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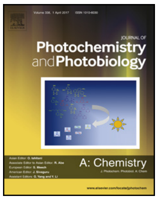

Invited feature article

Water splitting based on homogeneous copper molecular catalysts

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ABSTRACT

The future of energy supply depends on innovative breakthroughs regarding the design of cheap, sustainable, and efficient systems for the conversion and storage of renewable energy sources. In the past few years, many efforts have been devoted to the development of alternative catalysts for water splitting based on transition-metal elements. In this review, we largely focus on homogeneous copper-based catalysts for water oxidation and water reduction in both electrochemical and photochemical means. Particular attention is paid on evaluation of molecular catalysts' activity, stability and brief mechanism. Finally, challenge and prospective in this field is highlighted and we hope that more promising copper-based homogeneous catalytic system can be further developed.

1. Introduction

Nowadays, global energy utilization patterns largely depend on traditional fossil fuel, but it is reported that the current available energy supplies are estimated to be depleted in 50–150 years [1,2]. The continuously increasing energy demand and consumption causes severe depletion of fossil fuel and serious environment problems [3–5]. Therefore, it is urgent to develop alternative and sustainable energies, especially environmental-friendly energy conversion and storage technologies [6,7]. Renewable solar energy is regarded as the most abundant and promising alternative energy [8,9]. Thus lots of efforts will be made to explore and make use of it, among of which developing the conversion and storage of solar energy with economic and high efficiency occupies the most attention. In the artificial photosynthesis system, the overall process may consist of the light-harvesting, charge separation, proton-coupled electron transfers process, and chemical conversion [10]. The integrated components should be stable, efficient, cheap and robust including photosensitizer, sacrificial electron donor or acceptor and catalyst. Each part of this system functions in a coordinated and united manner, otherwise the system may lose efficiency or even collapse. Although artificial photosynthetic system for water splitting attracts lots of scientists' attention and significant achievements have been made, more works should focus on mimic natural PSII and PSI processes and explore fruitful catalysts with high stability, large efficiency, easy accessibility and low cost.

Besides, electrolysis of water has more than 200 years history and is regarded as one of the most attractive and convenient technology to produce hydrogen and oxygen. To date, most accessible water splitting catalysts are based on noble metals, but their widespread commercial applications are limited largely due to high cost and earth-scarce [11,12]. Consequently, extensive efforts have been made to replace these precious metals and exploit more abundant, robust, active and inexpensive transition metal catalysts.

Water splitting is divided into two half reactions water oxidation and water reduction. The former involves the O—O bond formation and four-electron coupled with four protons loss, which results in relatively slow kinetics, thermodynamics and large overpotential, which is a big bottleneck for the overall water splitting [13,14]. Compared with the water oxidation, water reduction is relatively accessible at a lower overpotential [15]. Water splitting catalysts consist of heterogeneous and homogeneous catalysts. For the former ones, transition-metal oxides or hydroxides and their derivatives are often the main active species, thus they have relatively high activity and greater durability, however, suffering poor elucidation for high activity. Compared to heterogeneous catalyst, homogeneous catalysts have many advantages. Assisted by molecular complex synthesis and design, with a wide range of active metal centers coupled with original and functional ligand, it would be highly desirable to facilitate mechanistic study and further provide an opportunity to design

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new efficient catalysts through well-tunable fundamental coordination chemistry.

In recent years, some reviews referring to the first transition-metal catalysts including iron, cobalt and nickel have been published [16–22]. Copper-based water splitting catalysts have become promising candidates because of their relatively high reactivity, stability and relatively low light absorption. Since Cu is biologically relevant and earth-abundant with well-defined redox properties [23–26], it is necessary to focus on the recent development on the copper-based homogeneous catalysts for water splitting in both electrochemical and photochemical systems. It is noteworthy that molecular Cu-based catalyst for water oxidation was firstly reported in 2012 [27], however, research on water reduction Cu-based molecular catalyst just occurred three years ago [28]. Therefore, developing molecular copper catalysts enjoys tremendous potential. In this discussion, much attention is paid on some general methods from literatures to characterize the activity, stability, and mechanism of molecular catalysts. Finally, based on many achievements in molecular catalysts for water splitting, an outlook is proposed and we hope that more promising copper-based molecular catalysts can be further developed.

2. Electrocatalytic parameters and methods for evaluating the performance of molecular catalysts

In order to evaluate performance of catalysts and further efficiently select desirable catalysts, typically, some parameters and methods should be well characterized including working overpotential, catalytic activity, turnover number, turnover frequency, and Faradic efficiency as well as stability.

2.1. Working overpotential

As we know, the thermodynamic potential of water splitting is 1.23 V at 25 °C and 1 atm. Since the inherent kinetic barriers exist on both anode and cathode coupled with other resistances from solution or contact, higher potential must be applied to achieve electrocatalytic water splitting. The difference between applied potential and the potential of the reaction at equilibrium is defined as overpotential [29]. The applied potential can be described as: $\eta = | E - E_{eq} |$. It is noted that E_{eq} is related to the pH and temperature of electrolysis system. It is considered that the overpotential may result from slow kinetics of charge transfer, mass and ionic transport [30]. Several methods are applied to reduce the overpotential of water splitting. Firstly, it is central issue to design efficient water oxidation and water reduction catalysts, preferably based on economic and earth-abundant transitional metal elements. Secondly, gas bubbles generated from the catalytic system concentrate on the surface of the electrode, leading to the reduced active reaction area and increased overpotential. Therefore, removal of bubbles to leave more active sites for the catalysis is an essential way to enhance the efficiency.

Notably, in homogenous system, the overpotential is expressed by many ways including onset overpotential, half peak overpotential and peak overpotential. Among them, onset overpotential is primarily used and is determined by measuring the applied potential at which a catalytic current density just occurs. In this review, for the main themes water splitting, we only concentrate on the aqueous solution.

2.2. Catalytic activity

The evaluation for catalytic activity of electrocatalytic reactions depends on many factors, and it is often estimated by carrying on cyclic voltammetry (CV) or linear sweep voltammetry (LSV). Under certain potential, the latitude of current density is usually used to judge and compare catalytic activity of catalysts. Of course, the only method is not sufficient. In order to compare the activities between the samples, onset overpotential and the media of catalytic system are also considered. Some complexes were initially reported as molecular catalysts, but under high applied voltage or harsh environment, heterogeneous copper oxide or hydroxide is regenerated and acts as active species for water splitting [31–34], therefore, it is crucial to determine the real active species [35–37]. The free ligand, metal salt, and a mixture of the free ligand and metal salt should be measured under identical conditions. To determine the true active species can be assisted by comparing the shape of catalytic wave as well as the current density at same potential.

2.3. Turnover number and turnover frequency

The evaluation of catalytic rates is a crucial step for the judgement and comparison of electrocatalysts. In molecular system, turnover number (TON) is defined as the amount of hydrogen or oxygen that a catalyst can convert to a desirable product per mol catalyst. Turnover frequency (TOF) is on the base of TON, which is divided by time, representing the intrinsic catalytic rate of catalyst. Sometimes it is relatively difficult to get a precise TOF. Generally, two methods were used to calculate and determine the TOF. Firstly, under electrolysis with a constant potential, the buildup charge versus time can be figured out. Two values can be both calculated based on the following Eqs. (1) and (2), where ΔC is the total buildup charge during electrolysis after deducing the blank charge, F means Faraday's constant, n_1 represents the mount of catalyst, n_2 indicates the number of moles of electrons for oxygen or hydrogen evolution, and t is the electrolysis time.

$$TON = \Delta C/(F * n_1 * n_2) \tag{1}$$

$$TOF = \Delta C/(F * n_1 * n_2 * t) \tag{2}$$

In practice, in the overall bulk solution, only the small fraction of catalyst molecules contribute to water splitting, thus calculations are slightly lower than the real conditions. Nevertheless, it is still conducive to compare similar catalysts. On the other hand, the kinetic study reveals another method with relatively more precise estimation. The current enhancement (i_{cat}/i_p) is expressed in the following Eq. (3):

$$\frac{i_{cat}}{i_p} = \frac{0.359 n_c}{n_p^{\frac{3}{2}}} \sqrt{\frac{K_{obs}}{\nu}} \tag{3}$$

Where n_c represents the number of electrons transferred for water oxidation or water reduction, n_p means the number of electrons transferred in the non-catalytic wave, ν is the scan rate, and k_{obs} is regarded as the apparent rate constant for a first-order or pseudo-first order H_2 or O_2 evolution reaction. By plotting the catalytic current over the diffusive peak current i_{cat}/i_d as a linear function of $\nu^{-1/2}$, the slope of the plot represents k_{obs} and it is usually referred as TOF of the catalyst in the literature [38]. In fact, TOF calculation is based on assumption and estimation, thus a relatively lower catalytic rate might be illustrated. Many reason and methods are uncovered to address this issue [35,38–40]. Firstly, the local consumption effect leads to the decrease or increase of pH, which dramatically influences catalytic behavior. Although this problem can be solved by increasing buffer concentration, the decrease in the solubility of catalysts could be further resulted from. Secondly, the low TON and TOF values are attributed to slow diffusion of the catalyst to the electrode surface and only the small fraction of