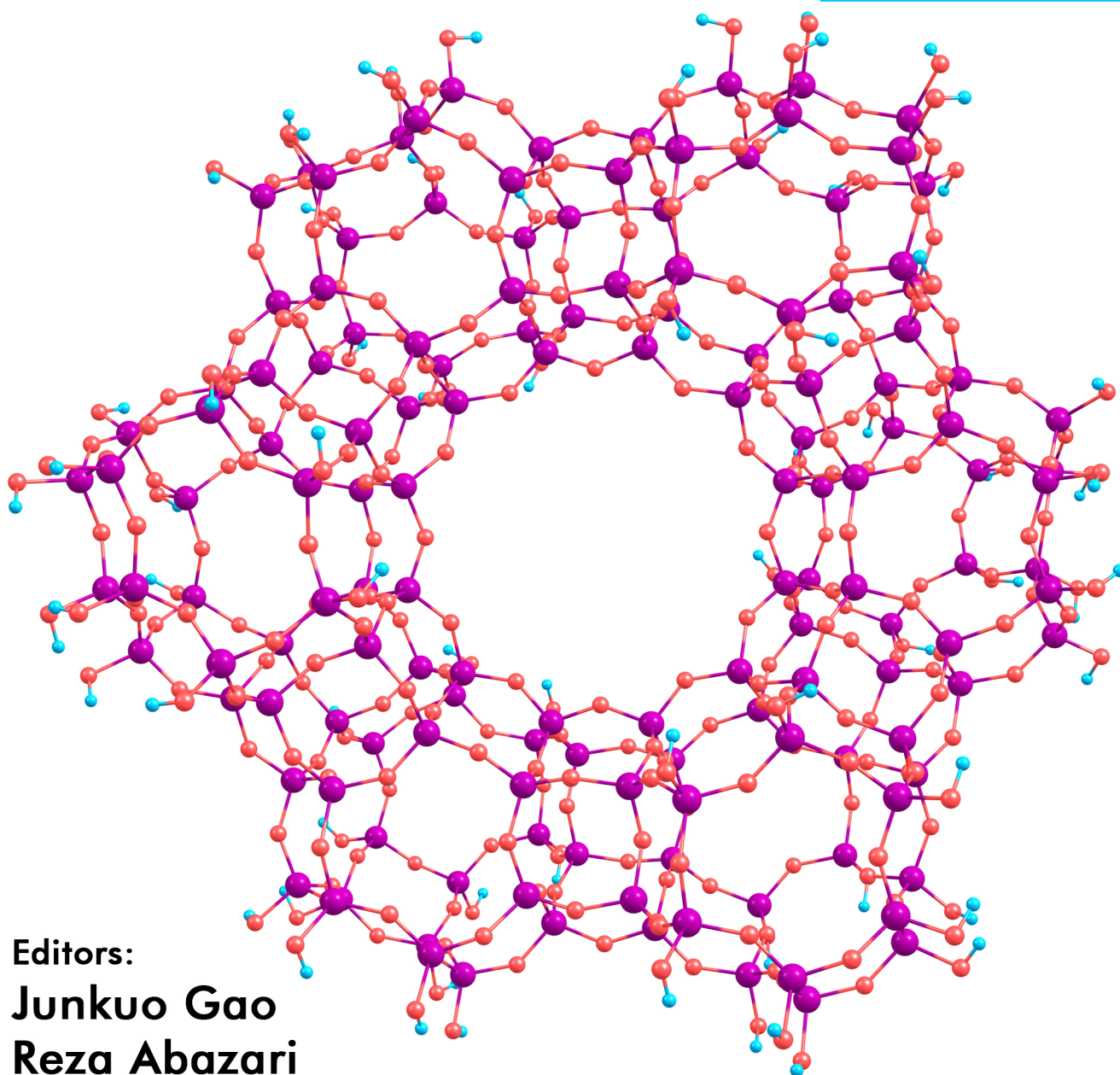


ADVANCED CATALYSTS BASED ON METAL-ORGANIC FRAMEWORKS

PART 2



Editors:

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Advanced Catalysts Based on Metal-organic Frameworks (Part 2)

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PREFACE

As a new type of functional molecular material, the design and synthesis of MOFs with the desired structure and properties have become one of the frontier fields of coordination chemistry, supramolecular chemistry, crystal engineering and materials science. The research of MOFs spans many disciplines, such as inorganic chemistry, organic chemistry, coordination chemistry, supramolecular chemistry, crystal engineering and materials science. The design, synthesis, and applications of MOFs have attracted tremendous attention in broad scientific areas. Therefore, it is worth releasing a professional publication to elucidate many related issues.

In addition to catalysis, MOFs have found increasing applications in photocatalysis and electrocatalysis. Thanks to their remarkable features, MOFs have opened new horizons in solar photocatalysis for hydrogen generation, CO₂ reduction, and removal of inorganic/organic pollutants. Their excellent photocatalytic behavior could be assigned to the interactions between the organic linkers and the metallic nodes. Photo-induced linker-metal single electron transfer is one of the most general mechanisms which can result in enhanced carrier mobility, decreased recombination rate, and improved charge separation efficiency. Visible light absorption can be enhanced by substituting the linkers with those having higher surface absorbance; while more efficient electron transfer can be achieved through nodes' modification by ion exchange.

MOFs and their composites have been lately used as a precursor for electrocatalysis of hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR), and CO₂ reduction reaction (CO₂RR) owing to their superior electrical conductivity and uniform active site distribution. Thanks to their tunable and porous crystalline structure, excellent surface area, feasible mass transfer routes, and atomic dispersion of metallic active sites, MOFs are promising structures for future electrocatalysis.

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CHAPTER 1

Metal-organic Frameworks and their Derived Structures for Photocatalytic Water Splitting**Reza Abazari^{1,2,*}, Soheila Sanati² and Junkuo Gao^{1,*}**¹ *Institute of Functional Porous Materials, School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China*² *Department of Chemistry, Faculty of Science University of Maragheh, Iran*

Abstract: Fossil fuels are non-renewable energy sources and may cause environmental pollution. One of the appropriate solutions is to develop clean and renewable sources of energy as an alternative to fossil fuels. Environmental pollution and lack of renewable energy sources are two significant problems affecting the current life of human society and economic progress. Researchers have addressed semiconductor-oriented heterogeneous photo-electrocatalysis, photocatalysis, and electrocatalysis by the fuel cells to solve these crises. Photocatalytic water splitting is a promising approach in resolving the energy crisis. This process involves harvesting solar light, charge transfer and separation, and evaluation of catalytic reactions of H₂ and O₂. In this regard, the main challenge is to find an efficient, environmental-friendly, cost-effective, and easily fabricated photocatalyst with high stability and corrosion resistance in different media. Thanks to their tunable structure, structural flexibility, high specific surface area, tunable pores, and unsaturated metal sites, metal-organic frameworks (MOFs) could be an efficient photocatalyst for hydrogen production under UV, NIR, and visible radiation. Therefore, MOFs and MOFs-based compounds are widely utilized as alternatives for expensive commercial catalysts developed based on rare elements such as Pt and Au. They can also be employed as precursors for the synthesis of different types of materials with different structures, sizes, and morphologies. This chapter summarizes MOF-based photocatalysts for the splitting of water are MOFs modification strategies.

Keywords: Charge Separation, Composites, Materials Derived, Metal-organic Frameworks, Photocatalytic Water Splitting, Synergistic Effect.

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1. INTRODUCTION

The inappropriate application of fossil fuels has led to significant environmental problems and energy crises, raising serious concerns [1]. Currently, fossil fuels are the source of more than 80% of the utilized energy in the world [2]. Excessive exploitation of fossil fuel reserves will soon result in serious shortages [3]. On the other hand, solar energy is a stable, safe, and clean energy source which has been proposed as a gleam of hope and a suitable alternative to fossil fuels [4, 5]. Some technologies have been developed for the conversion of solar energy into chemical energy and electrical energy. Low-temperature photocatalysis/electrocatalysis-based water splitting is highly promising [6, 7]. Hydrogen generation from water splitting using sunlight can be an efficient strategy to resolve the energy crisis and environmental pollution [8]. The increasing popularity of hydrogen generation through photocatalytic water splitting can be assigned to the following reasons: 1) water is the cleanest and most abundant source on earth, 2) water is produced as a result of hydrogen re-burning, releasing a lot of energy with no environmental consequences, and 3) the repeated application of hydrogen as fuel causes an efficient energy cycle that involves sunlight and efficient catalysts. Water splitting involves two half cathodic reactions: hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER) [9, 10]. However, these reactions are kinetically slow and require catalysts [11]. Photocatalytic splitting of water through semiconductor-based photocatalysts involves the following steps: (i) When the photon energy is higher than the band-gap of the photocatalyst, the electrons are excited from the valence to the conductive bands, leaving a hole in the valence band. (ii) The charge carriers reach the surface of the photocatalyst. (iii) The protons of the water molecules absorb the released electrons and are converted into hydrogen, while the holes and oxygen atoms combine to produce oxygen molecules (Fig. 1) [12, 13]. In these half-reactions, the potential of the conductive bond must be more negative than the energy level of H^+/H_2 (0 V vs. NHE, pH = 0) while the potential required for the valence bond must be higher than the energy level required for O_2/H_2O oxidation. Therefore, the minimum required bandgap for photocatalytic splitting of water should be equal to 1.23 eV [14]. Moreover, the variation in the free energy should be equal to 1.23 kJ/mol for the overall splitting of water [15, 16]. According to the Nernst equation, the overall splitting of water requires 1.23 eV energy. Semiconductors with a band-gap equal to or higher than 1.23eV are ideal photocatalysts for water splitting. Semiconductors with a band-gap of 1.23 eV are not suitable candidates for photocatalytic splitting of water as the overpotential of interfacial charge transfer should be also considered [17 - 19]. The minimum band-gap for photocatalytic splitting of water is about 2eV [20]. The band structure plays an important role in the determination of the photocatalytic performance of semiconductors. In a semiconductor, potential positions of valence and conductive

bands determine the oxidation and reduction capabilities [21, 22].

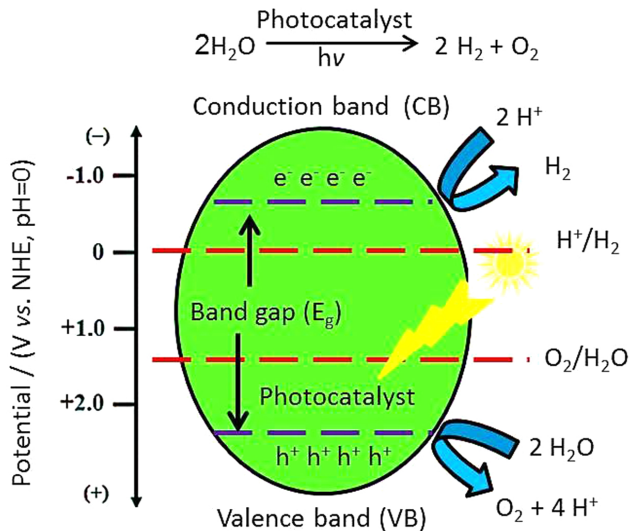


Fig. (1). The principle of photocatalytic water splitting based on semiconductors.

Metal oxide-based photocatalysts play an effective role in water splitting under UV light [23 - 25]. For instance, TiO_2 has been used in water splitting under UV light due to its low cost and nontoxicity as well as photostability [26]. Fujishima claimed the use of TiO_2 in the photocatalytic splitting of water for hydrogen generation in 1972 [27]. Due to its large band-gap (3.2 eV), TiO_2 can be only used under the UV spectrum of solar energy. Therefore, the efficiency of semiconductors decreases due to the fast rate of recombination of electron holes as well as the poor intensity of light in the UV region [28]. High-performance, visible-range photocatalysts can be helpful in photocatalytic water splitting [29, 30]. Conventional water-splitting photocatalysts are mostly inorganic compounds based on rare elements, making their mass production a costly process [31]. For instance, the high cost and instability of Pt nanoparticles have limited their application [32]. In this regard, the focus of future research should be on inexpensive and stable catalysts [33].

Metal-organic frameworks are a group of photocatalysts that have attracted the attention of research communities [34, 35]. These photocatalysts are benefited from a large surface area, suitable band-gap, the ideal structure for charge transfer, and high photo-corrosion resistance [36]. The application of MOF-based photocatalysts in water splitting was first reported in 2009 by the Mori Group [37]. Xu *et al.* reviewed MOFs-based catalysts for hydrogen generation from

CHAPTER 2

Metal-organic Frameworks and MOF-based Materials for Photocatalytic CO₂ Reduction

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Abstract: Owing to the undeniable emission of anthropogenic CO₂ emission into the atmosphere, the world has witnessed a continuous upsurge in the issue of global warming and energy insecurity. Numerous efforts have been adopted to alleviate these crises, but the most viable method is converting CO₂ into value-added chemicals or fuels. Considering the cleanness of solar energy and the corresponding renewable energy sources, various novel classes of metal-organic framework materials were developed for CO₂ photoreduction to energy-rich chemicals. This has made the study into different MOFs and MOF-based photocatalysts remain the hottest topics to date. The uniqueness of MOF materials over other photocatalysts includes their exceptional compositions, tuneability, larger surface areas, higher porosities, homometallic/heterometallic cluster as a secondary building unit, and diverse structural uniqueness. The development of these MOFs and MOF-based photocatalysts is essential to overcome the large and intrinsic thermodynamic barriers. Based on the considerable interest in these photocatalysts for CO₂ reduction (CO₂R), this chapter began with a brief insight into fundamental principles of photocatalysis, the process of photocatalytic conversion of CO₂, thermodynamics aspects of CO₂ photoreduction, mechanisms, and kinetics behind the photocatalytic CO₂R. We further highlight some progress and the associated challenges with the applicability of MOFs and MOF-based photocatalysts for CO₂R into energy-rich chemicals. Despite some challenges and hitches with MOFs for CO₂ reduction, their future in combating global warming and energy insecurity is promising.

Keywords: CO₂ Photoreduction, Energy-rich Chemicals, Metal-organic Frameworks, Photocatalysis.

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1. INTRODUCTION

The issue of global warming from greenhouse gas emissions has nowadays become a complex phenomenon. The omnipresent CO₂ emission *via* fossil fuel combustion is the major cause of global warming. Several approaches ranging from separation and sequestration to mitigation of the consequential effect of CO₂ emission have been adopted but the use of CO₂ as the chemical feedstocks for other processes remains a vibrant and reliable technique to ensure a “carbon-neutral cycle”. Thus, making a photocatalytic conversion of CO₂ to useful fuels and chemicals a desiring and appealing approach to mitigate the “greenhouse effects” and therefore relieve the global shortage of energy. However, CO₂ reduction (CO₂R) to chemicals or fuels is extremely challenging due to its stable structure with the chemical stability of C=O bond and higher dissociation energy than 805 kJ/mol, which requires higher energy inputs to break the cleavage and enabling the conversion of CO₂ to products [1]. Therefore, this necessitates the development of photocatalysts that can address this challenge. Numerous photocatalysts have been developed including “homogenous “metal incorporated zeolites”, molecular complexes”, and semiconductors but their performances are quite very low. Therefore, there is a need for the development of efficient photocatalyst materials for CO₂R to chemicals.

Over the past years, MOFs have been classified among the top emergent materials with exceptional photocatalytic functionalities, attractive crystallinity, and their coordination chemistry, self-assembly organic-inorganic hybrid unit with “metal nodes” or “polynuclear secondary building units (SBUs)” that produce porous with periodical frameworks [2]. These units are known to possess preferential coordination between the rigidity, metal ions, and the organic ligand lengths. MOFs possess distinctive structural topologies with remarkable surface areas, and ultra-higher porosities. Their various ranges of applications in catalysis (such as energy conversion and storage), wastewater treatment, medical application, *etc.* have drawn the attention of different researchers from various fields for wider laboratory and industrial applications.

From catalysis viewpoints, MOF materials have presented numerous fascinating merits as photocatalysts, cocatalysts, *etc.* over the other traditional materials including zeolites, silica, or clay. Notable potentialities of MOFs as multifunctional photocatalysts include the ability to tune their structures, diverse components (pores, nodes, and linkers), adjustable and well-defined frameworks for the proper understanding of the photocatalytic mechanisms, abundant active sites, uniform porosity; and tunable environment, transport and recognition of the substrate(s) and product(s), structural-functional relationships at the molecular levels, and rigorous photocatalysis in a wider array of the photocatalytic reaction

[3 - 8]. This chapter discussed MOFs and MOF-based photocatalysts for CO₂R. It started with a brief insight into fundamental principles of photocatalysis prior to the process of photocatalytic conversion of CO₂, thermodynamics aspects of CO₂ photoreduction, mechanisms, and kinetics behind the photocatalytic CO₂R. Finally, we highlighted some progress and the associated challenges with the applicability of MOFs and MOF-based photocatalysts for CO₂ reduction into energy-rich chemicals and therefore offer some promising strategies to foster the improvement in the field.

2. FUNDAMENTAL PRINCIPLES OF PHOTOCATALYSIS

Numerous review articles have explained the basic principle of photocatalysis [9], so our focus here will only base on the short introduction of the field to enable the readers to gain insight into the necessity of employing MOF photocatalysts for constructing the “solar-driven photocatalysts”. Photocatalysis is the process of inducing the targeted redox reaction(s) on the light absorbers and cocatalysts on it with the photogenerated electron(s) and hole(s). It comprises the following unique steps including (i) the light absorption, (ii) the charged separations and photogenerated transport charged carrier in the bulks, and (iii) the catalysis on the light absorbers and cocatalysts surfaces as presented in Fig. (1). Thermodynamically realizing this effectively is challenging because (a) extremely high solar energy (*i.e.* visible light) harvest is needed for generating necessary energetic electron-holes, (b) the higher mobility and longer diffusion lengths are involved in the photogenerated electron-holes for suppressing the bulk recombination, (c) highly redox powers of the photogenerated electron-holes make the reaction occurs since water oxidation reaction requires 4 electrons, (d) abundantly active surface site for the target forward reaction instead of the backward reaction (*e.g.* H₂+ O₂ →H₂O). Therefore, all these challenges required further research efforts with the 3 steps span from 10⁻¹⁵ to 10⁻¹ time scale [10]. Meeting the requirements for these steps is an inherent conflict that involves 3 factors including (i) decrease in bandgap (*i.e.* rise of absorption light ranges) leads to the decrease in the reductive capability of photogenerated electron and decrease in oxidation power of the photogenerated hole [11, 12], (ii) in many semiconductors, there is very high electron mobility than that of the hole mobility which is not favorable to the rate-determining steps for oxidation reaction involving H₂O [13, 14]. (iii) there are mismatching challenges amongst the random distribution of oxidative and reductive sites of reaction with the desired “electron-hole” migrations in a different direction [15]. The vital fundamental bottlenecks associated with catalysis principles, electronic property, and the photophysical process make it more challenging to realize the higher efficiency in photocatalysis. This can be addressed by precisely controlling each of the

Electrocatalytic Metal-organic Frameworks and OER Based on Metal-organic Frameworks and their Structure

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Abstract: Electrochemical water splitting has received extensive attention and research due to its ability to effectively produce and store clean energy. Water splitting includes hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The complex reaction mechanism of the two half-reactions leads to slow kinetics and high overpotentials, which need to be mitigated and reduced by increasing effective active sites and accelerating electron transfer. Hence, the development of favorable prices and robust electrocatalysts has become a research hotspot. Owing to a large specific surface area, regulatable chemical composition, pore structure, controllable topological structure, and clear surface function, metal-organic framework-based materials (MOFs) have been widely studied. Herein, we summarize relevant references in MOF-based materials with outstanding performance in water splitting and report the design, structure, and activity of a large number of MOF-based materials. In addition, great expectations are placed on the future development and application prospects of MOF-based electrocatalytic materials.

Keywords: Active Sites, Carbon Materials, Electrocatalysts, Faraday Efficiency, Mechanism, Metal Carbide, Metal Nitrides, Metal Oxides, Metal Phosphides, Metal Selenides, Metal Sulfides, Metallic Compounds, MOF, MOF Composites, MOF-derived Materials, Overpotential, Single Atom, Tafel Slope, Turnover Frequency, Water Splitting.

1. INTRODUCTION

The global energy crisis and environmental pollution have promoted the development and utilization of renewable resources and clean energy. Hydrogen

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is one of the most potential clean energies, which is expected to replace the traditional fossil fuels [1, 2]. Electrochemical water splitting has been deemed an effective technology for hydrogen production and involves two half-reactions that are OER on the anode and HER on the cathode [3, 4]. Currently, noble metal (NOM) electrocatalysts have been extensively studied and applied in the industry to accelerate the slow process and reduce the reaction over-potentials for promoting the reaction of electrochemical water splitting, such as IrO₂ and Pt/C [5]. However, the shortage and expensive price of NOM have greatly restricted their wide practical applications. Therefore, low-cost and plentiful catalysts for water splitting have been widely studied recently, such as MOFs have been extensively used as an advanced water-splitting catalyst.

MOFs are a class of porous coordination polymers composed of organic ligands and metal centers constituted by coordination bonds. Currently, because of their large specific surface area, regulatable chemical composition and pore structure, controllable topological structure, and clear surface function, MOFs are seemed as one class of the most promising candidates for electrocatalyst. Particularly, MOFs with the high surface area and the porous structure can expose plentiful active sites and accelerate mass transport [6]. In a broad sense, MOFs can be divided into three types: pristine MOFs, MOFs composite and MOF-derived materials. Benefiting from the above features, abundant active species can be introduced into the metal nodes and linkers, which can effectively promote electrochemical water splitting [7 - 10].

In recent years, MOFs have been extensively applied to OER and HER electrocatalyst. Moreover, coupling various conductive materials, including carbon nanotubes (CNTs), carbon cloth (CC), graphene and other conductive materials, can enhance the electrocatalytic activity of MOFs. For example, Yan and co-workers coupled MOFs with a 2D reduced graphene oxide (rGO) to form a 3D film through pyrolysis [11]. Furthermore, MOFs, as precursors, can be derived into various electrocatalysts [12], such as heteroatom doped porous carbons [13, 14], metal chalcogenides [15], metal nitrides [16], metal phosphides [17], atomic dispersed metal N-C sites [18]. For example, Shi and coworkers used ZIF-67 as precursor to synthesize nitrogen(N)-doped carbon-decorated CoP@FeCoP yolk-shelled micro-polyhedrae (CoP@FeCoP/NC YSMPs) [19]. Its unique structure and N-doped carbon optimized electronic structure improving its electrocatalytic performance.

This chapter reviews the recent research progress for MOF-based materials with high catalytic performance in water splitting. We focus on summarizing the mechanism of water splitting, the structure and performance of MOF-based

materials. Finally, the modification of excellent MOF-based electrocatalytic materials and its future development direction are prospected.

2. MECHANISM OF WATER SPLITTING

The main reaction path of electrocatalytic water splitting is:



It encompasses two half-reactions: OER and HER (Fig. 1a), which can occur in acidic and alkaline electrolytes [20]. Owing to the difference in ion content under acidic conditions and alkaline conditions, the reaction paths of the two half-reactions will be slightly different.

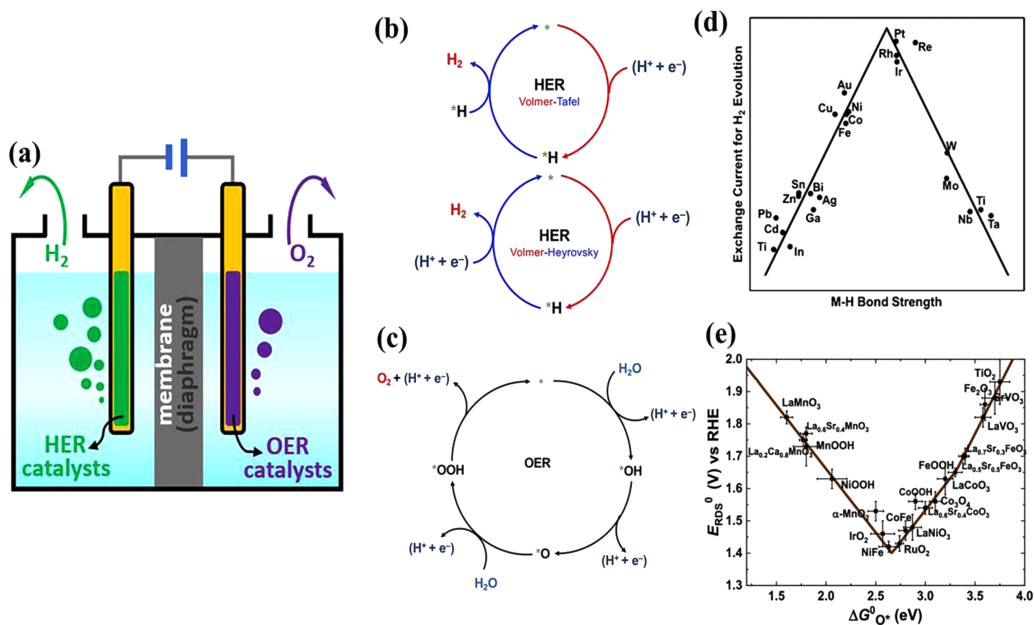


Fig. 1. (a) Water splitting electrolyzer. Reproduced with permission from ref [4]. Copyright 2018, American Chemical Society. (b) mechanisms for HER in the acid electrolyte, (d) Volcano plot for HER. Reproduced with permission from ref [29]. Copyright 2020, American Chemical Society. (c) mechanisms for OER in the acid electrolyte. Reproduced with permission from ref [28]. Copyright 2015, American Chemical Society. (e) Volcano plot for OER. Reproduced with permission from ref [30]. Copyright 2019, American Chemical Society.

2.1. Mechanism of HER

HER is usually considered a two-electron transfer reaction. The first step is to absorb hydrogen atoms released by H_2O or H_3O^+ on the active site, and the second

CHAPTER 4

Recent Progress in Metal-Organic Frameworks and their Derivatives as Advanced Electrocatalysts for Oxygen Reduction Reactions

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Abstract: Oxygen reduction reaction (ORR) plays an important role in clean energy storage and conversion devices, such as metal-air batteries and fuel cells. However, the slow kinetic has impeded their large-scale applications. Hence, it is necessary to develop highly efficient electrocatalysts to accelerate the reaction rate of ORR. Owing to their ordered structure, ultrahigh specific surface area, abundant channel and functional adjustability, metal-organic frameworks (MOFs) and their derivatives were explored to catalyze ORR. In this chapter, we present a timely review of pristine MOFs and MOF-derived porous carbon-based materials as advanced electrocatalysts for ORR. We start with the introduction of the fundamentals of electrochemical oxygen reduction reaction (ORR), followed by surveying various forms of MOFs and MOF-derived nanomaterials as advanced electrocatalysts towards ORR, including metal-free heteroatom-doped carbon-based materials, transition metal and nitrogen co-doped carbon (M-N_x-C), carbon-supported single-atom catalysts (SACs). Additionally, we briefly outline the challenges and prospects of this research filed.

Keywords: Carbon-Based Materials, Carbon-supported Single-Atom Catalysts (SACs), Heteroatom-doped Metal-Free Materials, Oxygen Reduction Reaction, Transition Metal and Nitrogen co-Doped Carbon (M-N_x-C).

1. INTRODUCTION

Faced with the rapid development of modern society and the growing environmental problems, various energy storage and conversion systems have

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emerged in order to replace traditional fossil fuels, including Li-ion batteries, Na-ion batteries, K-ion batteries, Li-S batteries, metal-air batteries, fuel cells, *etc* [1 - 4]. Among them, metal-air batteries and fuel cells have drawn widespread attention because of their high energy density and environmentally friendly features. However, the sluggish oxygen reduction reaction (ORR) at the cathode impedes their commercial applications. Currently, commercial Pt/C catalysts have been recognized as the state-of-the-art ORR catalysts. Nevertheless, Pt-based materials are faced with low reserves, high cost, susceptibility to CO poisoning and poor stability. Given this, much effort has been devoted to improving ORR catalytic performance in intrinsic electrocatalysts and support materials, including that: (1) reducing the loading of Pt by alloying Pt with other transitions; (2) developing novel support materials to increase the active catalytic sites, such as forming single-atom Pt catalysts and improving the utilization efficiency of Pt atoms; (3) exploring non-noble metal electrocatalysts with low cost and excellent catalytic performance.

Recently, metal-organic frameworks (MOFs), as a new class of porous materials, have attracted extensive attention in various fields, such as heterogeneous catalysis, clean energy, biochemical sensing, and so on [5 - 7]. Since the first discovery of MOFs in 1990, rapid progress has been made on the development of MOFs during the past decades [8 - 10]. MOFs are comprised of transition metal ions and organic ligands with a regular framework structure, which possess these unique features, including the high porosity, low density, large specific surface area, adjustable pore size and ordered crystal structure. These unique properties could make more active sites exposed and promote mass transfer rate, which make MOFs-based materials exhibit great application potential in a heterogeneous catalysis field. Pristine MOFs directly as a novel ORR catalyst can be traced back to the pioneering research reported by Mao's group in 2012 [11]. In their work, water-stable Cu(II)-based MOF, copper (II) benzene-1,3,5-tricarboxylate (Cu-BTC, BTC=1,3,5-tricarboxylate), was successfully prepared by hydrothermal method, which offers a new avenue of MOFs as direct electrocatalysts towards ORR.

In addition, the ordered structure consisting of metal nodes and organic linkers make MOFs as ideal precursors to prepare porous carbon materials. In 2008, Xu *et al.* reported the first example of MOF-5 framework ($Zn_4O(OOCC_6H_4COO)_3$) for the synthesis of nanoporous carbon, which demonstrated excellent performance as an electrode material for electrochemical double-layered capacitor (EDLC) [12]. Since then, there have been a lot of reports on various MOFs as templates or precursors for the synthesis of porous carbon. So far, several MOFs such as ZIF-7, ZIF-8, ZIF-67, MOF-5 and MIL have been regarded as excellent precursors to construct porous carbon materials for ORR in metal-air batteries and

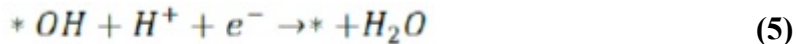
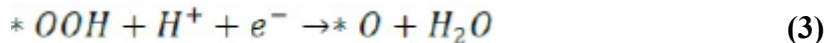
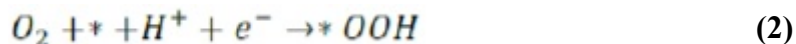
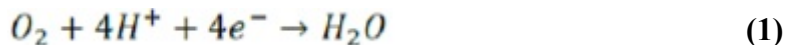
fuel cells [13 - 15]. Porous carbon-based materials derived from MOFs as high-performance electrocatalysts for ORR could be divided into three categories: metal-free heteroatom-doped carbon materials [16 - 19], transition metal and nitrogen co-doped carbon materials (M-N_x-C) [20 - 23] and carbon-supported single-atom catalysts (SACs) [24 - 28].

In this chapter, we start with introduction of fundamental principles of ORR in alkaline and acid conditions. Then, pristine MOFs and various MOFs-derived carbon-based materials as high-performance electrocatalysts for ORR are surveyed, which contain metal-free heteroatom-doped carbon materials, transition metal and nitrogen co-doped carbon materials (M-N_x-C) and carbon-supported single-atom catalysts (SACs). To elicit fundamental insights, the performance enhancement mechanisms are highlighted. Moreover, the challenges and prospects of this research area are also deliberated.

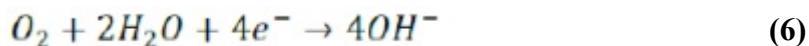
2. FUNDAMENTAL PRINCIPLES FOR OXYGEN REDUCTION REACTION (ORR)

ORR is a reaction converting oxygen molecular into water through several proton/electron coupled processes. In acidic conditions, the reaction operates through reduction of an oxygen molecule (O₂) and four protons (H⁺) by getting a total of four electrons. In basic conditions, hydroxyl groups (OH⁻) are obtained by two molecules H₂O and O₂ with the same number of electrons being involved. A 4-electron pathway of ORR in alkaline media or acid condition has been well-established, which involves the generation of at least three oxygen-containing intermediates (*OOH, *O and *OH) [29 - 34]. The detailed reaction formulas are described as follows:

Acid media:



Alkaline Conductions:



MOFs and their Derived Structures for Multifunctional Electrocatalysis

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Abstract: Multifunctional catalysis attracts great interest due to the opportunity to apply one compound in different types of reactions, and particularly its role in energy conversion reactions, such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR). The requirements of several catalysts are combined in one molecule, which allows utilizing these compounds at both cathode and anode sides for a variety of energy devices. However, seeking optimal catalysts with multifunctional applications and appropriate activity and durability is a difficult task. One of the promising candidates is metal-organic frameworks due to their unique structure and high-specific surface area. Utilization of MOFs and their derivatives as multifunctional catalysts for HER/OER, OER/ORR, HER/ORR/OER, and corresponding energy provision technologies, such as water splitting electrolyzers, metal-ion batteries, is the top area of modern research. Herein, the recent examples of MOF-based electrocatalysts for HER/OER/ORR activity in terms of their bifunctionality and trifunctionality and further application at both cathode and anode sides of water electrolyzer and metal-ion battery are summarized.

Keywords: Hydrogen Evolution Reaction, Metal-ion Battery, Metal-organic Frameworks, Multifunctional Electrocatalysis, Oxygen Evolution Reaction, Oxygen Reduction Reaction, Water Splitting.

1. INTRODUCTION

Hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR) are the most important electrocatalytic transformations that underlie a rational, environmentally friendly path to sustainable and efficient development of a modern energy system. In addition, most energy conversion systems are based on these reactions; for example, fuel

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cells are based on ORR-OER-HER reactions, rechargeable metal-air batteries - on ORR-OER, and water electrolyzers - on OER-HER [1 - 6]. As a rule, catalysts based on noble and expensive metals are used for these reactions. Pt-based catalysts are effective for ORR and HER, while IrO₂ and RuO₂ are widely used for OER. The high cost and limited reserves of these metals in the earth's crust significantly limit their large-scale application in renewable energy technologies [2 - 5]. Thus, the question of finding new alternative equally effective catalysts based on cheaper and more widespread metals in nature for their use in various energy devices becomes acute.

So-called multifunctional electrocatalysts are of particular interest. These are the catalysts that combine the ability to catalyze several reactions simultaneously due to their unique structure. However, the creation of multifunctional catalysts is not an easy task, since in this case, it is necessary to combine in one catalyst molecule the requirements for the structure, stability, and catalytic efficiency required for catalysts of different reactions. Bifunctional electrocatalysts used simultaneously for HER and OER, are now widely represented [6]. Some of these have been tested in water electrolyzers for overall water splitting reactions. In this case, the water electrolyzer was equipped with electrodes (the cathode and the anode) modified by a bifunctional catalyst instead of the standard Pt||RuO₂ system. Another type is bifunctional catalysts for OER/ORR. This kind of oxygen electrocatalysts has found application in metal-air batteries, the most common of which are zinc-air batteries. In addition, the literature contains examples of bifunctional catalysts for HER and OER, which have not found further application in any energy devices, although it should be noted that these examples are few. However, the greatest excitement is caused by trifunctional catalysts, effective at the same time for HER/OER/ORR, which allows them to be used simultaneously for several energy storage devices, such as water electrolyzers, fuel cells, and metal-air batteries. The most sought-after trifunctional catalysts exhibit excellent catalytic activity in all three reactions, as well as excellent stability, making them versatile and desirable catalyst systems for energy conservation devices.

Metal-organic coordination polymers (metal-organic frameworks, MOFs) are a promising new class of compounds based on inorganic building blocks, consisting of one or more metal cations connected to each other by organic linkers [7]. This class of compounds attracts the special attention of researchers due to the practically unlimited possibilities of the structural design of new compounds, and hence a wide range of functional properties. Functional materials of a new generation are being developed on the basis of MOFs, for example, for storing various gases, for separating complex mixtures, as chemical current sources, sensors, and catalysts. Due to their unique porous structure and ultra-high surface area, which provides access to multiple catalytic sites for the substrate, MOFs are

the ideal catalyst candidates for multiple reactions. The combination of these advantages has led to a wide study of MOFs as electrocatalysts for energy storage reactions [8 - 21].

Recently, Zhu *et al.* presented a review on the bifunctional catalytic activity of MOFs and their derivatives in ORR/OER and HER/OER reactions and described the possibilities of their further use in energy devices such as metal-air batteries and water electrolyzers [22]. In this review, the authors analyzed the various design approaches and structural features of MOFs that provide bifunctional activity. It has also been shown that MOFs can be used as support substrates to accommodate metals, metal oxides, and semiconductors, and can be used as sacrificial materials for the generation of different types of nanostructures for energy applications [22, 23].

Pristine MOFs, despite their original structure and properties, have many disadvantages, such as low conductivity and stability issues, which significantly limit their use directly in OER and HER, ORR [22 - 24]. However, several important approaches to their modification, aimed at increasing the number of active sites, improving the intrinsic conductivity of MOFs, as well as creating advanced self-supporting electrodes based on them, will significantly improve the electrocatalytic characteristics of pristine MOFs [15 - 17].

Thus, an integrated approach to the regulation of morphology and electronic structure, combined with the design of self-supporting MOF electrodes, opens up wide horizons for the creation of new MOF-based materials with excellent catalytic characteristics, excellent stability, and multifunctionality for energy storage devices [18]. The latest top-notch approaches to the creation of electrocatalysts based on organometallic frameworks and their derivatives were summarized in the review [25]. There are three main strategies for modifying natural MOFs leading to an improvement in their efficiency, selectivity, and resilience, namely structural, composition, and substrate engineering. The electroactivity is highly dependent on the conductivity of the electrocatalysts. Rational substrate selection, namely substrate engineering, is one of the simplest and most popular ways of modifying MOF-based electrocatalysts leading to an improvement in their catalytic properties. The method is based on the direct growth of MOF precursors on conductive substrates (graphene, glassy carbon, nickel foam (NF), *etc.*) in order to improve the conductivity, stability, and catalytic activity of MOF-based electrocatalysts. In this regard, great efforts have been made toward the search and development of substrates leading to an improvement in the activity of MOF-based electrocatalysts. Excellent conductivity is another important characteristic that ensures the high catalytic activity of electrocatalysts. A structural engineering approach has been proposed

Metal-Organic Frameworks and their Derived Structures as Catalysts for Electrochemical Sensors

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Abstract: Metal-Organic Frameworks are innovative materials that display interesting redox properties with multiple applications in electroanalytical chemistry and storage purposes. MOFs metal nodes present a redox pair (M^{2+}/M^{3+}) in the presence of alkaline electrolytes, which catalyse the electro-oxidation or a reduction of diverse kinds of molecules. This behaviour is used as the basic principle in the design of electrochemical sensors (modified electrodes) for the smart recognition and quantification of biomolecules and hazardous compounds by using inexpensive techniques such as voltammetry or chronoamperometry. In this regard, MOFs are combined with high conductive nanomaterials to create hybrid composites that increase the electron conductivity to macroscopic levels, and enhance the electro-analytical signal in comparison with the use of pristine MOFs. MOFs are also used to produce other kinds of framework structures such as carbonaceous frameworks embedded with nanoparticles. These derived materials have extensive applications in glucose electrochemical sensors. Herein, the principle of electrocatalysts with MOFs and their derived materials, the elaboration of electrochemical sensors and the recent application of MOFs materials as a catalyst on electrochemical sensors will be presented in this section.

Keywords: Electrochemical Sensors, Electronanalysis, MOF-Composites, MOF-Modified Electrodes.

1. INTRODUCTION

Metal-organic frameworks (MOFs) are inorganic polymers obtained by the coordination of metallic cluster nodes with organic linkers that create 2D or 3D networks with several topologies [1]. In the literature, reported MOFs have tetra-

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hedral or octahedral coordination environments depending on the metal coordinated in their structure [2]. Applications of MOFs in separation engineering are fundamentally based on their porous structure and specific pore size, where guest molecules can be selectively adsorbed without collapsing the framework structure [3].

On the other hand, the application of MOFs and their derivatives in electrochemical applications is a new and interesting topic. Electrochemical research based on MOFs is extensively focused on energy storage applications [4 - 7]; however, at present, there is a growing trend of the application of transition-metal based MOFs and their derivatives in the design of electrochemical sensors [8 - 10]. In this matter, Metal-Organic Frameworks have demonstrated to be excellent candidates owing to their extraordinary internal surface area ($> 6000 \text{ m}^2/\text{g}$)³, chemical resistance, electro-active behaviour and selective absorptivity of molecules which enhance the limits of detection, sensitivity and current density on electrochemical sensors [11].

Despite the interesting electrochemical properties of MOFs, their low overlap between electronic states and frontier orbitals in MOFs induces low electron conductivity [12, 13]. As a result, the use of pristine MOFs for electro-analytical applications is scarcely reported [8, 14, 15]. A smart strategy to solve conductivity problems is to combine pristine MOFs with nanomaterials or carbon allotropes. As a result, hybrid and highly conductive MOFs composites are obtained, and can be used as active materials in electrochemical sensors [10, 16] and devices for energy storage or production.

Currently, MOF based electrochemical sensors are becoming important in quantifying important analytes like biomolecules, pharmaceuticals, nitroaromatic compounds, heavy metals, *etc.* These sensors are basically modified electrodes that are incorporated in electrochemical workstations or portable devices for detecting analytes in real-time by using electroanalytical techniques such as voltammetry or chronoamperometry. On the electrode's surface, MOFs composites are directly involved in the selective electro-oxidation or electro-reduction of molecules in the presence of a specific potential window, scan rate and an accurate electrolyte.

In this chapter, we present the use of MOFs composites and derived structures as a catalyst in electrochemical sensors, hoping that the information found here, will inspire new research in this interesting topic. The first part of this chapter is an overview of MOF composites, their use in the fabrication of modified electrodes and their evaluation as electrochemical sensors. The second part is about the key role of MOFs as electrocatalysts and their proposed reaction mechanism. Finally,

in the third part, we discuss several examples of MOF composites used as an electrochemical sensor of biomolecules, and pollutants.

2. ELECTROANALYTICAL APPLICATIONS OF MOF COMPOSITES

MOF composites are derivatives formed by two or more substances that retain their properties and contribute to the entire system [17]. On electroanalytical application, MOFs composites are fabricated by combining pristine MOFs with innovative materials that display high electron conductivity and redox properties which allow increasing the analytical signals, modulating the oxidation/reduction potentials and inducing the selective catalyst of analytes even in the presence of other analogous molecules.

In the last years, researchers started to synthesize hybrid MOF composites based on carbon nanomaterials such as CNTs, fullerenes, graphite, graphene, graphene oxide or reduced graphene oxide [9]. These novel composites combine the highly porous properties of MOFs with the high-electron conductivity of carbon nanomaterials, providing the bulk electrical conductivity inside the modified electrode [10] whereas the deficiency of each component in the composite is moderated by each other, resulting in synergistic effects and attractive functions [18].

In addition, other nanomaterials like noble metal nanoparticles, and nickel or copper metal-oxide nanoparticles are also used in the elaboration of redox-active composites based on MOFs, where NPs are immobilized inside the porous frameworks to bring selectivity and high sensitivity to the sensors. Additionally, the main function of the nanoparticles in the MOF composite is to mediate the oxidation or reduction reactions toward specific analytes whereas the MOFs work only as a support matrix.

2.1. Fabrication of Electrochemical Sensors Based on MOF Composites: An Overview

Loading MOF composited on an electrode's surface is a big challenge that researchers have to face during the elaboration of electrochemical sensors based on MOF materials. On the development of electrochemical sensors, there is a diversity of electrodes that can be modified with MOF composites, and the modification process may vary according to the selected electrode. Most of the reported MOF electrochemical sensors are built on glassy carbon electrodes (GCE). The election of this particular kind of electrode is due to its low cost, chemical inertness, and wide electrochemical window. Its modification with MOF composites is carried out *via* drop-coating process. In this process (Fig 1), the

Metal-organic Frameworks and MOF-based Materials for Electrocatalytic CO₂ Reduction

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Abstract: Numerous CO₂ conversion strategies including thermochemical, photoelectrochemical, electrochemical have been adopted extensively in the last decades. However, the electrochemical CO₂ reduction (CO₂R) to energy-rich chemicals and fuels remains alternative promising technology owing to its ease of operations with an effective green approach. Compared with other energy conversion technologies, the electrochemical reaction conditions are comparatively mild with the ability to operate the reactions in a room temperature and pressure, thereby bringing better feasibility for alleviating anthropogenic atmospheric CO₂ emission that threatens global peace. The reaction processes and directions involved can be controlled freely by tuning reductive potential and temperature. In addition, the process of electrochemical reaction is usually proceeded by reactants to gain or lose electron(s) at the surface of the electrode without the need for redox agents, through which the required electricity is derived from some renewable energy sources (solar, wind, geothermal, *etc*) which do not generate any additional CO₂. This makes electrochemical CO₂R a green approach with no generation of contaminants. This chapter, therefore, highlighted different metal-organic frameworks (MOFs) and MOF-based materials for electrocatalytic CO₂R to energy-rich chemicals. Various strategies for designing MOFs, challenges, and prospects of MOF materials for better improvement of the CO₂R were also discussed.

Keywords: Electrochemical CO₂ Reduction, Energy-Rich Chemicals, Metal-

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Organic Frameworks, Renewable Energy, Strategies for Designing MOFs.

1. INTRODUCTION

Renewable energy sources have been posited as a fast-growing avenue for electric power generation. When coupled along with renewable sources of energy, an electrochemical oxidation-reduction reaction occurs at the electrode interface to achieve the conversion of renewable energy [1] for a sustainable energy generation cycle (Fig. 1). From practical application viewpoints, unlike the chemical reaction(s), the electrochemical system is known for simple reaction rate controllability through changing of applied bias and also possesses the simpler way of separating the product(s) from the half-reactions. Electrochemical reaction involves a consecutive conductive diffusion-reaction process that exhibits interactions between electrolyte, electrode, and dissolved products or reactants [2-8]. However, the performance of electrochemical reaction displayed low efficiency and high overpotential consequent to the high activation energy barrier between the intermediates and dissolved reactants thereby necessitating a high demand for ionic and electric conductivity along with a high surface area to ensure phase interactions [9]. Therefore, research into electrocatalyst development to abate the activation energy barriers and stimulate intermediates with low energy is now on the rise to meet the practical/industrial expectation of the field.

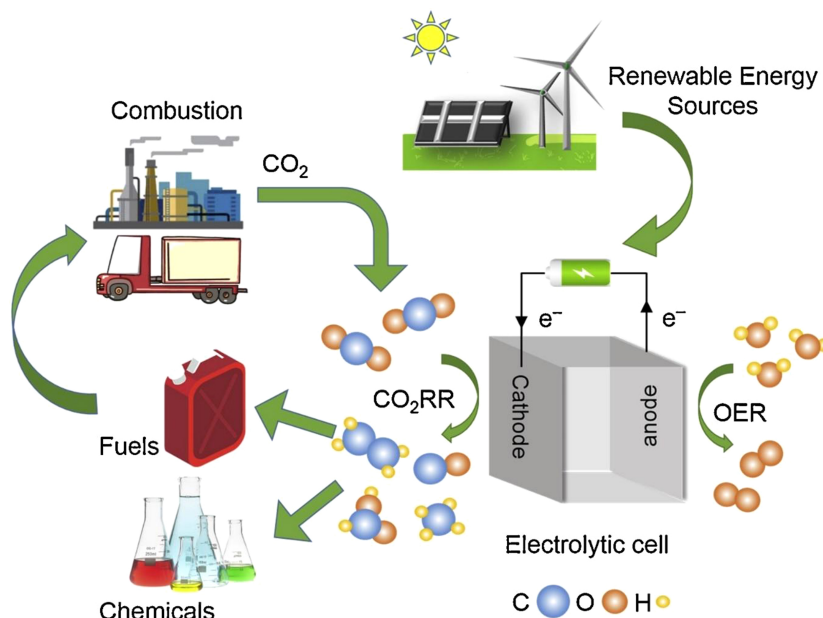


Fig. (1). Schematic illustration of the carbon cycle in electrochemical CO₂R. Reproduced from [13] with permission from Elsevier, Copyright A(c) 2020.

For efficient electrochemical reaction, the electrocatalysts employed and the applied potential are crucial for the efficiency and selectivity of CO₂R. However, at a specific fixed overpotential, various products rather than a single product are usually produced at electrodes which often leads to the poor selectivity of the desired product(s). Also, in a simple batch reactor which is commonly used across the globe, the rate of reaction is always confronted with the lower solubility of CO₂ in the reaction system especially at high overpotential, thus resulting in low current density or degradation of electrocatalytic activity [10 - 12]. Considering the poor stability and selectivity of existing electrocatalysts, the state-of-the-art technology is still unable to adequately meet/address the requirements for large-scale industrial applications. This chapter discussed MOFs and MOF-based electrocatalysts for CO₂R. It includes major significant advantages of the electrochemical approach over other methods of CO₂ conversion. Prior to discussion of different pristine MOFs nanocrystals, MOFs, and MOF-electrocatalyst materials, the basic concept of electrocatalytic reduction of CO₂ and the design of MOFs and MOF-based materials for the electrocatalytic reduction of CO₂ were discussed for proper insight and understanding of the process. Lastly, we highlighted some progress and the associated challenges with the applicability of MOFs and MOF-based electrocatalysts for CO₂R into energy-rich chemicals and therefore proffer some promising strategies to foster the improvement in the field.

2. MAJOR SIGNIFICANT ADVANTAGES OF ELECTROCHEMICAL APPROACH OVER OTHER METHODS OF CO₂ CONVERSION

Conversion of CO₂ to fuels can be achieved through different approaches including thermochemical [14 - 16], and electrochemical [2, 17 - 20], photochemical [21 - 23], and photoelectrochemical [24 - 26]. By the way of required operational conditions, an electrochemical conversion could be achieved at ambient pressure and room temperature [9], thereby bringing greater feasibility for a reduction of atmospheric CO₂. Also, the conversion of CO₂ through the electrochemical method is known to have a highly controllable characteristic and also the potential for very high conversion efficiencies. Its industrial prospects and practicability provide the electrochemical approach with numerous advantages over other methods. The electrochemical method has a wide range of conversion products such as formic acid esters [27], formamides [28], carbon monoxide [29, 30], methane [31 - 33], methanol [34 - 39], formic acid [11, 40-43], dimethylcarbonate [44, 45], alkylene carbonates [28], carbamic acid esters [27], lactones [27], and aliphatic polycarbonates [27] while photochemical conversion produces only limited products such as formate [46], formic acid [47], carbon monoxide [48 - 50] and methanol [47, 51].

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