



Review

Strategies to improve metal organic frameworks photocatalyst's performance for degradation of organic pollutants



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ARTICLE INFO

Article history:

Received 23 April 2018

Accepted 7 August 2018

Keywords:

Metal-organic framework

Photocatalyst

Modified strategy

Organic pollutant degradation

ABSTRACT

Researches on metal-organic framework (MOF) materials have gathered increasing interest in the field of photocatalysis due to their large surface area, well-ordered porous structure, and tunable organic bridging linker/metal clusters with a tailorable capacity to absorb light. The development of inexpensive, stable, efficient, and band-gap tunable MOF-based photocatalysts is still a great challenge. The selection of central metal ions and organic ligands is of great importance for the fabrication of MOFs with excellent photocatalytic properties. This review aimed to summarize the strategies of improving photocatalytic activity under light illumination, including optimization, modification, doping and imperfection, mainly in structure, light absorption, band gap and stability. In addition, the applications of various modified MOFs are also introduced. Finally, the future developments of MOFs are discussed.

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1. Introduction

Energy shortage is a serious social problem in the world today, which interferes with sustainable development [1,2]. Due to high utilization of light, heterogeneous photocatalysis has been seen to be a green and environmental, scientific and efficient method. Fujishima et al. devoted themselves to the pioneering work on the process of changing light energy to chemical energy by photocatalyst. Then, TiO_2 [3], ZnO [4], CdS [5] and Fe_2O_3 [6] as the representative of photocatalysts have been explored. Because of the limited tunable functionality and the instantaneous separation of electron-hole pair, the application of traditional semiconductor as photocatalyst is limited, and the researchers are devoting to develop novel, efficient, and tunable functional photocatalysts. Metal-organic frameworks (MOFs) in topological structure are built by the metal ions/clusters of inorganic secondary building units (SBU) and organic linkers with moderately strong coordination bondings [7,8]. Furthermore, as a result of precisely predesigned structures with tailored functionalities, MOFs are able to achieve structural and chemical control that are specific to target function. These merits along with structural diversities, abundant active sites, highly thermal stability and permanent porosities endow them great application potential in gas storage, separation, sensing and catalysis, as well as several other unrelated applications [9,10].

Recently, reviews have been made on various aspects of MOFs. Some reviews focus on structural strategies to fabricate the nanoparticle/MOF composites, including decoration of organic linker or metal center, combination with semiconductors and metal nanoparticles loading applied to different MOFs [11–13]. The mechanistic, functionality and structural complexity of MOFs are the emphasis in the review of Kuaila et al. [14]. The optical properties of MOFs can be flexible modulated via incorporation of NH_2 group, conductor photocatalysts like ZnO and metal sulfides nanoparticles, noble metal nanoparticles and graphene oxide (GO). Further, controllable design of tunable nanostructures (such as metal nanoparticles, quantum dots, polyoxometalates, organic and metallorganic molecules, biomacromolecules, and metal-organic polyhedra) inside MOFs for the versatile functions was summarized [15], with special emphasis on the preparation and synergistic properties of these composites. Notably, defect engineering in MOFs is an exciting concept for tailoring material properties, which opens up novel opportunities not only in sorption and catalysis, but also in controlling more challenging physical characteristics. The review done by Zhang et al. closed that gap by providing both a concise overview of defects in MOFs, or more broadly coordination network compounds (CNCs), including their classification and characterization, together with the potential applications of defective CNCs/MOFs. Others focus on environmental and energy applications [16]. Wang's [17] group summarized the photocatalytic degradation in metal organic frameworks, which emphasized on the reaction mechanism and the influence of various factors on the catalytic performance. Specially, Cr (VI) as a research object by the photocatalytic reduction of MOFs have got consummated [18]. Meanwhile, the study of photocatalytic mechanism, which is equal to highly convert energy into chemical energy, have draw the attention. The fundamental principles of energy transfer was summarized and the latest progress in energy transfer, light-harvesting, photocatalytic proton and CO_2 reduction, and water oxidation using MOFs was provided [19].

The review chosen common environmental pollutants: organic pollutants as a research object, aiming to summarize the strategies of improving photocatalytic activity under light illumination, including optimization, modification, doping and imperfection. It is important to optimize the metal centers and appropriate ligand

for photocatalytic activity. In addition, metal semiconductor and metal-free semiconductor, specially, graphene and carbon nitride doping with MOFs has been pampered recently. Defective MOFs with magnetic metal Fe, Co, Ni are not only beneficial to the separation and recovery of materials, but also helpful to improve the photocatalytic ability. Secondly, the light absorption, band gap, stability and mechanism are emphasized. Finally, a personal perspective regarding the future developments of MOF is presented.

2. Optimization of MOFs photocatalyst

2.1. Optimization of MOFs photocatalyst on the basis of metal-clusters

MOFs emerged as a class of highly porous crystalline materials follow the principle of metal ions coordination with organic ligands [20,21]. As the core of the MOFs, the excited clusters are the main active sites of photocatalytic reaction, and it is important to choose the appropriate cluster to construct the MOFs with high photocatalytic activity [22]. Fe-based MOF materials taking (MIL-88A, MIL-53 MIL-68) as typical models on the basis of iron oxo-clusters may be a potential photocatalyst for dye degradation. MIL-53(Fe), a Fe (III) contained MOF build up from chains of Fe (III) octahedral and polycarboxylate ligands (1,4-benzenedicarboxylic acid), was endowed excellent optical properties. In the UV-vis, the band of MIL-53(Fe) at 224 nm is related with the ligand to metal charge transfer (LMCT) of $\text{O}(\text{II}) \rightarrow \text{Fe}(\text{III})$, which is derived from carboxylate oxygen to metal. Except the main peak, due to the transition in Fe(III), a small peak centered at 445 nm appears in MIL-53(Fe). By calculation, the band gap of MIL-53(Fe) is 2.72 eV which corresponds to absorption band edge [23]. The direct excitation of iron-oxo clusters is deemed as the main active site of photocatalytic reaction because of adsorption incident photons by the iron-oxo cluster instead of organic linker in MIL-53(Fe) [24]. Along with the generation of holes, the absorption of solar energy induces chemical reactions, showing that the photocatalytic cavitation is mainly responsible for the degradation of dyes. By changing the ration of precursor $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and ligand H_2BDC , MIL-53(Fe) changed to MIL-68(Fe) as a photocatalyst. The band in the low energy region between 452 and 600 nm is attributed to the $d \rightarrow d'$ transition of Fe^{3+} ions [25]. Slightly different from the MIL-53(Fe), the band gap of MIL-68(Fe) is 2.8 eV which corresponds to the absorption edge as 440 nm. However, consistent with MIL-53 (Fe), the iron-oxo cluster, not organic ligand are uses as excited cites that is responsible for the photocatalytic performance of MIL-68 (Fe). In addition, MIL-88A similar to MIL-68 (Fe) is also effective for decoloration of methylene blue (MB) under visible light [26]. The band gap is as low as 2.05 eV which corresponds to the extended absorption edge of 650 nm. However, MIL-88A showed inconspicuous photocatalytic activity, specially, the MB degradation rate is less than 20% within 20 min. The formed $\cdot\text{OH}$ possesses with oxidation capacity is responsible for oxidizing the surface adsorbed organic molecules [27]. Meanwhile, with the aid of H_2O_2 electron donor, the photogenerated holes can generate more $\cdot\text{OH}$ radicals which are helpful for the photocatalytic conversion of dyes. Different from (ST-MOF235) by traditional hydrothermal methods, MOF 235 crystals, a type of iron-based MOF, were synthesized using a microwave-assisted method was presented (MA-MOF235), which exhibits excellent photocatalytic activity for the degradation of rhodamine B (RhB) [28]. The main optimal absorption band for MA-MOF 235 and ST-MOF 235 were 650 nm and 640 nm, which is different from MOF 235. The band gap energies of MA-MOF 235 and ST-MOF 235 were estimated to be 1.94 eV and 1.98 eV, suggesting that the potential of to act as a photocatalyst. In the presence of catalyst and H_2O_2 without light irradiation,

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