



Research Highlight

Immobilizing [FeFe]-hydrogenase mimics to metal–organic frameworks for enhanced hydrogen production

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Production of hydrogen from water by solar-energy conversion has long been considered a promising way to solve the climate change and energy crisis [1]. However, some critical issues at this stage, such as catalysts for hydrogen evolution with high efficiency and low cost, definitely hinder the practical application of photocatalytic hydrogen production from water. [FeFe]-hydrogenase, an excellent natural biological enzyme catalyst bearing unique organometallic clusters with noble-metal-free element, is most efficient in reducing protons to hydrogen and demonstrates remarkable turnover frequencies (TOF 6000–9000 s^{−1} per active site) [2]. With the crystal structural elucidation of [FeFe]-hydrogenase, numerous [FeFe]-hydrogenase mimics have been synthesized to develop photocatalytic systems for hydrogen generation [3–5]. To date however, there are still no artificial [FeFe]-hydrogenase mimics that can reproduce the high reactivity of natural [FeFe]-hydrogenase, largely because of the low stability of [FeFe]-hydrogenase in photocatalytic process. Therefore, considering the fact that a natural [FeFe]-hydrogenase is deeply embedded within the protein matrix, it is important to explore the external matrix of the [FeFe]-hydrogenase mimics.

Emerging as an intriguing class of porous crystalline materials, metal–organic frameworks (MOFs) can be easily functionalized at the molecular level [6]. Pioneering works on the incorporation of [FeFe]-hydrogenase mimics into MOFs to create heterogeneous catalysts has been demonstrated improved photocatalytic activity and stability for hydrogen production [7–9]. Among these previously reported studies, [FeFe]-hydrogenase mimics were incorporated into a photosensitizing zirconium-porphyrin MOF by direct coordination or into a non-photosensitizing MOF by post-synthetic exchange/covalent bond with [Ru(bpy)₃]²⁺ as a photosensitizer. Although some achievements have been made in

combination of [FeFe] catalyst and MOFs, immobilizing [FeFe] catalyst to photosensitizing MOF by covalent bonds is still a challenging task.

Recently, Yuan's group [10] reported the incorporation of an [FeFe]-hydrogenase mimics into an [Ru(bpy)₃]²⁺-derived photosensitizing UiO-type MOF by a facile click reaction to generate a new hydrogen evolution catalyst UiO-MOF-Fe₂S₂ (Fig. 1) [10]. In this work, the construction of photosensitizer and [FeFe] catalytic active site in the same framework could enhance the electron transfer process in a local microenvironment by comparison to [Ru(bpy)₃]²⁺ as a photosensitizer. Besides, the incorporation of [FeFe] catalytic active site via click reaction is more efficient compared with ligand exchange or weakly coordination strategy. After 50 h of photocatalytic reaction, the UiO-MOF-Fe₂S₂ produced a total of 32 μmol H₂ with ascorbic acid as a proton source and a sacrificial electron donor. The good performance of UiO-MOF-Fe₂S₂ can be ascribed to greatly improved stability by the protection from the framework, as well as the efficient electron transfer between the photosensitizer and the [FeFe] catalytic site.

In summary, this work may provide a new solution for incorporation of the [FeFe] catalytic center into a photosensitizing MOF by judicious design of the ligands. Meanwhile, the good performance of this artificial [FeFe]-hydrogenase mimics system demonstrates that this approach is a promising strategy to stabilize the [FeFe] catalyst and improve the photocatalytic efficiency of hydrogen evolution in water.

Conflict of interest

The author declares that he has no conflict of interest.

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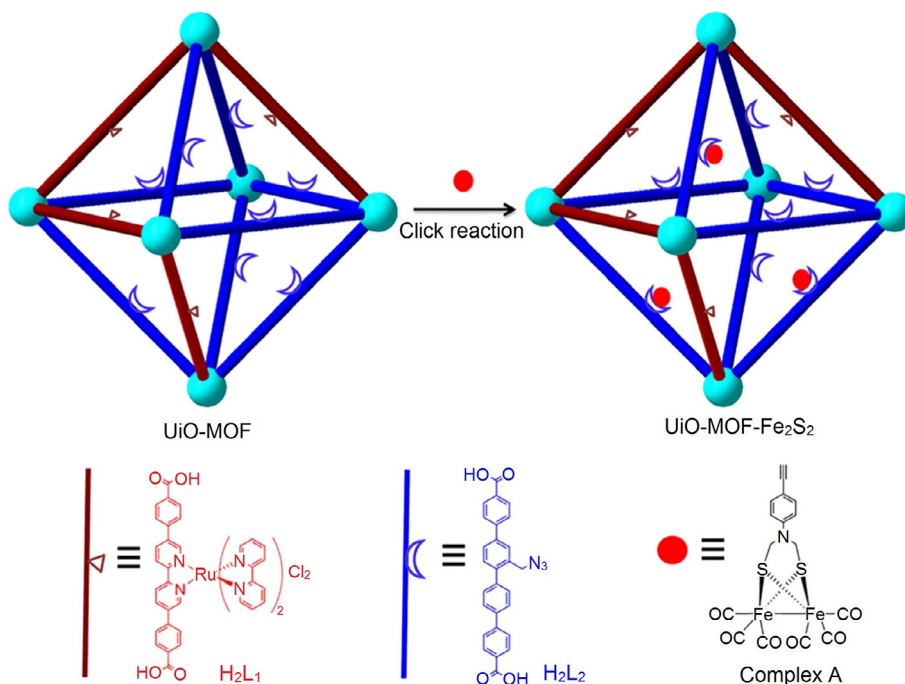


Fig. 1. Modification of UiO-MOF via a click reaction for incorporating [FeFe] catalytic sites to form new catalysts UiO-MOF-Fe₂S₂. Reproduced with permission from Ref. [10]. Copyright 2019 Elsevier.

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Daofeng Sun obtained his M.S. degree from Liaocheng Normal University, China in 1998, and graduated from Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences with a Ph.D. degree under the supervision of Rong Cao and Maochun Hong in 2003. After finishing three-year postdoctoral fellowship at Miami University, he joined Shandong University as a full professor in January 2007, then moved to China University of Petroleum (East China) in January 2013. His current research interest focuses on the design and synthesis of porous materials for clean-energy, catalysis and environmental-related applications.