Review

Metal–organic frameworks for solar energy conversion by photoredox catalysis

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ABSTRACT

Metal organic frameworks (MOFs) have received increasing attention in the field of photoredox catalysis, mainly due to the advantages of the highly porous nanostructure and tunable semiconducting properties. Thus, the essential roles of photocatalysis by MOF can be conventionally optimized toward addressing the environment and energy issues. In this review, the fundamental of the photocatalytic MOF is initially discussed. A range of the solar-driven applications by photocatalytic MOF are highlighted, including water contamination degradation, water splitting, CO_2 reduction and organosynthesis. In each chapter, a series of systematic investigations is presented, also involving a few recent results and unique phenomena that bestowed by the photocatalytic MOFs. The future prospects and challenges to use MOFs for each photocatalysis application are proposed.

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1. Introduction

Photocatalysis is generally defined as catalytic reaction driven by solar energy [1]. This topic is becoming increasingly significant to address the essential problems in the fields of energy and environment, due to the realizations of the advantages, for instance, the renewability, cost-effectiveness and minimized side-effects [2,3]. The developments of the green photocatalysis were mainly focused on four working directions worldwide, including water toxicity degradation [4], water splitting [5], CO_2 conversion [6] and organic synthesis [7]. In order to efficiently use the catalyst in such applications, a few common properties can be observed, for example, they should be stable in the general solvents, and can be tolerated under a strong light irradiation in air condition. Moreover, certain photocatalysis application still needs the catalyst to have distinct characteristics, for example, in terms of a powder photocatalyst for water splitting, in thermodynamic, it required their energy gaps that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are larger than water oxidative and reductive energy levels, respectively, which are 0 and 1.23 V (pH = 0) [8]. At the same time, under the considerations of the kinetic barrier and energy loss during the reaction, the corresponding energy levels are normally required to be as wide as 1.8–2.0 V. In the other situation, if the solar-driven water splitting is achieved through photoelectrochemical (PEC) approach, in which, water oxidation and reduction is independent through photoanode and photocathode under electric input, it requires the anodic HOMO level and cathodic LUMO level to engulf the water redox potentials. In comparison, the needs of a photocatalyst for CO_2 conversion are completely different. First, the thermodynamic energy required to reduce CO_2 is in a wide range depending on the aiming products, whereas, in general, easily to be satisfied by a photocatalyst in small energy gap. In contrast, the high kinetic barrier with complicated multiple-electron processes indeed restricts the photoconversion efficiency, thus determining the conversion rate [9]. In the meantime, the chemical activity of the CO_2 in the reacting medium is another factor to affect the photoefficiency, since the adsorption/activation is happened prior to the photoreactions.

As such, inevitably, any family of material with unitary property cannot fully satisfy all the requirements. For example, metal oxide semiconductors are normally quite inert in both the chemical structure and electronic/optical property [10]. Therefore, they generally possess quite good stability during photoreactions, but the photoactivity becomes difficult to further optimize. Despite introducing foreign elements, the capability to optimize the electronic/optical property of the materials is still quite narrow [11]. In contrast, the photoactivity of organic semiconductor can be readily tuned with a control of functional groups [12,13], however, in a typical one, the stability becomes a drawback hindering their developments [14]. As such, the family of metal organic frameworks (MOFs) is considered as a potential material consisting of advantages of both organic and inorganic semiconductors to overcome the systematic restrictions to achieve all these necessities, as it is possible to take features from both of them [15].

MOF is a family of materials consisting of organic ligands bridging metal clusters. The early excitements of MOFs were mainly due to the high surface area and large pore volume, and thus it was widely considered for the storage and separation of gas or liquid [16–18]. Upon these directions, achieving the semiconducting features in MOF opened a new avenue toward a wide range of applications, especially for photoredox catalysis [19]. In the structure of MOF, the HOMO of the organic ligand can be readily adjusted to maximize the solar energy harvesting, and the excited electron would be promoted to the certain location of the MOF, either on the metal node or on LUMO site of the organic linker [20]. The crystalline structure allows optimizing the migration distance of the photoexcited charge with controlled traveling distance and angles determined by the assembling units. In addition, the metal cluster could act as the structural center to strengthen the MOF structure. The integration of the optimized MOF with other functional materials also exhibits great advantages to approach the desired photocatalytic characteristics. For instance, with a conventional attachment of the semiconductor/metal nanoparticles into MOF, the aggregation of the nanomaterial can be minimized [21]. Also, more than one functions can be integrated with MOF by achieving the hybrid structures, for instance, the foreign materials can be functionalized as cocatalyst, sensitizer, or as extra energy gap to form heterostructure, or even enabled multiple-function by one specie [22–24].

This review will focus on the recent progresses in using MOF for photoredox catalysis [25–27]. The fundamental aspects in developing MOFs for efficient photocatalysts will be reviewed and discussed initially, ranging from the structural design and stability of MOFs to the formation of hybrid structures, such as integration with noble metals (NMs) and semiconducting materials. In subsequent, the photocatalytic applications of MOF will be summarized, including water purification, water splitting, CO_2 reduction and organic synthesis. Although a few very good publications reviewed the progresses of this area, we aim to present more recent developments of the photoredox catalysis, and specify the challenge and opportunity in the future [25,27–30]. By virtue of the photocatalytic MOFs, the possibility of photocatalysis was extensively widening toward addressing the human problems by breaking the limitation from the traditional materials and technologies.