early transition metal-based POMs, like polyoxotungstates and -molybdates, has largely been studied and reported but an increasing interest in this field has also led to the discovery of noble-metal-based POMs such as Pd, Pt and Au having different shapes, sizes and compositions [16–18]. They are discrete units with unique electronic/catalytic properties, i.e., appropriate band edge position and reversible multi-electron redox potential [19]. These properties are highly dependent upon the nature and number of the atoms in the core of the clusters [20]. Owing to these unique properties, POMs have potential applications in diverse research fields [21, 22], i.e., biomedical, catalysis, optics, electrochemistry, Li/Na ion batteries and magnetism [23]. Due to their high solubility and sensitivity to the reaction medium, POMs are even used as molecular catalysts in chemical industries while offering models for the exploration of structure-activity relationships at the interface of the extended solid materials and molecules [24]. The diverse aptitude of POMs as an essential multifunctional catalyst is superior as compared to the traditional photocatalysts and thus can be preferably used to catalyze the challenging photo-assisted water splitting reaction [25, 26]. Recently, various POMs composed of cost effective and Earth abundant metals are reported as efficient water splitting catalysts [27, 28]. They are equally important in both homogeneous and heterogeneous catalysis due to the reversible step-wise multi-electron transformation ability and tunable redox properties [29]. However, difficulty in separation for reusability, processibility [30], self-aggregation [31] and sometimes less accessibility of the core atoms in the large cage-like structures are the serious challenges associated with POMs, which severely hamper their catalytic potential in homogeneous catalysis. In order to address these challenges, immobilization/heterogenization of POMs and their coupling with solid supports is an appealing approach to effectively utilize/enhance their inherent catalytic potential and, therefore, have attracted much attention recently especially in photo-assisted water splitting [32]. The heterogenization of POMs on various support materials such as mesoporous silica [33], polymers [34], zeolites [35], metal-organic macrocycles [36], titanium oxide [37], graphene oxide [38], carbon nitride [39], activated carbon [40], and covalent organic frameworks [41], etc. have been extensively explored for various applications. The immobilization of POMs on the support surface not only facilitates their separation and reusability [42], but also increases their surface area [43], conductance [44], stability [45], processibility, selectivity and light harvesting ability and therefore

ensure the energetic electron hole pairs generation that are essentially needed for the water splitting redox reactions [46]. The supported POMs work on the principle of light absorption by the semiconducting supports followed by the charge transfer to the redox active POMs, where the respective redox reactions take place.

In this manuscript, we will review the major developments made in POMs research with specific reference to their immobilization on various porous supports including metal organic frameworks (MOFs), covalent organic frameworks (COFs), oxide-based semiconductors and carbonaceous materials as photocatalytic and photoelectrocatalytic system in separate sections for water splitting catalysis. We will also discuss their synthetic schemes, mechanistic role in photo/photoelectrocatalysis and energy conversion schemes. We believe, this mini review will provide guiding principles towards the development of new metal-oxo cluster with controlled size, shape and composition to subsequently extend their horizon in catalysis science.

2 Basics of photocatalytic water splitting and associated challenges

In photocatalytic process, light striking on the surface of photocatalyst leads to electronic excitation from ground to excited states, creating electron-hole pairs (e^-/h^+) in the conduction and valence bands respectively [47–49]. The generated electrons/holes pairs are responsible to execute the water splitting redox processes at the respective positions. The overall water splitting process can be written as $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$ that comprises of two half ‘oxidation’ and ‘reduction’ reactions. In principle, $\text{OH}^-/\text{H}_2\text{O}$ is oxidized at the valence band (VB) with the production of electrons, protons and O_2 , while reduction of protons takes place at the conduction band (CB) by coupling with photo-excited electrons for the ultimate production of molecular H_2 [50]. During photocatalytic process, three major steps are involved for the overall water splitting process after the interaction of solar flux with light harvesting/catalytic materials. (1) generation of e^-/h^+ pairs [51]; (2) successful migration of e^-/h^+ pairs to the surface of catalyst and their survival till their utilization in redox reactions [52]; (3) effective utilization of e^-/h^+ pairs in water reduction/oxidation reactions [53] (Figure 1). It is noteworthy to mention here that there is an equal probability of e^-/h^+ pairs recombination via surface and volume recombination processes instead of their

migration to the surface for catalysis. In addition, the redox position of the VB (+1.23 V vs. NHE) and CB (0.00 V) for the oxidation and reduction process respectively also plays a key role in photocatalytic water splitting reactions. Therefore, the competency of photocatalytic materials for the generation of fruitful e^-/h^+ is dependent on various factors including (i) good light harvesting capability in broad range of the spectrum to ensure the maximum photons conversion to charge carriers (e^-/h^+) [54]; (ii) the band gap of photocatalyst should be wide enough ($\Delta G^\circ = 237 \text{ kJ mol}^{-1} \approx 1.23 \text{ eV}$) to meet the thermodynamic demands to trigger overall water splitting reaction [55]; (iii) the conduction band edge of photocatalyst should be comparatively negative than H^+/H_2 redox potential (0.0 V vs. NHE) whereas the valence band edge should be comparatively positive than $\text{O}_2/\text{H}_2\text{O}$ redox potential (1.23 V vs. NHE), in addition, the redox potential for hydrogen and oxygen generation depends upon the pH value of electrolyte [56]; (iv) Most importantly, the photogenerated e^-/h^+ must migrate to the surface reaction sites earlier than their recombination.

It means that the lifetime of charges should be prolonged enough to take part in respective redox reactions [57]. However, the fast recombination process, low absorption ability, mismatch of redox potential and high diffusion barrier for the charge transfer of fruitful catalysis process are the major problems that need to be addressed. Therefore, various strategies have been employed to tune

Figure 1: Schematic representation of (e^-/h^+) pairs generation upon irradiation of photocatalyst, their subsequent migration to the surface and utilization for H_2 and O_2 production respectively on the surface of cocatalyst. Adapted with permission from the study by Yang et al. [53].

the desired properties of photocatalytic materials while addressing the associated challenges to improve the overall photon to hydrogen conversion efficiency.

3 Possible solutions of aforementioned challenges

3.1 Light absorption

During photocatalytic water splitting process, it is necessary to use light harvesting materials having a suitable band gap to meet the thermodynamic demand (1.23 V) in the visible spectrum. However, due to the kinetic barriers, some overpotential is required to overcome the kinetic constraints and successful release of molecular products [58]. According to Marcus theory, higher the overpotential, faster will be the electron transfer to the catalytic site to accelerate the redox process [59]. While on the other hand, high overpotential restricts the choice of photocatalyst to only wide band gap materials that need to utilize UV light covering small portion of the light spectrum. Keeping in view the thermodynamic

and kinetic constraints, various strategies have been employed to optimally extend the range of absorption of photocatalytic materials [60]. One of the most proficient approaches to extend the range of absorption is band gap engineering, i.e., doping/substitution of suitable heteroatom in the framework of photocatalysts which creates additional levels within the band gap and consequently widens the range of absorption [5, 61–63] (Figure 2a); another important approach is the use of photosensitizers, e.g., Ru(bpy)₃ [64], BiVO₄ [65] and dyes [66] which can push/transfer electrons/charges to catalysts upon photoexcitation (Figure 2b) [67]. Decoration of nanoparticles with surface plasmonic resonance (Figure 2c) [68–70], and the development of heterojunction and Z-scheme [71–73] by combining two suitable semiconductors to ensure the sufficient absorption of light in the desired range of the light spectrum [74, 75]. In addition, lifting of the valence band (Figure 2d) by hybridization with suitable metal and endorsement of interband states by lattice point defects are the important strategies for the extension of absorption range of photocatalysts (Figure 2e) [76–78].

3.2 Charge separation

After the generation of (e^-/h^+) pairs, its separation must be maintained till their effective utilization in desired redox reactions. However, majority of the charge carriers recombine prior to their participation in the redox reaction because of their short survival life (nanoseconds) compared to water reduction (milliseconds) and oxidation (seconds) reactions [79]. In order to address this challenge, various strategies have been adapted to prolong the lifetime of charge carriers [67]. The effective approaches for the extension of lifetime of (e^-/h^+) pairs are (i) development of heterojunction by combining two different photocatalysts (PC–PC), where charge transfer from one photocatalyst to the other takes place and consequently delays the recombination [80]; (ii) incorporation/use of co-catalyst which can easily accept electrons or holes by their reduction and oxidation respectively. Apart from that, doping, surface defects, size/morphology control and development of Z-scheme play an important role in the suppression of charge recombination [81].

Figure 2: Extension of absorption range of a wide band gap semiconductor (SC) by various band gap engineering strategies, i.e., (a) energy transfer (ET) by upconverting rare-earth metals, e.g., Ln³⁺ dopant (b) dye and other sensitization (c) sensitization through plasmonic material by electron transfer (d) orbitals hybridization by doping which leads to lifting of valence band by high energy orbitals (e) creation of the interband states by lattice defects. Adopted with permission from ref. [74].

3.3 Effective charge utilization

In photo-assisted water splitting process, the subsequent interfacial charges (e^-/h^+) transfer to the adsorbate molecules (OH₂/H⁺/OH⁻) resulting in the production of redox

products (H_2/O_2), which is the determining factor of the rate of reaction [82]. Generally, only one reaction, either oxidation or reduction, takes place to deliver the respective desired product efficiently, and meanwhile, the other half reaction is scavenged by the sacrificial agents [83]. During reduction half reaction (HER), the holes are scavenged by reductive sacrificial agents, for example triethanolamine and isopropyl alcohol (PVA), etc. [84]. In contrast, during oxidation half reaction (OER), electron acceptor scavengers (e.g., $\text{Na}_2\text{S}_2\text{O}_8$) are used to impede the HER process [85]. However, it is necessary that the redox potential of sacrificial agent must be higher than that of the photocatalyst, which can be finely tuned by pH adjustment.

While taking into account the above strategies, the major challenges associated with water splitting catalysts are: low absorption capacity, structural deterioration due to photo-corrosion and fast charge carriers (e^-/h^+) recombination. Apart from many other materials explored during the last decades, POMs are also the emerging materials with the potential to address the associated challenges due to their inherent catalytic potential and tunable properties.

4 Polyoxometalates (POMs) as photocatalytic materials

In photocatalysis, the optical band gap and band edge positions are the defining parameters for the efficiency and selectivity of a particular photo-redox reaction [86]. The promising photocatalytic water splitting ability of POMs is attributed to their ideal redox potential and multi redox active sites [87]. More promisingly, the tunable architecture of POM, where the selective hydrolytic removal of addenda atoms generates reactive multidentate lacunary species, offers limitless synthetic modifications prospects and tunable properties [88]. They can easily accommodate organic [89], inorganic [90] and organometallic moieties [91]. POMs have discrete number of atoms in the core of the clusters and their electronic/catalytic properties can be dynamically altered to improve their selectivity and charge carrier properties in the opposite directions. Most importantly the incorporation of chromophore possessing moieties leads to the development of light harvesting functional nanoscale systems [92], which are capable of photo-generated charge transfer from light driven antennae to the redox active POM core and, therefore, accelerate the respective redox reactions with high photon to hydrogen conversion efficiency [93–95]. However, their high solubility in aqueous medium is a formidable challenge, which can be realized by their loading on various suitable supports.

5 Immobilization of POMs on porous supports

Exploration of suitable substrates for the immobilization of POMs has always been a fascinating research area to make them more useful especially in heterogeneous catalysis. In this regard, various types of support materials including $\text{g-C}_3\text{N}_4$, SiO_2 , TiO_2 , CNTs, GO, MOFs, COFs, etc. have been used for the immobilization of POMs. The support materials not only provide stability and extension of light harvesting capability to POMs but also help tuning their activity and selectivity for various catalytic reactions. Mesoporous graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), for example, has recently been recognized as an ideal support for the immobilization of POMs. The mesoporous structure of $\text{g-C}_3\text{N}_4$ not only enhances the catalytic activity of POMs but also provides a method for the stacking of catalytic sites per projected geometrical area to effusively utilize the solar flux [96]. Another interesting example of support materials is TiO_2 , a well-known photocatalytic semiconductor firstly used for photocatalytic water splitting by Fujishima and Honda [97, 98]. TiO_2 acts as an ideal support for the immobilization of POMs, where the POMs accept the photo-excited electrons from the conduction band of TiO_2 and prevent the recombination, resulting in better efficiency of the POM@TiO_2 catalytic system [99]. Similarly graphene oxide is also a highly stable support material which significantly enhances the efficiency of POMs due to its high conductivity and ease of electron transfer [100].

Among the various support materials, MOFs have recently emerged as a new class of porous, crystalline, cage-like heterogeneous support for the incorporation of POMs. The pre-/post-synthetic strategies of encapsulation and functionalization have attracted enormous research interest in the design and heterogenization of such catalytic materials. The incorporation of POMs into MOFs leads to new materials (POMOF) possessing the synergistic effect of both materials [101]. The reactivity and selectivity of POMs can be further tuned by altering the microenvironment by changing the MOF functionality [102]. The judicious selection of light harvesting linker of the MOFs and the appropriate redox active POMs synergistically enhance the photocatalytic activity by the transfer of photo-generated charges from MOFs to the redox active center POMs [103]. The well-designed POMOF materials cross the borderline between homogeneous and heterogeneous catalysis [104] with immensely enhanced properties [105], which are superior than either of constituent components [106].

6 Strategies for incorporation/immobilization of POMs on supports

There are four general strategies for the incorporation of POMs in the support materials, i.e., dispersion, tethering, grafting and encapsulation. However, unlike other conventional support materials, MOFs as a support have distinct incorporation strategies due to their unique tunable framework. POMs can be incorporated in MOFs by three main strategies, i.e., impregnation, encapsulation and co-precipitation, which are briefly described below.

6.1 Dispersion

Dispersion is the spreading of POMs on the surface of support materials that have no specific anchoring sites. However, due to weak physical interaction between POMs and the support in case of dispersion, this process generally results in the leaching of POMs from support surface during reaction.

6.2 Tethering

Tethering is the attachment of POMs to the support surface through spacer species. This strategy is based on the surface functionalization and creating cationic functional groups on the surface of support, which further electrostatically interact with the anionic POMs. Amino-functionalization is one of the most widely used strategy in this regard, which can be generally realized by using amino-alkyl silane derivatives, where the $-NH_2$ groups of silane and POMs interact by acid-base phenomenon [107].

6.3 Grafting

Grafting refers to the covalent attachment of POMs to the support surface. This is one of the most promising methods for the heterogenization of POMs. There are, however, very few examples of grafting owing to the limited choice of anchors and method of surface modifications. Errington et al. [108], reported the grafting of $[TiW_5O_{18}]^{4-}$ POMs to alkanol-derived silicon surface attached to Si via covalent Ti-O-C fashion.

Unlike conventional supports, MOFs offer a highly tunable, crystalline scaffold for anchoring due to their well-ordered nature. Due to the unique framework topology and

adjustable porosity of MOFs, the incorporation of POMs into MOFs has distinct strategies from other conventional support materials. Based on the desired synthetic procedures, POMs can be incorporated in MOFs by three main strategies such as impregnation, encapsulation and co-precipitation [109].

6.4 Impregnation

Impregnation is the immersion of POMs into the MOFs cages that is achieved by soaking pre-formed MOFs in an appropriate solution of POMs. The main criterion of this method is the size matching and charge requirements, i.e., the cavity of MOFs should be large enough to accommodate POMs, and their window size should be appropriate to allow the entrance of POMs of different sizes. If the size matching conditions and charge balance are satisfied, this method is simple and widely applicable even for chemically sensitive POMs. The first POMOF was developed in 2005 by Ferey et al. [110], by impregnating Keggin polyanion in MIL 101 (Cr) MOF.

6.5 Encapsulation

Majority of POMOF synthesis involves assembling of MOFs around the POMs, while adding precursors of MOFs to the solution of POMs under solvothermal or mechanochemical conditions. This method is valuable in cases where the window size of MOFs is smaller than the diameter of POMs. In such a situation, POMs can be enclosed in cages of MOFs, and that is why this method is also known as bottle-around-ship method. Encapsulation method mostly results in the development of new crystalline material. The process is applicable under certain conditions, i.e., the POM must be stable under the synthetic conditions of MOFs and the ligand must preferably attach to the metal node rather than POMs [111].

6.6 Co-precipitation

The co-precipitation method has been rarely applied for the synthesis of POMOFs. In this method, synthesis of POMs and surrounding MOFs takes place simultaneously yielding co-precipitated composite material [112]. This method is the least applicable due to complicated synthetic conditions and phase separation [113]. Moreover, apart from physical interaction in all the aforementioned methods, development of electrostatic interaction is applicable everywhere by generating various types of positively charged functionalities

through surface functionalization of MOFs in order to ensure stability of negatively charged POMs, e.g., in case of MOF UiO-66-NH₂ [114].

7 Role of POMOFs in photocatalytic water splitting

Typically MOFs show a semiconducting behavior with large band gap and their activation relies on energetic (UV) light [115]. However, incorporating visible light-driven POMs having rich photoredox chemistry owing to their oxo to metal charge transfer ability extends the absorption capacity of POMOFs to the visible region of spectrum [116]. Apart from that, the MOFs provide stability and recyclability advantages to the POMs [117]. Moreover, supported POMs have great potential of inhibiting recombination of opposite charges during the light harvesting process and their effective utilization at the respective POMOF junctions for the corresponding water splitting reaction [118, 119]. The resulting POMOF hybrid materials work on the principle of light absorption by MOFs and subsequent photogenerated charge transfer to the redox active POMs where H₂/O₂ evolution takes place.

A significant body of POMOFs work is based on the incorporation of POMs in the scaffold of phosphorescent MOFs. Phosphorescent MOFs is a class of MOFs having chromophore derived ligands, and are produced by the incorporation of a chromophore moiety in the ligand structure. The incorporation of well-known photosensitizers, i.e., ruthenium- and iridium-bipyridine results in the

development of ligands having strong absorption in the visible region due to a metal-ligand charge transfer bands. The first example of chromophore derived POMOF for photocatalytic water splitting was reported in 2015 by Zhang et al. [120] by incorporating a Wells–Dawson type POM i.e., [P₂W₁₈O₆₂]^{6−} in the [Ru(bpy)₃]²⁺ derived UiO-MOF. The encapsulation method was used by treating anionic POMs with the precursor of MOFs i.e., ZrCl₄ and [Ru(bpy)₃]²⁺ derived dicarboxylate ligand resulting in the development of POMOF composite material. The UiO–MOF consists of octahedral and tetrahedral cavities with triangular open channels of cationic framework. The positively charged framework of UiO–MOF due to di-positive charges of ligand plays a key role in accepting anionic POMs during in-situ self-assembling process. Cyclic voltammetry measurements of [P₂W₁₈O₆₂]^{6−} provided vital insights into the HER process. The [P₂W₁₈O₆₂]^{6−} showed four reversible reduction peaks at 0.22, 0.04, −0.29, and −0.53 (V vs. NHE) along with an irreversible catalytic peak at onset potential of −0.63 V (Figure 3b). These results demonstrated the necessary injection of six or more electrons to each [P₂W₁₈O₆₂]^{6−} for catalytic proton reduction. The favorable behavior of POM@UiOs can be attributed to the ability of MOF for facile multi-electron injection to each POM, corroborating the requirement of multi-electron insertion, before the execution of HER catalysis.

The hybrid (POM@UiO) was evaluated for hydrogen evolution reaction (HER) in acidic aqueous electrolyte (pH 1.8) using methanol as a sacrificial electron donor under wide band visible light (λ > 400 nm) irradiation. The H₂ evolution rate was reported to be 699 μmol h^{−1} g^{−1} after 14 h illumination with maximum turnover number (TON) of 79.

Figure 3: (a) Schematic description of POM@UiO system, showing [P₂W₁₈O₆₂]^{6−}, green polyhedra; Zr, cyan; N, blue; Ru, gold; O, red; C, gray. Illustration of visible-light driven excitation of UiO framework followed by electron transfer to the encapsulated POMs for synergistically enhanced H₂ evolution. (b) Cyclic voltammogram of [P₂W₁₈O₆₂]^{6−} (2 × 10^{−4} M), showing four oxidation peaks in acidic aqueous electrolyte i.e., 0.2 M H₂SO₄ + Na₂SO₄ (pH 1.8) at the scan rate of 100 mV s^{−1}. Adopted with permission from ref. [120].

It was observed that by changing sacrificial electron donor to triethanol-amine, the TON reached to 307 with high stability. In contrast, no considerable activity was reported in case of pristine POMs and MOFs. The high catalytic efficiency was attributed to the synergism by visible light excitation of photoactive MOF followed by facile multi-electron transfer from the excited MOF to POM (Figure 3a). In addition, the charge carriers separation was reported due to formation $\text{POM}/\text{Ru}(\text{bpy})_3^{2+}$ ion pairs, explained on the basis of electron quenching and consequently a decrease of emission in photoluminescence spectroscopy.

Based on the same principles, Zhang et al. [119] reported another POMOF hybrid with Ni-containing POM i.e., $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ (Ni_4P_2) encapsulated in $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ derived UiO-MOF by same synthetic approach as described above. The photocatalytic HER activity was reported under similar conditions i.e., acidic aqueous solution (pH 1.2), visible light broad band irradiation source ($\lambda > 400$ nm) and methanol as a sacrificial electron donor with an extraordinary TON of 1476 with remarkable stability showing only 0.2% decrease in activity after 20 h HER. The high TON was ascribed to the proximity of Ni-POM to multiple photosensitizers in the Ni-POM@MOF structure (Figure 4), which can facilitate multi-electron transfer during catalysis (Figure 4a). The photocatalytic mechanism is based on the photoexcitation of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ followed by the transfer of photoexcited electrons to POM, which reduce protons (Figure 4b). Mechanistic investigation of electron transfer was carried out by photoluminescence studies. The luminescence quenching of MOF by the incorporation of Ni_4P_2 demonstrated that the HER process occurred by electron transfer from MOF to Ni_4P_2 . The Ni-POM was also encapsulated in the previously reported $[\text{Ru}(\text{bpy})_3]^{2+}$ derived UiO MOF to investigate the role of photoactive moiety in the MOFs framework, but no considerable efficiency was observed.

This can be explained on the basis of difference in energy gap of photosensitizer and Ni-POM i.e., the energy difference (ΔE) between $[\text{Ir}(\text{ppy})_2(\text{bpy})]^{+*}$ and $[\text{Ir}(\text{ppy})_2(\text{bpy})]^{2+}$ is -0.70 eV, which is negative enough (compared to -0.65 eV) for proton reduction by Ni-POM. In contrast, the ΔE between $[\text{Ru}(\text{bpy})_2(\text{bpy})]^{2+*}$ and $[\text{Ru}(\text{bpy})_2(\text{bpy})]^{3+}$ is -0.62 eV, which is not negative enough to reduce proton by Ni-POM.

The synergistic electron transfer and consequent photocatalytic efficiency and stability of POMOFs are directly dependent on the interactions between POMs and MOFs. The stronger interaction leads to facile electron transfer, high efficiency and stability. Han et al. [121] electrostatically incorporated cobalt-based POM, i.e., $[\text{Co}(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ (Co-POM) in the cavities of Cr-terephthalate MOF (MIL-101) by ion exchange impregnation method. The coordinatively unsaturated metal sites of MIL-101 were available for binding with anionic POM. The electrostatic interaction was confirmed from XPS shift of Co $2\text{P}_{3/2}$ from 781.1 to 781.6 eV and also Co K-edge shift in the XANES analysis. The photocatalytic activity was evaluated in pyrex glass reactor charged with 50 mL (10 mM) sodium borate buffer followed by the addition of synthesized photocatalyst material i.e., Co-POM/MIL-101 (12.5 mg) and $\text{Ru}(\text{bpy})_3^{2+}$ (0.05 mmol) as photosensitizer in the presence of $\text{Na}_2\text{S}_2\text{O}_8$ as a sacrificial reagent at pH 9.0 under visible light irradiation (300 W Xe-lamp $\lambda > 420$ nm). The TOF ($7.1 \times 10^{-3} \text{ s}^{-1}$) and oxygen yield (66%) of Co-POM/MIL-101 per cobalt atom was superior as compared to that of pristine Co-POM (TOF = $4.0 \times 10^{-3} \text{ s}^{-1}$ and O_2 yield of 49%) under the similar experimental conditions. The improved efficiency and stability of Co-POM was attributed to the electrostatic interaction with the MIL-101. Similar approach of electrostatic interaction of negatively charged oxo moieties on the surface of POMs with metal cation and organic linker have also been used in various studies [122]. This

Figure 4: (a) Schematic illustration of POMOF represents Ni_4P_2 POM green; Zr, purple; Ir, red, C, gray, the scheme shows photoexcitation of the MOF framework and subsequent multi-electron injection to the POM. (b) Proposed catalytic cycle for visible-light-driven hydrogen evolution catalyzed by Ni_4P_2 @MOF. Adopted with permission from ref. [119].

strategy enhances the stability and efficiency both for photocatalytic water oxidation [123] and reduction reactions [124].

Self-assembling of the simple linkers in the advanced and well-ordered supramolecular 3D architecture of MOF and subsequent incorporation of POM is an interesting area of research. In 2016, Tian et al. reported supramolecular metal-organic framework (SMOF) developed by self-assembling of hexa-armed $[\text{Ru}(\text{bpy})_3]^{2+}$ -based precursor and a macrocyclic molecule, i.e., cucurbit [8] and uril [125]. A Wells–Dawson-type POM (WD-POM) was encapsulated in SMOF through one-cage-one-guest pattern (Figure 5), by soft base $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ soft acid $[\text{Ru}(\text{bpy})_3]^{3+}$ ion pairs strategy. The synthesis of this unique hybrid was carried out while taking advantage of size matching of cubic cages of SMOF 1.5 nm and WD-POM 1.1 nm. The photocatalytic hydrogen evolution efficiency of synthesized photocatalyst (0.002 mM) was demonstrated in acidic aqueous solution (pH 1.8), using methanol as sacrificial electron donor with TON of 392, and also in organic medium i.e., (acetonitrile: dimethylformamide 3:7) with TON 1820 in the presence of triethanolamine as sacrificial electron donor under monochromatic ($\lambda = 500 \text{ nm}$) visible light irradiation. The highest occupied molecular orbital (HOMO) energy of SMOF and the lowest unoccupied molecular orbital (LUMO) energy of WD-POM, determined by UV–Vis spectroscopy and cyclic voltammetry measurements, were found to be -3.59 and -4.78 eV , respectively, which shows a favorable electron transfer from excited SMOF to WD-POM to consequently trigger the hydrogen production. The remarkable efficiency of POM@SMOF was attributed to unique pattern of encapsulation where each POM anion was surrounded by eight counterparts $[\text{Ru}(\text{bpy})_3]^{2+}$ at the vertices of cubic cage, such a pattern facilitates multi electron injection from photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$ units to the encapsulated WD-POM. Moreover, the homogeneity of the reaction system allows close contact and quick diffusion of hydronium ion to facilitate the HER with fast and better performance.

POMs have reductive nature and can reduce metal salts to metal nanoparticles (NPs) [126]. Taking advantage of this property, various types of metal salts have been reduced and stabilized on the surface of POMs and further encapsulated in MOFs to develop tricomponent systems having NPs, POMs and MOFs (NPMOF) [127, 128]. Using this approach Guo et al. reported Platinum incorporated polyoxometalate Pt-(POM) in the framework of $\text{NH}_2\text{-MIL-53}$ (MOF) [129]. In the composite material (PNPOMOF), POM plays multiple roles i.e., it reduces platinum salt to platinum nanoparticles (Pt-NPs), further stabilizes Pt-NPs against aggregation, and facilitates electrostatic association of negatively charged Pt-NPs with positively charged

Figure 5: A schematic illustration of POMOF, showing the encapsulation of WD-POM ($[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ purple polyhedra in the cubic cages of SMOF white; C, N, blue; light gray; O, red; Ru, cyan; for photocatalytic hydrogen evolution. Adopted with permission from ref. [125].

protonated $\text{NH}_2\text{-MIL-53}$ MOF. The photocatalytic H_2 production was assessed using 10 mg of synthesized photocatalyst (PNPOMOF) in 2 mL aqueous ascorbic acid (0.05–0.2 M) solution, which acts both as buffer and sacrificial electron donor at pH 4.5. The sample was irradiated for 6 h with visible light Xe-lamp (150 W, having a beam size of 0.2 cm^2 , emitting monochromatic ($\lambda = 400 \text{ nm}$) light). The yield of molecular H_2 was reported to be 1.2×10^{-4} with TON of 66, and no activity for hydrogen production was observed for the controlled samples based on each component (POM, MOF, Pt NPs) alone. The sequential catalytic mechanism was explained by the $n\text{-}\pi^*$ transition of amine-functionalized MOF with bathochromic shift, followed by the transfer of excited electrons to POM and then to Pt NPs, where H_2 evolution reaction takes place (Figure 6a). Moreover, the stability was investigated by gas chromatography (GC), where the GC signal of recycled and

Figure 6: (a) scheme showing mechanistic H_2 evolution by Pt NPs decorated POM encapsulated MOF PNPOMOF, represents POM $H_3PW_{12}O_{40}$, dark blue polyhedral; Pt NPs, gray ellipses; $AlO_4(OH)_2$, light blue clusters; carbon connectors, gray sticks; oxygen, red. (b) The H_2 peak in GC showing stability of PNPOMOF for three successive cycles. Irradiation time (6 h) and pH (4.5) catalyst conc. (10 mg). Adapted with permission from the study by Guo et al. [129].

reused catalyst up to three cycles (Figure 6b) demonstrated almost comparable efficiency for H_2 production.

The lacunary precursors show attractive reductive property and can even accommodate up to 32 electrons in case of Keggin-based polyoxomolybdate, when reduced. However, due to the high oxidation state of addenda atom, the POM precursors exhibit poor oxidative properties. Transition metal substitution is a unique strategy to tune the redox properties of POMs that leads to multi-electron oxidative behavior and stabilize transition metals over a wide range of oxidation states [130]. Li et al. [131] reported the substitution of three different metals (Co, Ni and V) in the phosphotungstate POM leading to three high negatively charged substituted POMs i.e., $P_2W_{17}Co$, $P_2W_{17}Ni$, and $P_2W_{15}V_3$. All the substituted POMs were incorporated in the framework of MIL-101(Cr) sensitized with $[Ru(bpy)_3]^{2+}$. The resulting POMOF materials i.e., $P_2W_{17}Co@MIL-101$, $P_2W_{17}Ni@MIL-101$ and $P_2W_{15}V_3@MIL-101$ were used for photocatalytic HER with TON of 49, 50 and 56, respectively. The photocatalytic experiments were conducted in reaction mixture having 16 mL DMF/ CH_3CN (7:3), 200 μ L H_2O (pH 2), 94 mM triethanolamine (sacrificial agent), 48 μ M $[Ru(bpy)_3]^{2+}$ (photosensitizer) and 3.1 μ M POMOF (photocatalyst), under visible-light irradiation of 300 W Xe-lamp ($\lambda > 420$ nm). The comparable photocatalytic efficiency of these substituted POMs demonstrates their potential applications in photocatalysis. The superior performance of these substituted POMs was due to the high negatively charged POMs, which electrostatically adsorb positively charged photosensitizers (PS) $[Ru(bpy)_3]^{2+}$ from the solution for charge compensation. Meanwhile, it leads to the development of heterogeneous catalytic system POMOF@PS producing effective contact between POMs and PS resulting in the ease of intersystem electron crossing from photoexcited PS to the POMs to facilitate HER. The role of MOFs in the catalytic system is to enable the uniform arrangement of POMs and providing platform for maximum PS adsorption. This strategy was further extended to the sequential

adsorption of another anionic hydrogen evolution catalyst i.e., $Mo_2S_{12}^{2-}$ over the cationic PS and in this case the H_2 evolution rate was enhanced to $25578 \mu\text{mol h}^{-1} \text{g}^{-1}$.

Selection of stable MOFs for the incorporation of POMs is an important criterion in the development of POMOF systems. Despite of huge library of MOFs, there are only a few examples of POMOFs due to limited chemical stability of MOFs. Among the various examples of MOFs, UiO-66 exhibits excellent chemical and thermal stability, which can even maintain their structural integrity in boiling water for hours. Li et al. reported $PW_{12}@UiONH_2$ as stable POMOF composite for photo-assisted HER, synthesized by impregnating Keggin POM units in the framework of UiO- NH_2 MOF [132]. The authors have claimed the covalent interaction between POMs and carboxylate groups of MOFs on the basis of XPS analysis. The UV-Vis absorption analysis of UiO-66- NH_2 shows absorption edge at 420 nm corresponding to the band gap of 2.86 eV while the absorption edge of $PW_{12}@UiO-NH_2$ was red shifted corresponding to the band gap of 2.66 eV (Figure 7b). This result illustrates that the introduction of PW_{12} improve absorption ability of UiO-66- NH_2 , which can ultimately resulting in the improvement of photocatalytic performance. The H_2 production rate for pristine UiO-66- NH_2 was reported to be $11.8 \text{ mol h}^{-1} \text{g}^{-1}$ while that of $PW_{12}@UiO-NH_2$ was $72.7 \text{ mol h}^{-1} \text{g}^{-1}$ accomplished in ethanol water mixture 1:3 (50 mL) using 20 mg of synthesized photocatalyst materials under visible light (500 W Xe-lamp) irradiation. The improved efficiency in case of POMOF can be explained on the basis of covalent interaction between POMs and MOFs, which significantly boost charge transfer from photoexcited MOF linker to POM unit that was confirmed by photoluminescence analysis. The photocatalytic mechanism was proposed on the basis photoexcitation of MOF linker, followed by electron transfer to the POM unit where proton reduction takes place (Figure 7a).

Figure 7: (a) Proposed mechanistic illustration of H₂ evolution by POMOF catalytic system having impregnated PW₁₂O₄₀³⁻ POM units in the framework of UiONH₂ MOF, photoexcitation of MOF and subsequent electron injection to POM. (b) Photoluminescence emission spectra with 375 nm excitation of MOF shows shift of band gap while incorporating POM. Adopted with permission from ref. [132].

Magnesium porphyrin is an important constituent of chlorophyll b, acting as light harvesting antenna complex. The mimicking of this system in the form of zirconium porphyrin (MOF-545) is indeed a credit to MOFs design. Paille et al. [133] designed photocatalytic system by impregnating sandwich-type cobalt containing POM i.e., [Co₄(H₂O)₂(PW₉O₃₄)₂]¹⁰⁻ in the hexagonal channels of (MOF-545). The final composite material, P₂W₁₈Co₄@MOF-545, was found to be photocatalytically active for oxygen evolution reaction upon exposure to visible light ($\lambda > 420$ nm, 280 W) in borate buffer (pH 8) containing Na₂S₂O₈ as an electron acceptor, executing O₂ with: TOF $\approx 40 \times 10^{-3} \text{ s}^{-1}$ and TON = 70). Oxygen evolution starts immediately upon exposure to light, increased linearly with time and reached a plateau after 1 h of reaction (Figure 8b). The high activity of the POMOF can be explained on the basis of enhanced oxidizing power of MOFs by incorporating porphyrin ligands. More importantly, the MOF stabilizes the cobalt POM and the POMOF offers -OH of MOF and labile water Co-OH₂ of POM at the interface of POMOF, thus facilitating OER. The sequential mechanism can be explained on the basis of light capture by porphyrin resulting in the excitation of MOF, followed by the capture of excited electrons by the sacrificial electron acceptor (Na₂S₂O₈), the resulting oxidized MOF in turns oxidizes POM that finally oxidize OH₂ to O₂ (Figure 8).

The activity of hybrid materials can be even improved by assembling them in the form of thin film, which provides the easy transfer of electrons at the interface, enhances the exposure of the active sites and reusability. In this regard, the same group reported the previous P₂W₁₈Co₄@MOF-545 material with improved efficiency by simply developing thin films on indium tin oxide support by drop casting and electrophoretic methods [134]. The

photocatalytic OER performance of both the films was multifold higher than that of the previously reported suspended catalyst under similar conditions. The random orientation of the active sites and hindrance in the light penetration of suspended catalyst are known to impede the efficiency of material. These limitations of suspended catalyst can also be overcome by the development of thin films. Design and assembly of unique POMOF with interesting structures and properties has been an attractive and challenging task recently. The POMOFs are mostly crystalline in nature, which provide uniform binding sites for structure property relationship. Zhao et al. obtained two different structures by encapsulating two Keggin-type POMs i.e., [α -SiW₁₂O₄₀]⁴⁻ and [α -PW₁₂O₄₀]³⁻ in the framework of same Cu-triazole MOF [135]. Both the materials have same MOF building units but different structures due to different charges and binding abilities of POM units. The final POMOF materials, i.e., Cu₁₂(trz)₈(H₂O)₂][α -SiW₁₂O₄₀].2H₂O were denoted by POMOF1 and [Cu₁₂(trz)₈Cl][α -PW₁₂O₄₀] POMOF2. In POMOF1, the POM units exist in nine-membered rings of MOF via Cu...O interactions resulting in the development of a 3D framework (Figure 9a). In POMOF2, the POM lies in the 2D bilayers of MOF through Cu...O interactions (Figure 9b). POMOF1 offered better photocatalytic H₂ evolution at the rate of 192.2 $\mu\text{mol g}^{-1} \text{ h}^{-1}$ in 100 mL aqueous solution of CH₃OH (20%) as sacrificial e⁻ donor in the presence of 100 mg synthesized photocatalyst under visible light irradiation 300 W Xe-lamp ($\lambda = 320\text{--}780$ nm), whereas lower photocatalytic activity was observed for POMOF2 due to the difference in their structure and band gap. It was further revealed, that the skeleton of PMOF2 is not suitable for the transport of excited electrons and adsorption/desorption of intermediate molecules. However, irrespective of structure, similar results i.e., low activity of phosphorous-based POMs has been reported by Hill et al. [136] compared to its isostructural silicon-based POMs [137] in two different studies possibly due to overall charges on the POMs and

Figure 8: Schematic illustration of proposed light-induced OER mechanism by $P_2W_{18}Co_4@MOF-545$ POMOF. (b) Kinetics of light-driven O_2 evolution (blue) $P_2W_{18}Co_4@MOF$ (red) 2nd cycle (pink) 3rd cycle. Measured by GC analysis using 0.5 mg of $P_2W_{18}Co_4@MOF-545$ in 2 mL of 80 mM borate buffer solution, $Na_2S_2O_8$ (5 mM), pH 8, visible light 280 W ($\lambda > 420$ nm). Adopted with permission from ref. [133].

the heteroatom. It was further observed that each additional electron increased the negative charge by one, which ultimately decreased the redox potential by almost 210 mV.

Based on the same structure properties relationship, Lu et al. recently reported five different novel Keggin-type POM-based MOFs, i.e., (1) $[CH_2L_1]_2[(CuL_2)(PMo_{12}^{VI}Mo_3^{V}O_{40})]$; (2) $(TBA)[Cu(H_2O)_2L_1][PMo_{12}O_{40}]$; (3) $[Zn_{0.5}(H_2O)(L_1)][Zn(L_1)_{1.5}Cl][H_2L_1]_{0.5}[PMo_{12}O_{40}] \cdot 1.25H_2O$; (4) $[Cu_2(H_2O)_2(L_1)_3][PM^{VI}_{11}Mo^{V}_{40}]$ and (5) $(H_2L_2)_{0.5}[(Cu^{II}L_2)(PMo_{12}O_{40})] \cdot H_2O$, where $L_1 = 4,4'$ -bis((1H-1,2,4-triazol-1-yl)methyl)-biphenyl, and $L_2 = 1,4$ -bis((1H-1,2,4-triazol-1-yl)methyl)-benzene [138]. All the POMOFs were synthesized in ionic liquids with unique crystal structures. POMOF 1 had molecular interlocked polyrotaxane architecture (Figure 10a), where POMOF 2 was composed of three-fold interpenetrating host guest polyrotaxane network (Figure 10b). The synthesized POMOFs showed fascinating photocatalytic H_2 production efficiency in 100 mL methanol water mixture (2:8), 100 mg synthesized POMOF 1–5, respectively, loaded with Pt 1.2%, under visible-light irradiation. The POMOF 1 produced $12.2 \mu\text{mol}$ of H_2 after irradiation for 6 h at the rate of $29.6 \mu\text{mol g}^{-1} \text{h}^{-1}$. The efficiency of POMOF 2–5 was, however, slightly lower than that of POMOF1. The difference in their photocatalytic activity may be due to the difference in their structure and the subsequent charge conductivity in the framework.

To maintain the catalytic efficiency, the POMs must not leach out of the MOFs framework, which means that the window size of the MOFs must be smaller than the diameter of POMs. Based on this principle, taking advantage of the size matching adjustment of Co-based POMs and Fe-based MOFs having cavity size of 25 Å and window size of 5.5 Å, Shah et al. reported two types of leaching free POMOFs by encapsulating two different cobalt-based POMs i.e., mixed valent $[Co^{II}Co^{III}W_{11}O_{39}(H_2O)]^{7-}$ and $[Co_4(PW_9O_{34})_2(H_2O)_2]^{10-}$ in iron-based MOFs i.e., MIL-100 (Fe) to obtain $[Fe_3(C_9H_3O_6)_2O(OH)][H_7Co_2W_{11}O_{39}]_{0.28} \cdot 9H_2O$ denoted as (1) and $[Fe_3(C_9H_3O_6)_2O(OH)][H_{10}Co_4P_2W_{18}O_{68}]_{0.21} \cdot 11H_2O$ denoted as (2) [139]. The percent loading of POMs was very high i.e., 48 and 54% for 1 and 2 respectively, which was due to high porosity i.e., 8 large and 16 small cages per unit cell of MOF. These POMOFs exhibited decent photocatalytic water oxidation efficiency with the yield of 41% with TOF of 0.53 for 1 in sodium borate buffer solution (18 mL, 80 mM), catalyst 5.6 mg, at initial pH 9 having $Na_2S_2O_8$ (5 mM, 1.19 g) and 1.0 mmol $[Ru(bpy)_3]Cl_2$. The reported yield for 2 was 72% with TOF $9.2 \times 10^{-3} \text{ s}^{-1}$ in sodium borate buffer solution (50 mL, 10 mM), catalyst (12 mg), pH 8, containing 1.0 mmol of $[Ru(bpy)_3]Cl_2$ and 5 mM of $Na_2S_2O_8$ under visible light illumination 300 W Xe-lamp having cut-off filter at >420 nm. Both POMOFs 1 and 2 are having higher

Figure 9: Structural difference of $[\alpha-SiW_{12}O_{40}] \cdot 2H_2O$ encapsulated in nine-membered $[Cu_{12}(trz)_8(H_2O)_{24}]^{3+}$ (a) POMOF1 and $[\alpha-PW_{12}O_{40}]^{3-}$ encapsulated in 2D bilayer of $[Cu_{12}(trz)_8Cl]^{3+}$ (b) POMOF2. Adopted with permission from ref. [135].

Figure 10: Structural difference of five different POMOFs synthesized ionothermally for photocatalytic H_2 evolution. (a) POMOF1 (b) POMOF2, (c) POMOF3, (d) POMOF4, (e) POMOF5. Adopted with permission from ref. [138].

efficiencies than their individual counterparts (POM and MOF). The enhanced efficiency of POMOFs was attributed to an increase in the absorption capacity and charge separation (e^-/h^+ pairs) at POMOF junctions by the transfer of electrons from conduction band of MOFs to that of POMs. The electron transfer was assisted by the proximity of POMs to the μ_3 -O bridged Fe_3 units of MIL-100 due to electrostatic interaction of anionic POMs and acidic Fe_3 units of MOFs. The catalytic mechanism can be explained on the basis of photoexcitation of MOFs in the presence of photosensitizer (Figure 11) followed by electron transfer to the POMs, where water oxidation takes place.

Most promisingly, such hybrid materials can also be modified and can extend their ability to simultaneously catalyze both HER and OER. In this regard, Shi et al. have reported two different types of oxidative POMs i.e. $[W_{12}O_{40}]^{8-}$ and $[W_6O_{19}]^{2-}$ in the framework of Cu-based MOF (composed

of $\{Cu^{I}_{24}(\mu_3-Cl)_8(\mu_4-Cl)_6\}$ clusters linked by TPB ligand where ligand = TPB = 1,3,5-tris (3-(1,3,4-triazol-1-yl)phenyl)-benzene [140]. Both polyoxoanions were associated with cationic cavities by electrostatic interactions with the MOF. The tri-component POMOF composite i.e., $H_{48}[Cu^{I}_{24}(\mu_3-Cl)_8(\mu_4-Cl)_6]-(TPB)_{24}[Cu^{II}(CH_3OH)_6][W_{12}O_{40}]_8[W_6O_{19}]_3$ was photochemically active both for HER and OER and H_2 and O_2 were produced at the rate of 6614 and 1032 $\mu\text{mol g}^{-1} \text{h}^{-1}$ respectively in separate experiments only after 6 min of irradiation. The visible-light-driven H_2 experiments were conducted in mixed solution H_2O/CH_3CH_2OH (3 mL, 1:1), in the presence of sacrificial electron donor triethanolamine (TEA), having fluorescein (Fl) as photosensitizer under visible light irradiation (300 W Xe-lamp). The O_2 evolution experiments were performed in sodium borate buffer ($8.0 \times 10^{-2} \text{ M}$, 10.0 mL), photosensitizer $[Ru(bpy)_3]Cl_2$ and electron acceptor $Na_2S_2O_8$ illuminated by light-emitting diode (LED) lamp (beam diameter = 2 cm; light intensity = 16 mW; $\lambda \geq 420 \text{ nm}$). The oxidative nature of POMs and reductive nature of Cu clusters of MOFs offers dual functionality to the composite POMOF for simultaneous water reduction and oxidation reactions (Figure 12). The role of MOFs in the photocatalytic activity of POMOF is the light absorption and photoexcitation, which subsequently transfers the excited electrons to the POMs. While the POMs act as redox active centers where respective redox reaction takes place by the transfer of electrons to the adsorbate resulting in the release of respective product. The MOFs frameworks provide porous support for stabilization, heterogenization and recyclability of the highly soluble POMs and present a new class of emerging POMOF materials with superior properties than either of constituent components. Many MOFs having pi conjugated (e.g., porphyrin) and photosensitizers derived ligands (e.g., ruthenium- and iridium-bipyridine, etc.) act as light harvesting frameworks, which enhance the adsorption capacity of POMs.

Figure 11: A schematic representation showing encapsulation of cobalt-based POMs in the cavities of iron-based PMOF (MIL-100) for photocatalytic OER process. Adopted with permission from ref. [139].

Figure 12: Bifunctional photocatalytic system in which the POM act as oxidizing component and MOF as reductive component facilitating OER and HER respectively. Adopted with permission from ref. [140].

The synergistically enhanced photocatalytic activity of POMOFs are, therefore, mainly attributed to the transfer of electron from MOFs to POMs and meanwhile, the life time of charge carriers (e^-/h^+) at the POMOF junctions is also prolonged. These findings offer insightful guidelines about the immobilization of robust homogenous POMs on porous support materials, especially MOFs to rationally design recyclable and heterogenized photocatalysts for overall water splitting catalysis.

8 Immobilization of POMs on semiconductors/support for water splitting

Being metal-oxo-anions, POMs have strong affinity towards cationic surfaces for electrostatic stabilization [141] and, therefore, can be immobilized on various semiconducting materials [142]. The heterogenization of POMs on the surfaces of ammonium functionalized cationic silica has recently been reported for the oxidation of various reactants [33, 143–145]. TiO_2 is an interesting support material that can be modified by cationic moieties i.e., aminopropyltriethoxysilane (APS) and subsequent electrostatic immobilization (tethering) of Ru-based POMs for photoinduced water oxidation has provided new insights for the immobilization of POM [146]. Similarly, the ease of functionalization of carbon nitrides (C_3N_4) due to the presence of amine ($-\text{NH}_2$) groups on their surface has offered a new dimension to the heterogenization of POMs. Various types of POMs have been immobilized on the surface of $\text{g-C}_3\text{N}_4$ by simple protonation

of amine groups on the surface of $\text{g-C}_3\text{N}_4$ ($-\text{NH}_2 + \text{H}^+ \rightarrow -\text{NH}_3^+$) for water splitting [147]. Similarly the functionalization of carbon nanotubes (CNTs) by cationic polyamidoamine dendrimer (PAMAM) leads to the heterogenization of various POMs for water oxidation [148, 149].

Zheng et al. reported for the first time the immobilization of iron substituted POMs i.e., $[\text{Fe}_4^{\text{III}}(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{12-}$ on the surface of (3-aminopropyl triethoxysilane) APTS-functionalized mesoporous silica (SBA-15) for photocatalytic water oxidation [150]. Pristine POM was assessed in homogeneous environment for photocatalytic water oxidation in the presence of $\text{Ru}(\text{bpy})_3^{3+}$ as photosensitizer and $\text{S}_2\text{O}_8^{2-}$ electron acceptor, which demonstrated catalytic efficiency with O_2 yield of 48%, TON 900 and TOF five under visible-light irradiation. The photocatalytic efficiency mechanism is based on the photoexcitation of $\text{Ru}(\text{bpy})_3^{3+}$ followed by the oxidation of POM, which further oxidizes H_2O (Figure 13a) and the overall process is shown below:

The heterogenization and recovery of POM was realized with complete separation and reusability with no capacity loss up to four cycles (Figure 13b). The four electrons oxygen reduction mechanistic study was carried out by flash photolysis which revealed that oxo-to-metal-charge-transfer (OMCT) takes place in POM followed by electron transfer to photogenerated $[\text{Ru}(\text{bpy})_3]^{3+}$ and then oxidized POM execute water oxidation process. The redox potential of photosensitizer must be high enough to oxidize POM, and in this case the potential difference i.e., ($\Delta E = \text{HOMO}([\text{Ru}(\text{bpy})_3]^{3+}) - \text{HOMO}(\text{POM})$) of photosensitizer was suitable to oxidize POM.

Taking advantage of the anionic nature and extended reactive surface of POMs and positively charged surface of carbon nanodots, Choi et al. have developed self-assembled supramolecular hybrid material of $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ (Co-POM) and alginate-based carbon nanodots (CDs) by exploiting electrostatic interactions (Figure 14) [151]. The visible light driven water oxidation performance of the donor acceptor type composite material i.e., CD/Co-POM showed high oxygen evolution efficiency with TON of 522 in the presence of $\text{S}_2\text{O}_8^{2-}$ (0.15 M) as electron acceptor under visible light irradiation (300 W Xe-lamp) with a 400 nm cutoff filter and IR filter. Such an excellent performance is due to the self-photosensitizing capability of CDs, rapid transfer of photogenerated holes from CD to POM,

Figure 13: Mechanistic representation of photo-driven water oxidation cycle showing the role of functionalized (apts) support (SBA-15) photosensitizer $\text{Ru}(\text{bpy})_3^{3+}$ and POM $[\text{Fe}_4^{\text{III}}(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{12-}$. (b) Stability of supported POM for four cycles, catalyst concentration (10 mg), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (1.0 mM) and $\text{Na}_2\text{S}_2\text{O}_8$ (5.0 mM) under photoirradiation of LED lamp ($\lambda \geq 420$ nm) at room temperature. Adopted with permission from ref. [150].

appropriate band gap and comparatively more positive band edge position of CDs than water oxidation potential.

9 Incorporation of POM in covalent organic framework (COFs)

COFs, being an emerging class of porous crystalline polymers, have attracted widespread attention because of their structural robustness and tunable properties. The encapsulation of POMs in the scaffold of COFs has recently opened new opportunities for the heterogenization of POMs. Recent reports have demonstrated that COFs can encapsulate a variety of POMs and may endorse a suitable interaction. In this regard, Zhu et al. have reported the impregnation of phosphotungstate POM i.e., $[\text{PW}_{12}\text{O}_{40}]^{3-}$ in the covalent triazine framework (Figure 15) and indicated new platform for the immobilization of POMs [152].

Figure 14: Electrostatic interaction of POM with CDs and their mechanistic illustration for photoinduced water oxidation. Adopted with permission from ref. [151].

In a recent report, Young et al. have incorporated Mn-based Anderson POM in COF to form Mn-Anderson-COF (Figure 16) that has shown exciting photocatalytic performance, which suggests that COFs can provide effective platform for the heterogenization of POMs [153].

The luminescent properties of COFs have also attracted significant interest in the field of optoelectronics, solid state light emitters and photocatalysis. Based on these properties, the 3D COFs have been regarded as potential substrates for heterogenization of POMs for photocatalytic water splitting, which is totally unexplored area of research. However, despite of remarkable achievements in photocatalytic water splitting, the main challenge that still persists is the lower efficiency and selectivity towards H_2 evolution under solar energy and, therefore, efforts are underway to enhance the conversion efficiency for practical applications. The efficient visible-light-driven photocatalysts and new insights into the water splitting mechanism are required, particularly with regard to the identification of thermodynamic and kinetic constraints, to facilitate the design of an effective photocatalytic water splitting system for real applications.

Figure 15: Encapsulation of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ POM in the framework of cationic COF. Adopted with permission from ref. [152].

Figure 16: Synthetic approach and structural evaluation of POMCOF M-Anderson-COF. Adopted with permission from ref. [153].

Photoelectrochemical (PEC) oxidation and reduction of water is, however, still considered a more competent approach to fulfill the future energy demand.

10 Photoelectrocatalytic (PEC) water splitting

Photoelectrochemical water splitting is based on the principle of excitation of electrons from valence to conduction band of photoelectrode material upon irradiation along with small additional bias, resulting in the generation of e^-/h^+

Figure 17: Schematic representation of photoelectrochemical water splitting adopted with permission from ref. [156].

pairs [154]. Oxidation of water takes place at holes and the resulting generated electrons move through the external circuit towards cathode, where reduction of hydrogen ions take place (Figure 17). Photoelectrochemical phenomenon has some advantages over the photocatalytic process, owing to the use of photoanode as a working electrode, instead of direct addition of the catalyst to the reaction medium. Furthermore, there is no need of gas separation in PEC systems because O_2 and H_2 production can easily be separated by using proton exchange membrane electrode.

For efficient and sustainable process, a PEC needs to generate sufficient voltage in order to split water upon irradiation of solar flux. Photoanode materials, which are responsible for oxidation, are n -type semiconductor having favorable band gap for the absorption of a wide range of spectrum and capable of efficient charge collection and carrier motilities. While photocathode materials are generally p -type semiconductors and must generate the required cathodic current to reduce water to hydrogen [155]. The prerequisite of photocathode material is to have conduction band edge potential more negative than the hydrogen redox potential. Generally, photoelectrode materials need to possess high stability in aqueous medium, be of low cost, and environmentally benign. Though remarkable achievements have been reported in the development of photoelectrode materials, however, there are still several persisting issues that need to be addressed for their practical applications [156]. Various types of photoanode materials have been reported including bismuth vanadate ($BiVO_4$), titanium oxide (TiO_2), iron oxide (Fe_2O_3), tungsten oxide (WO_3), zinc sulfide (ZnS), cadmium sulfide (CdS), graphitic carbon nitride ($g-C_3N_4$), and tantalum nitride (Ta_3N_5), etc. [157]. But these materials have some limitations such as low absorption capability, high charge recombination, and photocorrosion [158]. Various strategies have been adopted to overcome the aforementioned limitations that include structure and morphology control, development of heterojunction, doping, co-catalyst deposition, and passivating surface. The incorporation of co-catalyst into photoanode is one of the most effective strategies for improving the PEC performance [159]. Recently, POMs have been recognized as promising co-catalytic materials, which significantly enhance the range of absorption and synergistically improve the charge separation and migration phenomenon in photoanode materials. The higher solubility of POMs, however, required them to be supported on various supports and the following sections will highlight some of the strategies to immobilize POMs on various semiconducting photoanode materials such as, $BiVO_4$, TiO_2 , Fe_2O_3 , CdS , and $g-C_3N_4$.

11 Immobilization of POMs on Bismuth Vanadate BiVO_4

Bismuth Vanadate (BiVO_4) has been recognized as one of the most widely used semiconducting materials in photoelectrochemical water oxidation due to its favorable band-gap (2.4 eV), which can be photoexcited by visible light irradiation. Furthermore, BiVO_4 has appropriate valence band edge with strong oxidation capability [160]. So, benefitting from such valuable properties, many significant systems of PEC water oxidation have utilized BiVO_4 as a central catalytic material. However, the quick surface charge recombination impairs its photoelectrochemical oxidation performance and still the photocurrent density of pristine BiVO_4 is far lower than its theoretical photocurrent (7.5 mA cm^{-2}) under AM 1.5 G filter. Recently, POMs have been introduced as effective co-catalyst materials coupling with BiVO_4 to significantly enhance the photocurrent response by reduction of charge recombination and broadening of absorption range. For example, Fang et al. [161] have recently demonstrated that cobalt containing polyoxometalate ($\text{Ag}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$, (PW_9Co), work as a hole extraction material on the surface of photoanode BiVO_4 . The composite material was synthesized by depositing BiVO_4 on the surface of FTO through electrodeposition followed by developing a layer of PW_9Co via spin-coating. The composite material i.e., $\text{BiVO}_4/\text{PW}_9\text{Co}$, exhibited high photocurrent density of 3.06 mA cm^{-2} compared to that of pristine BiVO_4 (0.93 mA cm^{-2}), which showed 3.3-fold enhancement at the bias of 1.23 V versus RHE in three-electrode system (Ag/AgCl as reference and Pt as counter electrodes) under visible light intensity of 100 mW cm^{-2} with an AM 1.5G filter in aqueous solution of 0.5 M Na_2SO_4 (pH 5.8). The surface photovoltage study (SPS) showed the absorption edge of pure BiVO_4 at 502 nm and the corresponding band-gap of BiVO_4 was acquired as $E_g = 2.47 \text{ eV}$. Accordingly the top of valence band (VB) and bottom of conduction band (CB) was calculated to be 2.95 and 0.48 V versus RHE, respectively. The UV-Vis absorption studies of PW_9Co showed absorption edge at 652 nm, representing the E_g of $\text{PW}_9\text{Co} = 1.9 \text{ eV}$. The Mott-Schottky plot shows that the VB and CB of PW_9Co are inferred to be 1.93 and 0.03 V versus RHE, respectively. The VB of PW_9Co lies between the VB of BiVO_4 and potential of $\text{O}_2/\text{H}_2\text{O}$, which is favorable for hole transfer and thus the PW_9Co can serve as a mediator for the hole extraction and transfer from BiVO_4 to facilitate the water oxidation.

In another report, Xi et al. [162] adopted a rational design of dual modification of BiVO_4 photoanode by polyoxometalate $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW_{12}) acting as electron capture

and nickel (II) phthalocyanine tetrasulfonic acid (NiTsPc) acting as hole extractor for the photoelectrochemical water oxidation. They reported the transient photocurrent response of $\text{BiVO}_4/\text{PW}_{12}/\text{NiTsPc}$ at constant bias of 1.0 V for several cycles demonstrating 13.4-fold enhancement in photocurrent response compared to that of pristine BiVO_4 photoanode. All PEC measurements were conducted in aqueous solution of 0.5 M Na_2SO_4 (pH 4.9), using electrochemical workstation (CHI 660C) with three-electrode system. The light source was 400 W Xe-lamp coupled with an AM 1.5G filter. The average intensity reaching the films was 100 mW cm^{-2} while illumination area was fixed at $0.8 \times 0.8 \text{ cm}^2$. The energy band distribution of PW_{12} , BiVO_4 , and NiTsPc (Figure 18) allow the photoelectron transfer from BiVO_4 to PW_{12} and transfer of holes to NiTsPc , which is responsible for boosting the photochemical response of BiVO_4 .

It is very important to study the effect of the nature of POMs on the photoelectrochemical performance of BiVO_4 . Xi et al. [163] incorporated two different types of POMs i.e., $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW_{12}) and $\text{K}_6[\text{CoW}_{12}\text{O}_{40}]$ (CoW_{12}) with BiVO_4 . The photocurrent response of pristine $\text{BiVO}_4 = 5.2 \mu\text{A cm}^{-2}$ at 0.7 V versus SCE) was enhanced to $12.0 \mu\text{A cm}^{-2}$ for $\text{BiVO}_4/\text{PW}_{12}$ and $18.9 \mu\text{A cm}^{-2}$ for $\text{BiVO}_4/\text{CoW}_{12}$. The photocurrent response was measured in 0.1 M Na_2SO_4 solution at constant bias of 0.8 V in three-electrode system under visible light intensity of 100 mW cm^{-2} ($\lambda > 400 \text{ nm}$). The improvement of photocurrent response was attributed to the charge separation by the transfer of electrons from BiVO_4 to the POM. The superior enhancement of 2.6-fold in case of $\text{BiVO}_4/\text{CoW}_{12}$

Figure 18: A schematic illustration showing charge transfer processes between $\text{BiVO}_4/\text{PW}_{12}/\text{NiTsPc}$. Adopted with permission from ref. [162].

compared to that of 1.3-fold in case of $\text{BiVO}_4/\text{CoW}_{12}$ has been attributed to the matching of energy bands of CoW_{12} and BiVO_4 .

Development of multicomponent photoanode material is a promising strategy to further improve the photochemical response of BiVO_4 . In a recent report, Fan et al. [164] have developed tricomponent anode material comprising of bismuth vanadate (BiVO_4), nitrogen doped carbon (N/C) and cobalt-based polyoxometalate (CoPOM) i.e., $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]$ for photoelectrochemical water splitting. BiVO_4 film was developed by electrodeposition on the surface of FTO glass followed by the growth of N/C layer and deposition of CoPOM. The negatively charged CoPOM was electrostatically interacted with positively charged protonated pyridinic nitrogen. The layer of N/C facilitated charge transfer and further endorsed uniform distribution of CoPOM while the molecular CoPOM acted as co-catalyst and significantly enhanced the hole injection efficiency and effectively reduced the water oxidation energy barrier resulting in lower onset potential and consequently improving the kinetics of BiVO_4 photoanode for PEC water splitting. The desired assembling of tricomponent anode enhanced the photocurrent density of BiVO_4 up to 1.93 mA cm^{-2} at 0.63 V , which is 11.4 times higher compared to that of the pristine BiVO_4 . The PEC measurements were evaluated using electrochemical workstation (CHI 660) at 1.23 V versus RHE (three-electrode system) in 0.5 M phosphate buffer solution having pH 7, under visible light intensity of 100 mW cm^{-2} (300 W Xe-lamp with an AM 1.5G filter).

12 Immobilization of POMs on titanium oxide (TiO_2)

Among the large family of semiconducting materials, TiO_2 has shown a remarkable promise owing to its decent PEC properties such as high surface activity, high chemical and mechanical stability, and nontoxicity, etc. [165]. However due to the high band gap (3.2 eV) and poor conductivity, the PEC performance of pure TiO_2 is not well-pleasing. Therefore, numerous efforts have been made to overcome the associated challenges including high charge recombination and narrow absorption capability. Among many other cocatalysts, POMs have also been demonstrated as promising cocatalyst to enhance the photocatalytic performance of TiO_2 . For example, Lauinger et al. have stabilized POMs on the surface of functionalized TiO_2 as efficient photoanode material for water oxidation [146]. Electrostatic interaction was developed between surface functionalized TiO_2 with

3-aminopropyltrimethoxysilane (APS) having quaternary ammonium cationic side chain, which preferentially binds the negatively charged POMs i.e., $[\text{Ru}^{\text{IV}}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_4(\gamma\text{PW}_{10}\text{O}_{36})_2]^{9-}$ denoted as (Ru_4P_2). The targeted photoanode was found to be oxidatively stable under homogeneous conditions resulting in enhanced current density in photoelectrochemical water oxidation that is attributed to the improved electron transfer dynamics. The structural integrity of the immobilized POM and evidence for stability of the films after long photoelectrochemical measurements has also been reported in 160 mM sodium borate buffer (pH 8), having 0.1 M KNO_3 electrolyte at the scan rate of 10 mV s^{-1} in three-electrode system under visible light source (150 W Xe-lamp) equipped with 400 nm cut-off filter, focused on the flat quartz window.

Similarly, Liu et al. [166] fabricated nanocomposite photoanode comprising TiO_2 nanotubes modified with polyoxometalate $(\text{Bu}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$ (PW_{12}) and Co_9S_8 , in which PW_{12} facilitate charge separation and Co_9S_8 play the role of electron transport mediator. The composite photoanode $\text{TiO}_2/\text{Co}_9\text{S}_8/\text{POM}$ was found to have superior photocurrent density at 1.23 V versus RHE under simulated solar light illumination, low onset potential (using 0.5 M Na_2SO_4 electrolyte in three-electrode system with Ag/AgCl as reference and Pt as counter electrodes) and high photoconversion efficiency compared to that of pristine TiO_2 , which implies that the composite material has lower band bending requirements for charge separation. The proposed mechanism of action for the composite material has been explained on the basis of band energy positions i.e., the conduction band (CB) edge of TiO_2 ($\text{ECB} = -0.5 \text{ V}$) lies higher than that of PW_{12} ($\text{ECB} = 0.22 \text{ V}$) and valence band (VB) of Co_9S_8 ($\text{EVB} = -0.015 \text{ V}$). The photoexcited electrons in the CB of TiO_2 are preferentially injected to the CB of PW_{12} as well as to the VB of Co_9S_8 (Figure 19). Based on these two aspects, the targeted composite material was found to synergistically enhance the electrons transfer resulting in boosting photoelectrochemical water oxidation.

Light harvesting capability in the broad range of spectrum is an important criterion for the PEC performance of the photoanode material. In this regard, Yang et al. [167] modified TiO_2 nanorods with cobalt substituted polyoxometalate i.e., $\text{Na}_2\text{Co}_4[\text{Co}_4(\text{PMo}_9\text{O}_{34})_2] \cdot 14\text{H}_2\text{O}$ (denoted as Co-POMs), and reported that the incorporation of Co-POMs enhanced the photocurrent density by 1.4 times compared to that of pristine TiO_2 at the applied bias of 0.8 V (vs. RHE) under AM 1.5G illumination. Mott-Schottky (MS) characterization was carried out to get the flat band (FB) and energy structure (Figure 20) for Co-POMs and TiO_2 . The E_{FB} of TiO_2 and Co-POMs was found to be 0.59 and 0.41 V , respectively in 0.5 M Na_2SO_4 (pH 7.4), using electrochemical

Figure 19: Schematic diagram showing electron transfer from CB of TiO_2 to the CB of PW_{12} and VB of Co_9S_8 . Adopted with permission from ref. [166].

work station with three-electrode system (Ag/AgCl as reference and Pt as counter electrodes) under 300 W Xe-lamp (100 mW cm^{-2}) with AM 1.5G filter. The conduction band potential of n -type semiconductors is approximately 0.1–0.3 V lower than E_{FB} . Based on this assumption, the conduction band potential of TiO_2 and Co-POM were assumed to be 0.29 and 0.11 V respectively, while the valence band positions were assigned according the E_g values, which are 2.45 V for Co-POMs and 3.31 V for TiO_2 . The Z scheme energy structure showed light absorption and corresponding electronic excitations, and the relatively negative conduction band of Co-POM favored the injection of electrons to TiO_2 under applied bias, which further led to the reduction of water. While on the other hand, the relatively positive valence band of TiO_2 stimulates the accumulation of holes which consequently oxidizes water. The aforementioned favoring electron/hole transfer route potentially enhanced the catalytic efficiency of the composite material.

13 Immobilization of POMs on other semiconductors

Recently, the incorporation of POMs as a co-catalyst in various semiconducting materials such as iron oxide (Fe_2O_3), cadmium sulfide (CdS), and graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) have been demonstrated to improve the PEC response of the aforementioned semiconductors. For example, Wang et al. [168] reported the incorporation of ammonium metatungstate

Figure 20: Mott-Schottky diagrams of Co-POMs and TiO_2 , in 0.5 M Na_2SO_4 (pH) 7.4 three-electrode system under 300 W Xe-lamp with AM 1.5G filter (100 mW cm^{-2}). Adopted with permission from ref. [167].

$(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$ POM denoted as $(\text{H}_2\text{W}_{12})$, in cadmium sulfide (CdS) quantum dots and further composited with reduced graphene oxide (rGO). The electrostatically interacted tri-component layer-by-layer film was fabricated by the immersion of APS (3-aminopropyltrimethoxysilane) modified ITO glass in the suspension of rGO, amine modified CdS and anionic H_2W_{12} , respectively. A five-fold enhancement of photocurrent response of rGO-CdS- H_2W_{12} composite film was attributed to the charge separation efficiency by the transfer of electron from CdS to POMs. The conduction band level (CB) of CdS (-0.8 V) is more negative compared to the reduction potential of H_2W_{12} , which enables the transfer of photoexcited electrons from CB of CdS to H_2W_{12} . The introduction of rGO further facilitated charge propagation from H_2W_{12} to ITO linked through the external circuit.

Molecular POMs as WOCs are quite susceptible to degradation via detachment from electrode surface under operating conditions in aqueous electrolytes and the stabilization of POMs is an important parameter in the design of catalyst material. Lauinger et al. reported the stabilization of ruthenium-based POM, i.e., $[\{\text{Ru}^{\text{IV}}_4(\text{OH})_2(\text{H}_2\text{O})_4(\gamma\text{-SiW}_{10}\text{O}_{34})_2\}]^{10-}$ (Ru_4Si_2) on the surface of hematite photoelectrode, which was pre-functionalized with 3-aminopropyltrimethoxysilane (APS). The electrostatically immobilized Ru_4Si_2 POM on the surface of Fe_2O_3 was further protected by Al_2O_3 layer coated by atomic layer deposition [46]. They further reported that special design of ternary catalytic system, i.e., hematite-APS- $\text{Ru}_4\text{Si}_2\text{-Al}_2\text{O}_3$, promisingly prolong the durability of photoanode architecture for extended period ($>12 \text{ h}$) of photoelectrolysis with 100% Faradaic efficiency and without this protection layer, POM experienced rapid detachment from the hematite surface.

Jeon et al. [169] developed a photoanode by depositing thin film of cationic branched poly(ethylenimine) (b-PEI) and anionic POM, i.e., $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ as water oxidation catalysts on the surface of photoelectrode (Fe_2O_3), through layer-by-layer assembly technique. The performance of the composite material was significantly enhanced compared to the bare Fe_2O_3 with the cathodic shift of onset potential by 400 mV and the pronounced increase of photocurrent density (0.94 mA cm^{-2}) with an applied bias of 1.23 V versus RHE, in three-electrode system (Ag/AgCl reference and Pt counter electrodes), using 80 mM phosphate buffer (pH 8) under visible light source, 300 W Xe-lamp equipped with 400 nm cut-off filter under visible light illumination. It was due to the synergistic effect and improvement of charge transfer between Fe_2O_3 and electrostatically interacted anionic POM with cationic PEI. Furthermore, a dramatic enhancement of stability has been reported and attributed to the protective layer formed by PEI between Fe_2O_3 and POM.

More recently, Yousefi et al. [170] explored the compositing effect of POMs on the efficiency of g- C_3N_4 as a photocatalyst. The composite material was developed by hydrothermal synthesis of a Preyssler-type POM, i.e., $(\text{Na}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]\cdot x\text{H}_2\text{O}) (\text{P}_5\text{W}_{30})$ and g- C_3N_4 . The high photo-conversion efficiency and smaller slope of transient open circuit potential decay for the composite material i.e., $\text{P}_5\text{W}_{30}/\text{g-}\text{C}_3\text{N}_4$ demonstrated better charge transfer and lower rate of recombination, which was explained on the basis of negative shift of flat band potential V_{fb} of $\text{P}_5\text{W}_{30}/\text{g-}\text{C}_3\text{N}_4$ (-0.58 V versus Ag/AgCl) compared to that of g- C_3N_4 (-0.37 V versus Ag/AgCl). The V_{fb} was calculated from the extrapolation of Mott–Schottky plot. The negative shift in the V_{fb} demonstrates larger carrier density and effective charge transfer in the composite material resulting in boosting photoelectrochemical response. The Mott–Schottky plots were acquired in 0.5 M Na_2SO_4 solution (pH 6.5), using three-electrode system with scan rate of 10 mV s^{-1} and frequency 500 Hz over the potential range 0.6–0.8 V versus Ag/AgCl in the dark.

14 Conclusion and future perspectives

The rapid development in molecular and nanoscale science has offered enormous opportunities to develop highly effective photo/photo-electrocatalysts for water splitting. At present, POMs-based nanohybrids are among the most promising yet emerging photo-assisted redox mediators for photo-driven water splitting for the production of hydrogen

as a sustainable energy source. This review summarizes recent developments in the heterogenization of POMs on various types of porous supports, such as MOFs, COFs, SiO_2 , TiO_2 , CNTs, C_3N_4 and GO, etc. These supports not only offer better stability and ease of accessibility of active sites on supported POMs but also extend the absorption range of light radiations and synergistically enhance the photo/photo-electrocatalytic efficiency. Such hybrid materials are indeed very promising to facilitate the transfer of electrons from photoactive support material to the redox active POMs for photo-driven water splitting. Their properties can be easily controlled and significantly improved by varying the nature and number of the atoms in the core of the clusters. From the experimental results, it has been found that photocatalytic properties and redox potential are highly sensitive to the support materials. Therefore, growing a library of POMs and support materials, especially MOFs and COFs, are the worth exploring strategies to develop several novel combinations of POMs and COFs/MOFs. Their distinctive and selective catalytic properties can be further ameliorated by the judicious selection of photoactive linkers of the MOFs (e.g., porphyrinic and bipyridine, etc.), COFs (e.g. conjugated triazines) and redox active POMs. We believe that heterogenization of POMs on various porous supports, especially in the 3D framework of crystalline COFs, is relatively an underexplored area, which has a great potential in photo-assisted water splitting and beyond.

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