



Metal–organic frameworks for electrochemical applications

Wei Liu, Xue-Bo Yin *



Nankai University, Research Center for Analytical Sciences, College of Chemistry, State Key Laboratory of Medicinal Chemical Biology, Tianjin Key Laboratory of Biosensing and Molecular Recognition, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, China

ARTICLE INFO

Keywords:

Metal–organic frameworks
Electrochemistry
Redox-active complex
Mass or energy conversion
Electrochemical sensor

ABSTRACT

Electrochemical devices are fast, sensitive, accurate, and convenient as sensing and mass or energy conversion platforms. Metal–organic frameworks (MOFs) attract much attention because of their intriguing properties. MOFs have great potential for electrochemical applications, but two challenges are confronted, including the design of redox-active MOFs (ra-MOFs) and the improvement of MOF conductivity. Redox or catalytic active sites can be introduced using active ligands or metal ions, and active complexes as building blocks. MOFs can also hold active guest molecules, enzymes, bacteria, and nanoparticles and promote electrochemical activity. In order to improve MOF conductivity, conductive ligands and metal nodes are rational choices to form long-range delocalized electrons for charge mobility. Integrating guest molecules or mixing with electrical conductors is the alternative. The MOF film attached on the substrate surface facilitates direct electron transfer and device building. High sensitivity and selectivity of MOF-based electrochemical sensors and improved mass or energy conversion are anticipated.

© 2015 Elsevier B.V. All rights reserved.

Contents

1. Introduction	86
2. Design of electrochemically active MOFs	87
2.1. Organic ligands or metal ions as the active sites of MOFs	87
2.2. Redox-active metal complexes as the active sites of MOFs	87
2.3. Redox-active species-loaded MOFs for electrochemical applications	90
2.4. Integration of nanoparticles in MOFs for electrochemical applications	91
3. Enhancement of conductivity of MOFs	91
3.1. Electronic conductivity of MOFs	91
3.2. Mixing MOF with conductive materials	92
3.3. MOF thin film on a substrate for direct electron transfer and device building	92
4. Selectivity and sensitivity of MOF-based electrochemical systems	93
5. Applications of MOF-based electrochemical systems	93
6. Conclusions and future outlooks	94
Acknowledgments	95
References	95

1. Introduction

Metal–organic frameworks (MOFs) consist of metal nodes connected by organic ligands, bearing structures ranging from microporous to mesoporous scale [1,2]. Their flexible and porous structures allow easy diffusion of guest molecules into the infinite and highly ordered frameworks and thus promote host–guest in-

teractions [3–5]. All these merits encourage further study of using MOFs in separation [5], gas storage [6], and catalysis [2,7,8]. The optical, electrical, and magnetic properties of MOFs extend their applications to chemical sensing [9,10] and bioimaging [11], including magnetic resonance imaging [12] and optical imaging with phosphorescent MOF [13].

Electrochemical devices are versatile, reliable, attractive, highly sensitive, easy-to-use tools having specific recognition and wide applications [14]. In view of these advantages, electrochemiluminescence (ECL) sensors have been developed in order to detect metal ions, small molecules, and biomacromolecules

* Corresponding author. Tel.: +86 13820376212; Fax: +86 22 2350 3034.
E-mail address: xbyin@nankai.edu.cn (X.-B. Yin).

in our group [15–19]. It is easy to envision the versatile applications of MOF-based electrochemical systems, but the topic has received far less attention than other MOF applications [4,20]. After conducting a search on the ISI web of science (retrieved on Jan 7, 2015), 17,802 papers were reported with MOFs as the subject, among which only 547 papers contain “electrochemical” or “electrochemistry”. Electrochemical systems are often used to probe local environment, structure, and guest species in MOFs; however, applications based on the direct use of the electrochemical properties of MOFs were less [4].

Some MOFs meet the requirements of electrochemical applications and are used as advanced electrode materials and matrices [4]. The pore and channel of MOFs offer radius and volume exclusion for the targets with different size, shape, polarity, and conformation [21]. The host–guest interaction further enhances the selectivity by Lewis acidic or basic sites in ligands, open metal sites, hydrophobic interactions, and aromatic π groups in MOFs [22]. Moreover, the incorporation of electron-donating or electron-withdrawing groups in the ligands results in the formation of donor–acceptor structures in the MOFs and thus tunes electron orbital energy level of the electrochemical devices. The substrate specificity of the catalytic site improves the selectivity of electrochemical response [24]. Thus, using MOFs as electrode materials and matrices would further extend the applications of electrochemistry. Electrochemistry has been broadly discussed; however, electrochemical sensing and mass or energy conversion using MOFs as electrode materials or matrices have been primarily included in this review.

The design of redox-active MOFs (ra-MOFs) and the improvement in the conductivity of MOFs are the challenges for the development of MOF-based electrochemical systems [4,23]. The basic requirements and structural elements of ra-MOFs are discussed in this review with an emphasis on the potential applications of electrochemical sensing and mass or energy conversion [14]. Most MOFs are insulators or semiconductors [23,25], but their porosity favors the introduction of nonnative conductivity by infusing the accessible volume with the guest molecules [26]. Deposition of an MOF film enhances the direct electron transfer between the film and substrate. Thus, the merits of both MOFs and electrochemical devices are anticipated, including the permselectivity and catalytic activity of the former, as well as the simple instrumental set-up and high efficiency of the latter [27]. Directions for future research are proposed with an emphasis on the desired functionalities and the structure–property relationships of MOFs, and designing and rationalizing the functional devices for practical applications of electrochemistry.

2. Design of electrochemically active MOFs

Electrochemical activity, the pre-requirement of MOFs for electrochemical applications, can be achieved by introducing redox-active or catalytic sites [4]. Electrochemically active MOFs provide the selectivity to target for sensing. The electrocatalytic properties of MOFs facilitate mass or energy conversion. The electrochemical activity within MOFs is considered to manifest via three processes [28]: 1. The rapid extension of ionic permeability in MOFs; 2. Electrochemical mechanisms causing phase change; and 3. Restructuring of the framework as a result of electrochemical activity.

2.1. Organic ligands or metal ions as the active sites of MOFs

The incorporation of redox-active organic ligands represents a strategy to prepare ra-MOFs by taking advantage of the ligand π – π^* bands [29–31]. Extension of the conjugated system of the ligand is a potential approach for construction of ra-MOFs, such as the derivatives of benzene, pyridine, imidazole, and thiophene. The large dislocation area facilitates UV absorption, luminescent emission, and

charge mobility, which are the important information sources monitored by chemical sensors. The long-lived excited state is stabilized by charge delocalization via extensive π – π^* and/or π – n stacking interactions [28–30]. MOF-based electrochemical systems are constructed based on the ligand-mediated response (ligands such as DPNI and DPMNI; Fig. 1) to the electrochemical stimuli of MOFs [29]. Solid-state cyclic voltammetry (CV) study of porous micron-thick $[\text{Zn}_2(\text{NDC})_2(\text{DPNI})]$ MOF film reveals the reversible and irreversible peak from DPNI, while $[\text{Zn}(\text{DMF})(\text{NO}_3)_2(\text{NDC}')(\text{DPMNI})]$ MOF exhibits two redox-accessible states [30,31]. The color of MOFs varied from yellow to intense brown, while the mono- and dianion species were formed. The charge transition for optoelectronic and sensing application derives from the color-tunable electrochromic property of the ligand [29]. Moreover, the organic ligands contain large π bonds, or the large conjugation areas support the photoinduced charge-transfer process, which is the potential source of ra-MOFs. An in situ solid-state spectroelectrochemical method is used to elucidate the redox-accessible states of metal and ligands by coating the MOFs on indium tin oxide (ITO)-coated quartz working electrode [29]. While near-infrared (NIR) emissions are assigned to $D_0 \rightarrow D_n$ transition, the overlapping bands in the UV–Vis region are ascribed to the HOMO–LUMO (highest occupied molecular orbital/lowest unoccupied molecular orbital) transitions.

If redox-active metal ions are used to prepare ra-MOFs, the open metal sites provide a polarized surface in tailored pores to interact with small molecules and ions. The metal ions used as catalytic sites receive electrons to effect chemical reaction. Electrochemical reduction of Fe^{3+} to Fe^{2+} in MIL-35(Fe) facilitated the simultaneous insertion of Li^+ in the porous structure [24]. As the electrons occupied the lower-energy 3d orbital, higher M–O bond stability toward charge variations was achieved for the reversible conversion/decomposition [24]. MOF-5, HKUST-1, and M-MOF-74 (M = Mg, Mn, and Co) were used as electrode materials for O_2 evolution (Fig. 2a–c) [32]. As illustrated in Fig. 2d,e, the accessible open metal sites in the uniform channels increased the number of O_2 molecules and improved the reaction efficiency [32]. The accessible pores, high surface areas, and adjustable chemical environments of the MOFs acting as electrode materials facilitated the interaction with the guest molecules [32]. The diversity and capacity of the MOFs extend their applications to Li– O_2 batteries and mass evolution electrode materials [24,32].

Electrocatalytic reduction of CO_2 was observed in a $[\text{Cu}_3(\text{BTC})_2]$ MOF film-modified electrode; well-defined Cu(II)/Cu(I) and Cu(I)/Cu(0) reversible redox responses were indicated [33]. As illustrated in Fig. 2f, the mechanism shows that Cu(I), as the active species, catalyzed the reduction and transferred CO_2 to oxalic acid [33]. Enhancing conductivity and efficiency of the MOF-modified electrode will generate long-lasting current for practical purposes. The MOFs contribute to the reverse process of immobilization of atmospheric CO_2 and conversion of CO_2 to useful organic molecules, which have the potential to decrease adverse impacts on the environment by lowering the CO_2 level [33]. $[(\text{HOC}_2\text{H}_4)_2\text{dtoaCu}(\text{II})]$ MOF was used as a catalyst for ethanol electrooxidation; higher tolerance to the oxidation products and lower ethanol electrooxidation potential were observed compared to those while using Pt-based catalysts [34]. Better knowledge about the redox properties of the building blocks facilitates the development of ra-MOFs with higher efficiency for specific electrochemical procedures.

2.2. Redox-active metal complexes as the active sites of MOFs

Fabrication of ra-MOFs with metal ions or organic ligands is easy but primeval. Changing the valence state of the metal ions and the oxidation state of the ligands may lead to the structural collapse of MOFs. Metal complexes made from stable ligands provide optional blocks for building steady ra-MOFs. The metal ions in the

Download English Version:

<https://daneshyari.com/en/article/7689145>

Download Persian Version:

<https://daneshyari.com/article/7689145>

[Daneshyari.com](https://daneshyari.com)