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Featured Letter

Photosensitive titanium and zirconium Metal Organic Frameworks: Current research and future possibilities

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ABSTRACT

The sustainable production and storage of energy is one of the most important scientific and technological challenges to ensure the energy availability for the near future. For that matter, light-driven photochemical reactions, such as water splitting and CO_2 reduction with water, can transform sunlight energy into chemical energy. Designing an efficient porous organic/inorganic hybrid material (known as Metal-Organic Frameworks (MOFs)) that features molecular functional components for light harvesting and catalysis can address the challenges of the field and create a technological breakthrough to convert sunlight into solar fuels. The latest achievements in MOFs for artificial photosynthesis and photocatalysis are presented with emphasis on bulk MOFs and thin film MOFs deposition. This review is focused on robust Zr and Ti MOFs for water splitting reactions and CO_2 reduction, which are the most promising materials for this purpose. New directions are evaluated and the challenges for photocatalytic MOF are also discussed.

1. Introduction

Energy is now the main concern of several researchers since late studies have demonstrated a tendency on the decline of the oil and gas production [1] as well as the negative effects on the environment due to the use of these energy resources [2]. For this reason, alternative energies have been one of the focusing points of several studies during the last decades. The discussion surrounding these alternatives has been focused on the efficiency, the availability and the impact that these energy resources will have on the environment and on human activity. While several options have been studied, such as nuclear energy, solar thermal energy, wind energy or hydroelectric energy [3], the use of solar fuels seems to be one of the most promising options, since the sun represents an “infinite” source of energy and solar fuels can be easily stored. However obtaining a material that can convert efficiently solar energy into chemical energy still remains a challenge [4].

Plants can use solar energy to convert CO_2 and water into glucose. Three steps can be distinguished in this photosynthetic process to produce chemical energy from solar energy: light harvesting process by photosensitizers to generate a charge separation, electron transfer from redox cofactors and migration to a reactive center (Scheme 1). Several molecular systems have been developed to mimic nature and to reproduce the photo-driven water splitting or CO_2 reduction. Photocatalysis has been first demonstrated by Fujishima and Honda in the 1970s with the use of TiO_2 under UV light [5]. The use of photocatalysis in the visible light spectra represents a great improvement in this area, even though most of the systems described in the last decades respond to the UV spectra of light. Promising results regarding solar fuels have been obtained by improving the light absorption with the use of transition metals [6]. One of the current challenges is to integrate all of the components inside a single material to avoid the use of a sacrificial reagent to regenerate the catalyst.

Metal Organic Frameworks (MOFs) or porous coordination polymers are a new class of porous materials [7]. Since the term MOF was adopted in 1999 by Yaghi and co-workers [8], this field has grown exponentially. The versatility in the structure of MOFs has allowed scientists to study them for diverse applications such as gas storage [9], heterogeneous catalysis [10], metal extraction [11], drug delivery [12], sensing [13] among others. Another application that has shown promising results, even in early stages of development, is artificial photosynthesis. The number of publications in this field has rapidly increased as noted by Fresno in 2014 [14]. MOFs structure can be controlled to contain a photosensitizer and a catalytic center, all in the same material as plants can do. Due to this characteristic, MOFs have a great advantage over other materials such as TiO_2 based photocatalyzers [15,16].

Also, two recent methods have increased the possibilities to obtain new photocatalytic MOFs and will be discussed: Post-

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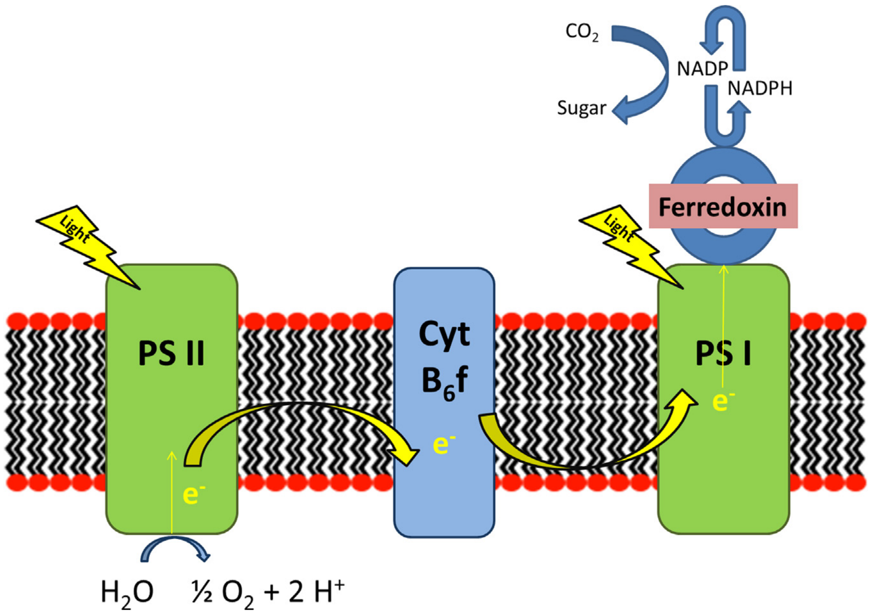

Scheme 1. Schematic representation of the photosynthetic chain.

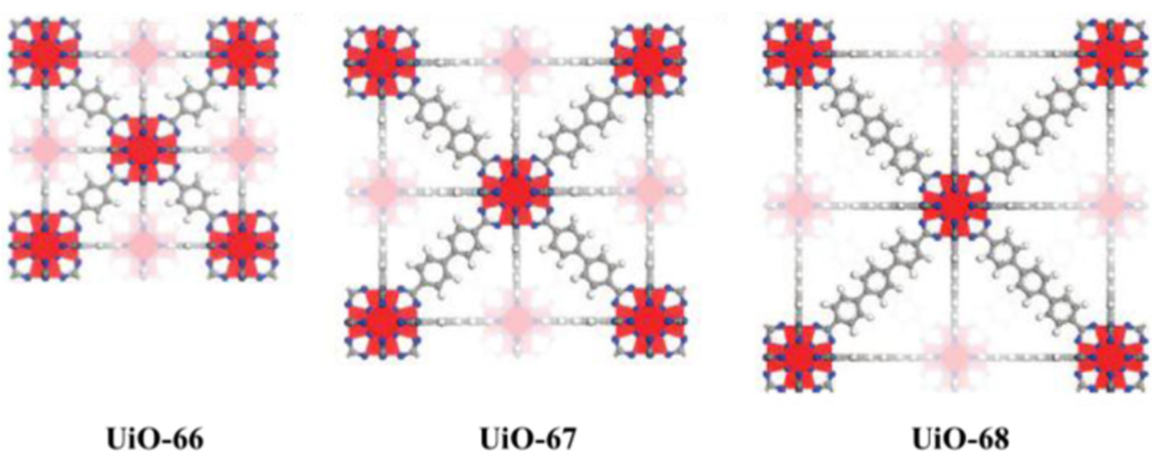

Fig. 1. Structure of the UiO-66, UiO-67 and UiO-68. Reprinted with permission from [25]. Copyright 2015 American Chemical Society.

Synthetic Modification (PSM) and Post-Synthetic Exchange (PSE). PSM consists in the synthesis of known crystalline MOFs but with active sites on the ligands to add a desired functionality [17,18], while PSE consists in the exchange of either, the metal center or the ligand, without a crystallinity loss [19,20].

Another possibility is the deposition of MOFs on a solid surface to increase the stability and the possibilities of application of classical MOFs [21]. This process allows to keep the photocatalytic properties of the original framework but at the same time to use a material that can withstand the harsh conditions of the environment [22].

These areas have been mostly developed with Zr and Ti MOFs due to their high stability under light excitation or photocatalytic conditions. This review provides a small summary of very recent achievements with these materials for photochemistry (25% of cited papers are from 2015) and gives some perspectives and opportunities in this field.

2. Photocatalytic Metal-Organic Frameworks

2.1. Presentation

The first attempts to develop a MOF with photocatalytic properties was made by Chen [23] and by Natarajan [24]. In both cases, they took advantage of the photocatalytic activity of the metallic centers (uranyl center in the first case and Co, Ni and Zn in the second one) and measured the improvement of the activity of the new complexes in the degradation of some dyes. The development of MOFs for photocatalysis is focused on two different strategies: introduction of photosensitive metals inside the pore cavity or as metal nodes and the use of the organic bridging ligand as antennas for light harvesting to activate the metal nodes or a catalyst.

2.2. Zr based MOFs for photocatalysis

First reported by Lillerud and co-workers [25], the UiO family (Zr MOFs) possess high stability, structural resistance towards different solvents and to mechanical pressure due to the high connectivity of the secondary building unit (SBU) $[Zr_6(RCO_2)_{12}(O)_4(OH)_4]$ with open channels that can be easily tuned by varying the size of the organic linkers (Fig. 1). Incorporating functional groups on the MOFs backbones allows to generate different kind of materials with high rates of diffusion inside the MOF [26,27].

One of the first studies of the photocatalytic properties of the UiO MOF family has been made by Garcia and co-workers [30]. They used UiO-66 and the amino functionalized UiO-66 [UiO-66