Potential Application of Metal–organic frameworks for Photocatalytic Water Splitting

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Abstract. These days, the environmental pollution and energy shortage are the crucial global issues. Therefore, replacing the renewable source of energy with the fossil fuels is the most promising approach to solve the aforementioned problems. Hydrogen is an attractive source energy because of its high energy density and its combustion by-product is only water. Hydrogen production through photosplitting of water over a semiconductor based photocatalyst is a desirable approach to diminish the global energy and environmental problems. However, its low solar conversion efficiency and finding suitable photocatalyst still remain as the main challenge for this system. Recently metal–organic frameworks (MOFs) have received great attention for the photocatalytic hydrogen production due to their large surface to volume ratio, design flexibility, and well-defined porosity. In this short review, we focus on the previous studies on the various types of MOFs based photocatalyst in the solar hydrogen production system. The main intention of review is to highlight the importance of coupling molecular approaches of catalyst design with materials science strategies in the improvement of MOFs based photocatalysts, which will undoubtedly lead to a very bright future for photocatalytic water.

1. Introduction

The rapid development of the world’s economy increases the energy demand and consumption of fossil fuels. Converting solar energy to hydrogen as a clean source of energy through photosplitting of water in a photoelectrochemical (PEC) cell is a promising approach to overcome these challenges. This method is truly renewable with low environmental impact on both large and small-scales compared to hydrogen production from carbon-containing feedstock [1, 2]. Figure 1 shows the photocatalytic reactions over semiconductor photocatalyst for water splitting in the PEC cell. The first photocatalytic water splitting was conducted over TiO₂ photocatalyst under UV light irradiation by Honda and Fujishima in 1972 [2]. The photocatalytic water splitting occurs in three steps; (1) irradiating light on the surface of photocatalyst and generating electron hole pairs, (2) migration of photoexcited electrons to the conduction band (CB) and leave positive holes in the valence band (VB), and (3) reduction and oxidation of the adsorbed species on the surface by the photoexcited electrons and hole to produce hydrogen and oxygen, respectively [3, 4]. It is noteworthy to mention that the photocatalyst is core of each PEC with some requirements like an optimal bandgap energy approximately 2 eV to absorb maximum solar spectrum, high stability, long lifetime of generated charge carriers, low charge carrier recombination rate, and suitable CB level position [5]. Typically
the photocatalysts are made of metal oxides (TiO$_2$, SrTiO$_3$, ZnO, α-Fe$_2$O$_3$, WO$_3$, Ta$_2$O$_5$, VO, KTaO$_3$, and Fe$_2$O$_3$), metal sulfides (CdS and ZnS), oxynitrides, and oxysulfide (TaON and Sm$_2$Ti$_2$O$_7$) [6]. Up to date, there has not been found any photocatalyst that meet all requirements for photocatalyst applications in the PEC cell [5, 7, 8]. They mainly suffer from the wide bandgap group which absorb UV region as a small portion of sunlight, high charge carrier recombination rate, and chemical and photochemical corrosion. During last three decades, extensive efforts have been devoted to design semiconductor-based photocatalysts through developing heterogeneous systems such as the heteroatom-doped, metal oxide type, dye-sensitized, and Z-scheme types [9-16].

![Figure 1: Principle of photocatalysis process in the photoelectrochemical cell](image)

Several attempts have been reported to extend absorption edge to visible region and reduce the recombination rate by doping transition-metal ions with a d$^0$ (0<n<10) electronic configuration, valence band control by doping an anion's p or s orbitals of p-block metal ions and spectral sensitization [6-8]. Nevertheless, combining all-mentioned multiple modifications of the photoelectrode are still challenging and the photoconversion efficiency of this technique is low for it to be economically feasible [6]. Recently, MOFs with unique electronic, optical and catalytic properties have been investigated for light-harvesting (mimics of natural photosynthesis) to restrict this particular recombination process [17, 18]. MOFs have two main parts, including metal cations/clusters (divalent and trivalent ions of 3d transition metals (Zn, Cu, Fe, Ti, etc.), 3p metals, or lanthanides) and organic linkers (two or more carboxylate-, pyridyl- or azolate functions as coordinator to the cluster) [17-19]. During last decade, the design and synthesis over 20,000 MOFs for various application like gas storage, compound sensing, biomedical engineering, CO$_2$ capture, and catalysts due to the highly intriguing flexibility in which the shape, size, and functionality of the components are adjustable [20]. The unique properties of MOFs offers several advantages like high surface to volume ratio, low charge carrier recombination rate, design flexibility, extending absorption edge to visible region, shorten of diffusion length of charge carrier, and tunability of the porous frameworks for solar hydrogen production through photocatalytic process. These unique properties can inspire new ideas for fabrication heterojunction of metal oxide with MOFs and surface engineering study to enhance the efficiency of solar conversion efficiency in PECs [21, 22]. The goal of this short-review is to report some recent significant findings on the application of highly versatile and tunable MOFs component for photocatalytic solar hydrogen production.

2. Fundamental aspects of MOFs
Metal–organic frameworks (MOFs) as porous coordination polymers (PCPs) belong to a group of crystallized porous polymeric materials which form by combing of organic linker as bridge with metal ions as shown in Figure 2(a). The various catalytic activities of MOFs correspond to its high porosity, offering adequate spaces for the incorporation of functional groups as shown in Figure 2(b and c) [23]. MOFs need some requirements such as high stability under aqueous conditions at different range of pH in order to participate in the water splitting process [25]. Metal-organic frameworks (MOFs) such as MIL-125(Ti), UiO-66(Zr) [24, 27], MIL-53 (Al) [28], MIL-101(Cr) [29], PCN-222 [30], and ZIF-8 [31] are the most studied for photocatalytic hydrogen production. In the following section, we will summarize the reports on the photocatalytic reaction over MOFs materials as classified under four groups; (I) MOFs act as catalyst and photosensitizer is in the solution, (II) photosensitizers are
introduced in MOFs structure for light harvesting with external catalyst, (III) MOF is containing of both photosensitizer and catalyst, and (VI) MOF is mixed together with solid state material to create heterojunction active photocatalyst [32].

Figure 2: Formation of metal–organic frameworks (MOF) [24] and schematic diagrams of metal ion and organic linkers as potential catalytic sites within MOF structure [23]

2.1 MOF–catalyst with photosensitizers in solution supported electrocatalytically driven water splitting

We summarized some reported works of the molecular based water splitting system, including a non-semiconducting catalysts, photosensitizer, and sacrificial agent. Here the photosensitizers which are organic dyes and organometallic components can absorb and transfer visible light to a photocatalyst for generating electron and reduction process of water. While the presence of sacrificial agents provide electron for oxidized photosensitizer to return its ground state. Yamashita et al. reported visible light-driven hydrogen production over highly stable Pt/NH₂-MIL-101(Cr) as catalyst, Rhodamine B (RhB) as a photosensitizer, and triethanolamine (TEOA) as sacrificial agent. The catalyst was highly stable and it reused 5 times without loss of catalytic performance [25]. Pt/NH₂-MIL-101(Cr) composite produced more hydrogen compared to pure NH₂-MIL-101(Cr), Pt/TiO₂, and Pt/SiO₂, which might be corresponded to synergetic effect between Pt and MOF as shown mechanism in figure 3(a). In addition, they studied the effect of various Pt loadings (0.5, 1.0, 1.5, 2.0, 3.0 wt %) and RhB concentration on the photocatalytic performance of Pt/NH₂-MIL-101(Cr) composite. The NH₂-MIL-101(Cr) with the optimum amount of 1.5wt% Pt produced the highest amount of hydrogen. The increase in the amount of Pt until 1.5wt% had positive effect on the performance due to increase in the number of active sites on the surface of catalyst however, increasing the amount of Pt beyond the optimum level up to 3wt% had the negative impact on the catalytic performance due to agglomeration of Pt particles. In the another work, In 2014, He et al.[26] reported the application of UiO-66(Zr) and Pt@UiO-66(Zr), using RhB as photosensitizer for solar hydrogen production in the photoelectrochemical cell with catalytic activities of 33 and 116 μmol g⁻¹ h⁻¹, respectively. The proposed mechanism of photocatalytic hydrogen production over RhB sensitized Pt@UiO-66 (Zr) under visible-light is presented in Figure 3(b).
2.2 MOFs- Photosensitizer and external catalyst

In this strategy, the photosensitizers and external catalyst introduce in MOFs structures for light harvesting and photocatalytic activities. Lin and his co-workers [27] reported the photocatalytic hydrogen production over Pt nanoparticles@Photoactive (NPs@photoactive) MOFs. They photosensitized with highly chemically stable UiO(Zr) with Ir-phosphor-derived linear dicarboxylate linkers [Ir(ppy),(bpy)]- (ppy = 2-phenylpyridine; bpy = 2,2’-bipyridine) via hydrothermal process. Then the Pt NPs were deposited into the cavities of phosphorescent UiO MOFs via photo-deposition method. The photocatalytic hydrogen production reactions were performed using a 450 W Xe-lamp with a 420 nm cut-off filter in the presence of a mixed solvent of tetrahydrofuran (THF)/triethylamine (TEA)/H₂O (20:1:1) as sacrificial agent for 6 hours. Hydrogen production results showed that Pt NPs@MOF were active for both photocatalytic hydrogen reaction in the visible region with higher turnover frequencies and higher compared to homogeneous control. While the readily recycled and reused Pt@MOFs photocatalyst with larger linker could greatly enhance up to turnover number of 7000, which is five times the value afforded by the homogeneous control. They explained that the better photocatalytic performance of photosensitized Pt@MOF might be due to highly efficient electron transfer for unstable iridium organic linkers to Pt NPs which had positive effect on the photocatalytic hydrogen performance and reduce the decomposition rate of the Ir complexes.

2.3 Supported MOF with photosensitizer and catalyst

The MOFs researchers have developed frameworks with dual functionality, containing both photosensitizer and catalyst. The pioneer of using dual functionalized MOFs was Garcia and Co-workers in 2010 using two zirconium containing MOFs: UiO-66 ([Zr₆O₄(OH)₄(bdc)]₁₂) and UiO-66(NH₂) for hydrogen production in the presence of water and methanol [28]. The presence of the amino group in the BDC benzene dicarboxylic acid (DBC) ligand shift the absorbance of MOFs in the wavelength longer than 300 nm without altering the photochemistry properties. Highly porous titanium-based MOF (MIL-125-Figure4a) have received greatly attention owing to existence of titanium-oxo species. Ti-MOFs photocatalysts contains of cyclic octamers of TiO₂ octahedral with photochromic properties because of reduction of Ti⁴⁺ to Ti³⁺ under UV irradiation with higher photocatalytic activity [29].

Figure 3: Proposed mechanism of photocatalytic H₂ production over RhB sensitizer and Pt as co-catalyst for (a) NH-MIL-101(Cr) and (b) UiO-66(Zr) under visible-light

Figure 4: (a)(left) [001] and (right) [010] orientations of MIL-125. Ti, O, C, and H are depicted in blue, red, black, and beige, respectively [29], (b) schematic illustration of photocatalytic hydrogen production reaction over Pt-supported Ti-MOF-NH₂[30], and (c) concept of hydrogen of Co@MOF
Photocatalytic hydrogen production over Ti-MOF (1,4-benzenedicarboxylic acid linker-MIL-125) and amino-functionalized Ti-MOF under visible-light irradiation have been reported by Yu Horiuchi and his co-workers [30]. Ti-MOF-NH₂ was synthesized by a facile solvothermal and its absorbance edge shifted beyond 500 nm compared to its counterpart Ti-MOF. In addition, this photocatalyst is able to produce hydrogen without presence of noble metal but the quantum efficiency was low compared to that deposited with Pt. They reported hydrogen production rate of 366 μmol h⁻¹ g⁻¹ over Pt/Ti-MOF-NH₂ in the presence of triethanolamine (TEOA) as a sacrificial electron donor. Hydrogen is produced efficiently through the linker to-cluster charge-transfer (LCCT) mechanism as illustrated in Figure 4(b). In another work, the photocatalytic hydrogen production of modified NH₂-MIL-125(Ti) with Co-based electrocatalyst (Co-dioxime-diimine) was investigated by Nasalevich and co-workers [31]. The reported mechanism over this photocatalyst was depicted in Figure 4(c). This highly stable Co@MOF produced hydrogen under visible region 20 times higher than pristine NH₂-MIL-125(Ti) in the absence of noble metal. The stability report shows that this photocatalyst was recyclable without loss activity until 70 h.

2.4 MOF composite
The combination of MOFs with other semiconductor materials and catalysts in the form of heterojunction is another approach to make photocative materials with MOF. In this composite MOFs are considered as a template and it does not have an active role in photocatalytic process. Lin and his co-workers [32] reported the preparation process of crystalline FeO@TiO₂ composite nanoparticles by coating amorphous TiO₂ on the Fe₄-MOFs H₂BDC as organic linker-MIL-101 and calcination process. This Pt was deposited on the surface of this photocatalyst for visible light-driven hydrogen production process from water (Figure 5a). Diffuse reflectance spectroscopy was used to measure the UV-vis absorbance of MIL-101, MIL-101@TiO₂, FeO@TiO₂, a physical mixture of FeO and TiO₂, and FeO (hematite) alone are shown in Figure 5b. The absorbance spectrum for MIL-101@TiO₂ showed a combination of the spectral features of MIL-101 and TiO₂ alone, with TiO₂ absorbing mainly UV light while MIL-101 absorption extends into the visible range. Hematite FeO nanoparticles showed an absorption edge at 585 nm, corresponding to a band gap of 2.12 eV (2.1 eV typically reported). The photocatalytic activity of the FeO@TiO₂ material was tested under Xenon lap with filter of UV region by measuring photo-induced hydrogen production from water in the presence of triethylamine (TEA) as a sacrificial reducing agent and K₂PtCl₆ as co-catalyst reduced to Pt during the photocatalytic reaction, promoting surface of H₂ formation. Hydrogen production linearly increases after 48 h a total amount of 30.0 μmol h⁻¹ g⁻¹ was produced as shown in Figure 5(c).

Figure 5: (a) MOF-template synthesis of by FeO@TiO₂/Pt, (b) UV-vis diffuse reflectance spectra various prepared photocatalysts and the insects present a photograph of dispersions of MIL-101 (1), MIL-101@TiO₂ (2), FeO@TiO₂ (3), FeO@TiO₂/Pt (4), FeO@TiO₂/Pt (5), and TiO₂ (6) in ethanol, and (c) The H₂ peaks in GC traces of the headspace over photodriven reactions over FeO@TiO₂/Pt [32].
MOF template FeO$_2$ @TiO$_2$ is a heterogeneous catalyst which can be recovered from reaction mixture and reused in the fresh electrolyte. The MOF template FeO$_2$@TiO$_2$ photocatalyst is able to produce hydrogen from water splitting under visible region while single competent of TiO$_2$, FeO, and physical mix FeO$_2$@TiO$_2$ are not able to do so. In another work, Bala et al [18] reported the synthesis of Co$_2$O$_3$/TiO$_2$ p–n heterojunction using Co-based metal organic frameworks (Co-MOFs) as a TiO$_2$-absorbent for nanocomposite formation. The characterization results confirmed the presence of anatase TiO$_2$ nanoparticles and spinel Co$_2$O$_3$-like species. The photocatalytic hydrogen production in the presence of methanol as a sacrificial electron donor (SED) under 400 W xenon lamp with optimum of level Co-2wt.% had maximum rate of 7000 $\mu$mol g$^{-1}$ h$^{-1}$, which is almost 7 times higher than that of the conventional Co$_2$O$_3$/TiO$_2$ nanocomposite.

2.5 Challenges of MOF application for water splitting

The large varieties of MOFs owing to their rich diversity in the selection of inorganic and organic components will attract profound attention in the future for catalytic applications like water splitting. However the quantum efficiency of hydrogen production of MOFs is low and needs more efforts to be devoted to deep understanding the rich chemistry of MOFs for photocatalytic application. The water sensitivity of certain MOFs in which water involves has been well known as a major challenge and limits theirs applications perspective. Furthermore, most of reported MOF-based photocatalysts were shown better performance the presence of noble metals which are rare and expensive which are not economically desirable for large scale application. In addition, some complex and expensive organic linker of MOFs create problem for their application. In order to reduce the cost of the expensive co-catalysts and organic linker, design of mixed organic linker, exploring mixed-organic linkers and 1st-row transition metal-based catalysts derived, and using carbon based co-catalyst like graphene might be an attractive strategy in the future to reduce the cost of MOF based photocatalyst. In despite of all issues, very bright future for photocatalytic water splitting over MOFs based photocatalyst is predictable because of their unique properties like high surface area, adjustable pore volume, size, 3D structure, and rich coordinator chemistry.

3. Conclusion

The MOFs based materials in heterogeneous photocatalysis for water splitting have been intensively investigated due to the unique properties of MOFs. The tunable structure and high porosity of these crystalline materials provide a feasible approach to design highly active, recyclable, and environmentally benign MOFs photocatalysts. The impressive results have been reported for hydrogen production over MOF based photocatalysts however, this approach is still new and it has profound potential for further improvement. There are some problems with this system which can be addressed as follows;

- The number of MOFs which have been explored for photocatalytic application are not sufficient while a large amount of MOFs with redox active metals or functional organic linker are still remained for further study.
- The efficiency of these systems are low, and thus they should be remarkably developed for practically approach.
- The most of MOFs photocatalysts are constructed by noble metals which are rare and expensive.

We believe that further development of MOF based photocatalyst need the better understanding of photocatalytic systems with MOF-based materials. In addition, reducing the MOFs based photocatalysts to nano-size can create better interaction with the substrate and enhance light harvesting. Finally, we are confidence that the ability of design various MOF based photocatalysts provides an excellent platform to develop an ideal photocatalyst to solve energy and environment issues.

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