



MOF based composites with engineering aspects and morphological developments for photocatalytic CO₂ reduction and hydrogen production: A comprehensive review

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ABSTRACT

Recently, metal-organic framework (MOFs) based materials have gathered increasing interest in the field of photocatalysis for energy and environmental remediation. The discovery of the highly porous, flexible, modifiable structure with excessive active sites is effective for harnessing clean energy from the sun. Several MOFs have been successfully designed for CO₂ capture and H₂ production applications. This review highlights the engineering aspects, morphological developments, and efficiency enhancement for MOFs-based photocatalysts towards CO₂ reduction and hydrogen applications. In the first part of review characteristics, classification, band structures, morphological development, and visible light responsiveness of MOFs were critically discussed. The recent developments in MOF semiconductors ranging from single metal MOF to mixed metal is discussed. In the mainstream, enhancement approaches for photocatalytic performance of MOFs and expand their visible light absorption has been discussed. The commonly employed enhancement strategies include morphological alterations, Schottky junction, sensitization with polymers, plasmonic metals, or dye, and heterojunction formation including type I, type II, type III, and Z-scheme. The applications of MOFs based materials for photocatalytic CO₂ reduction, and hydrogen production were systematically discussed. This review will ultimately be useful for researchers looking to develop novel strategies to enhance MOF semiconductors composites for not only environmental and energy applications, but as well as other catalytic processes.

1. Introduction

The increasing emission of greenhouse gases (such as CO₂) continue to worsen the threats of climate change and global warming. To mitigate this impact, renewable and sustainable energy should supplement or replace the current fossil fuels. One evolving technology that can achieve this vision is photocatalysis, which has emerged as a green technology due to its possible utilization of renewable solar energy [1]. For instance, atmospheric CO₂ and H₂O can be converted into renewable fuel and chemicals such as methane (CH₄), formic acid (HCOOH) and methanol (CH₃OH) using photocatalytic strategies under low temperature and atmospheric pressure without further polluting the environment [2,3]. More importantly, photocatalytic water-splitting for hydrogen evolution reaction (HER) have been established as an effective

approach to meeting energy demand [4,5].

However, one of the major challenges in photocatalysis is the inefficient utilization of the solar spectrum, which is associated with their wide bandgap and lower photocatalytic efficiency due to the fast recombination of photogenerated electrons and holes [6]. Conventional inorganic semiconductors such as the popular TiO₂ are limited by their rapid charge recombination and low light absorption due to their wide bandgaps [7,8]. Light absorption, being the backbone of photocatalytic technologies, is highly dependent on the light harvesting properties of the photocatalyst material [9]. This reinforces the interest in MOFs for photocatalytic applications. Fig. 1 presents the result of the search on the Scopus database (with keywords Photocatalytic Metal Organic Frameworks) from 2009 to 2022. It shows the exponential growth in the contribution to research involving photocatalytic MOFs due to their

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