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Mini review

Metal Complexes as Molecular Electrocatalysts for Water Oxidation: A Mini-Review

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Electrocatalysts for splitting water into oxygen have increasingly attracted attention recently. First-row transition metal complexes (e.g., Cu, Fe, Co and Ni) have great potential to electrochemically catalyze water oxidation for oxygen evolution because of their abundance and cheapness. In this review, these metal complexes as water oxidation electrocatalysts were summarized. Their catalytic properties including overpotential, stability, and turnover rate were discussed.

Keywords: Electrocatalysts; water oxidation; oxygen evolution; metal complexes

1. INTRODUCTION

Water is one of the most common substances on the earth. With the depletion of resources such as oil and natural gas and the increasingly serious environmental pollution, hydrogen production by water oxidation and hydrogen evolution has become the focus area of renewable clean energy research, which is directly related to energy development and environmental protection. Water oxidation for oxygen evolution involves the loss of four electrons and four protons with formation of an O-O bond ($2H_2O = O_2 + 4H^+ + 4e^-$, $E^0 = 1.23$ V vs. NHE). Electrocatalysis for water oxidation has played a major function in renewable energy system [1-5]. The development of electrocatalysts such as metal oxides and non-metal oxide materials has been reviewed by several groups [1-3]. Since the first catalytic activity of homogeneous water oxidation catalyst (dinuclear pyridine ruthenium complex) has been reported in 1982 [6], metal complexes have been developed for electrocatalytic water oxidation [7]. On the basis of their abundance and cheapness, first-row transition metals, such as Cu, Fe, Co, and

Ni, have been emerged as water oxidation catalysts for practical applications. This review summarized the progress in the water oxidation electrocatalysts based on Cu, Fe, Co, and Ni complexes.

2. COPPER COMPLEXES

Copper is an earth-abundant and biorelevant redox metal. In some redox metalenzymes, copper is coordinated with a variety of nitrogen ligands to produce monomeric η^1- and η^2-peroxo complexes and dimeric bis(μ-oxo) and μ-η^1:η^2-peroxo complexes. Inspired by the fact, Mayer and co-worker reported the first copper-based electrocatalyst for water oxidation, named as copper-bipyridine-hydroxo complex [8]. The electrocatalyst generated by simply mixing a copper salt and bipyridine operates at pH 11.8 ~ 13.3 shows an overpotential of 0.75 V with a turnover frequency of 100 s^{-1} for water oxidation (Figure 1). Lately, many groups designed and synthesized a few of copper complexes with pyridine derivatives as the ligands (Figure 2) [9-15], in which the operation pH and/or overpotential decreased with high turnover frequency (Table 1). For example, Lin's group developed a copper-based electrocatalyst with 6,6′-dihydroxy-2,2′-bipyridine as the ligand [11]. Because of the hydrogen bonding interaction between the hydroxyl substituents and the bound hydroxo/aquo ligands (Figure 3), this complex exhibits a lower overpotential for water oxidation than that of copper-bipyridine-hydroxo complex. At the same time, Meyer's group reported a single-site copper complex with N,N-bis(2-(2-pyridyl)ethyl)pyridine-2,6-dicarboxamidate, denoted as Py_3P). In contrast to the previous two copper complexes, the electrocatalyst can work at low pH (~ 8.0) with $HPO4^{2-}$ as a proton acceptor [12]. Additionally, dinuclear copper complexes have been explored as electrocatalysts. Typically, Liao and Zhang reported a 1,8-naphthyridine-based dinuclear copper complex with 2,7-[bis(2-pyridylmethyl)aminomethyl]-1,8-naphthyridine. The complex catalyzed water oxidation at pH 7.0 without decomposition during long-term electrolysis. DFT calculations demonstrate that the O-O bond formation follows an intramolecular coupling mechanism but not a nucleophilic attack of water on the high-oxidation-state Cu^{IV}=O intermediate [13]. Kieber-Emmons and co-workers also reported a dinuclear copper water oxidation catalyst, $[(L)Cu(II)]_2$-$(\mu$-$OH)_2(OTf)_2$ (L = bis((6-methyl-2-pyridyl)methyl)(2-pyridylmethyl)-amine) [14]. The turnover rate was calculated to be 33 s^{-1} at an overpotential of ~1 V at pH 12.5. The experimentally calibrated calculations demonstrated that oxidation of both mononuclear and dinuclear species led to the generation of common dinuclear intermediates, avoiding the formation of terminal Cu(IV)=O/Cu(III)-$O^{\bullet}$ intermediates.

Besides binding to pyridine derivatives, copper can be coordinated with other nitrogen-containing ligands, such as peptide and imidazole derivatives [16-20]. Typically, Meyer and co-workers demonstrated the copper complex formed with triglycylglycine (GGGG) shows good electrocatalytic ability toward water oxidation at 1.32 V (vs. NHE) with a turnover frequency of 33 s^{-1} [21]. Note that the deprotonation of the third peptide NH is accompanied by extremely high pH value; thus, high pH (> 11) is required for the formation of the electrocatalyst. Imidazole is a good ligand for metal binding. It has been suggested that deprotonation of the ligand in the Cu complexes lowers water oxidation overpotential [20]. In particular, C-terminal His extension of two glycine (2GH) instead of three glycine (3G) in the copper complexes lowers the overpotential and improves the turnover frequency [18,19]. Amino terminal Cu(II) and Ni(II)-binding (ATCUN) motif is included in a protein or peptide including albumins (e.g., HSA, BSA, and RSA), neuromedins C and K, human sperm protamine P2a, and histatins [22]. It is characterized by comprising of a free NH_2-terminus, a histidine (His) residue in the third position and two intervening peptide nitrogens (denoted as NH_2-X-X-His sequence). Our group found that the ATCUN-Cu(II) metallopeptides showed similar attributes with those of Cu(II) complexes-based electrocatalysts toward water oxidation (not reported). However, the ATCUN-Cu(II) metallopeptides show good stability in a wide pH range (4.5 ~ 11) and exhibit good electrocatalytic capability toward water oxidation in neutral pH environment. This work will be helpful for design of novel metal-based water oxidation catalysts. Given that ATCUN-Cu(II) can be oxidized into Cu(III)-ATCUN *in vivo* via chemical or photochemical catalysis reaction, our result would be valuable for understanding the physiological functions of ATCUN-containing proteins or peptides.

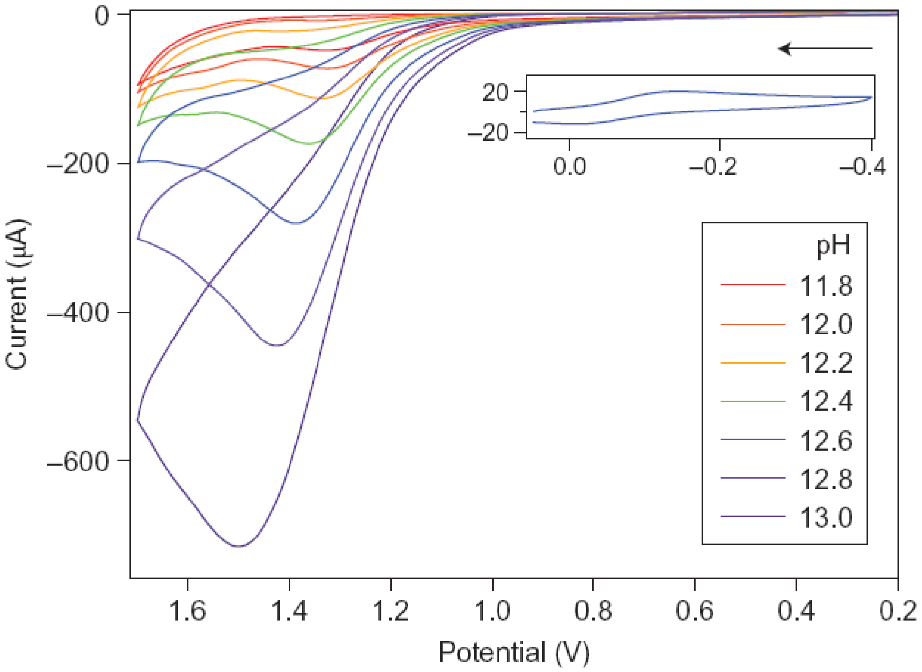
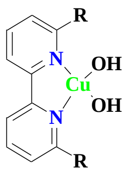
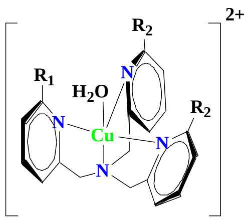


Figure 1. CVs of solutions containing 1.0 mM total Cu and bpy. These show large, irreversible pH-dependent waves that indicate electrocatalysis. Conditions: Cu and bpy added as $[(bpy)Cu(m\text{-}OH)]_2(OAc)_2$ and 0.1 M aqueous electrolyte (NaOAct/NaOH), 100 mVs21 on a GC electrode. The arrow indicates the sweep direction. Inset: a CV of the same solution at pH 12.5 under nitrogen, shown at the same scale as the irreversible anodic wave. Reprinted with permission from reference [8]. Copyright 2012 Springer Nature.



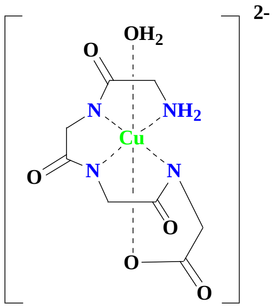
1, 2

1: R = H
2: R = OH



3, 4

3: R1 = H, R2 = Me
4: R1 = R2 = F



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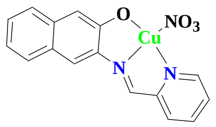

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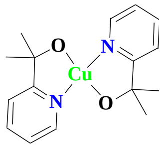

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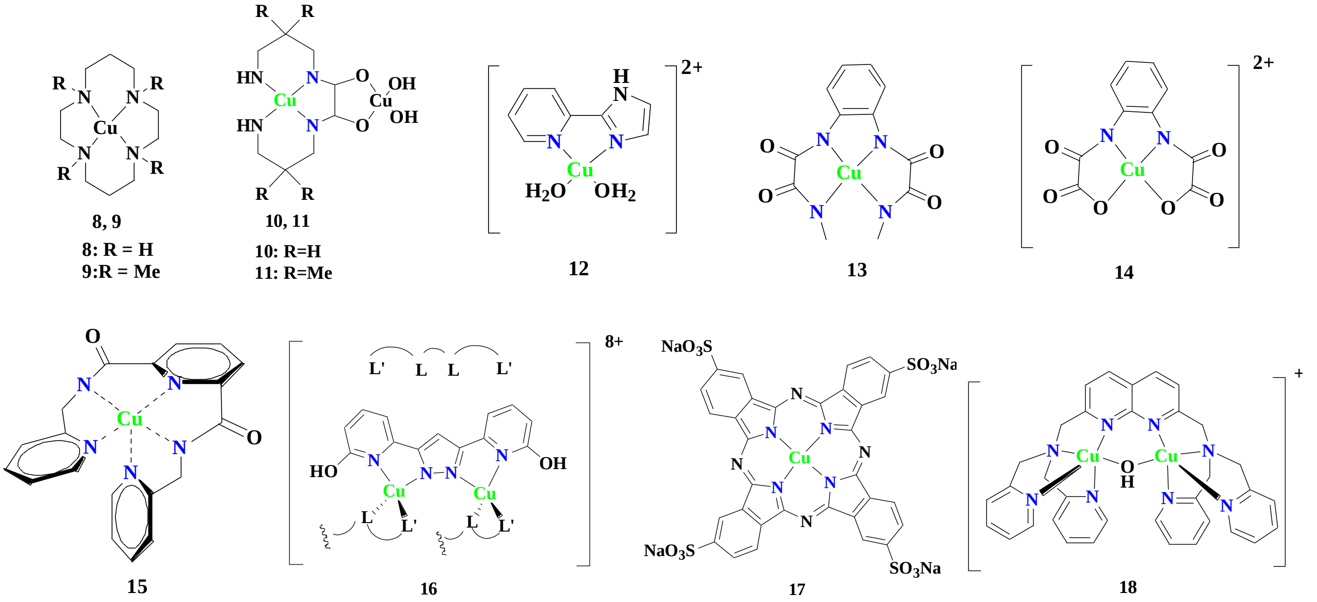

Figure 2. Chemical structure of the reported copper complexes-based electrocatalysts.

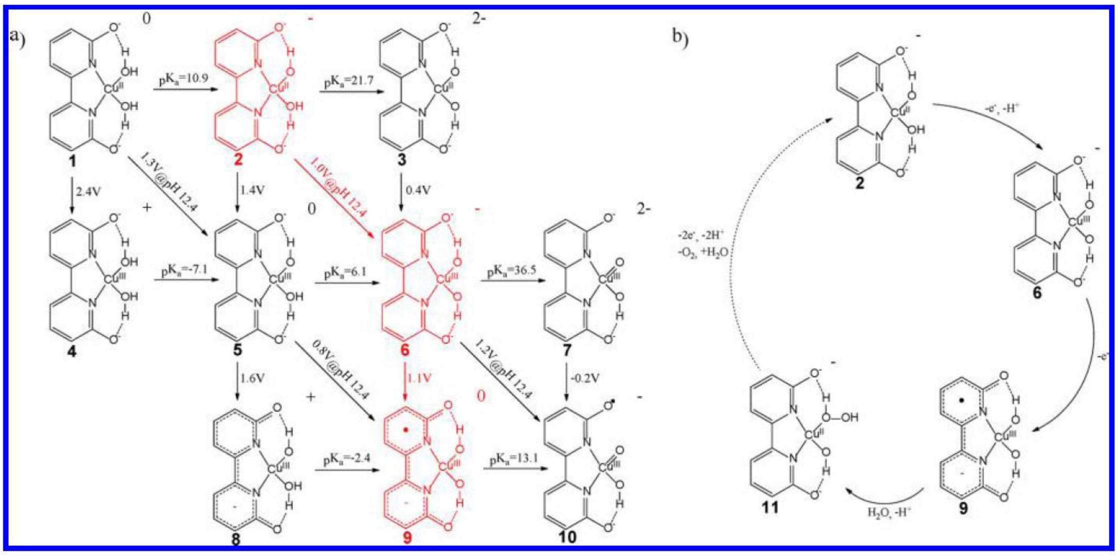

Figure 3. (a) Calculated thermodynamic pathways for the first and second oxidation of the Cu-L complexa and (b) proposed mechanism for water oxidation. Reprinted with permission from reference [11]. Copyright 2013 American Chemical Society.

Besides the above copper-pyridine and copper-peptide complexes, other N_4-copper macrocyclic complexes have also been reported as electrocatalysts [6, 23-28]. For example, Llobet and co-workers reported the copper complexes with tetra-anionic tetradentate amidate ligands H_4LY (Y = 1 ~ 4), L = N1, N1′-(1,2-phenylene)bis(N_2-methyloxalamide) [28]. At pH 11.5, the complexes exhibit an electrocatalytic water oxidation wave at 1.25 V with an overpotential of 0.7 V. The turnover rates for water oxidation were found to be 3.6 s^{-1} at pH 11.5 and 12 s^{-1} at pH 12.5. The overpotential is greatly decreased because of the increase of the electron-donating capacity at the aromatic ring. For this view, they further demonstrated that the catalytic ability of these complexes can be manipulated by modification or π-stacking of the ligand to graphitic electrode surfaces (Figure 4) [27]. The copper complex with 4-pyrenyl-1,2-phenylenebis-(oxamidate) that has extended π-conjugation via a pyrene moiety covalently connected to the phenyl ring can be anchored onto the graphene-based electrode surface through π-stacking interaction. The electronic perturbation donated by the pyrene group at this electrode lowed the overpotential by 0.15 V in contrast to the copper complex with o-phenylenebis(oxamidate) and led to the increase of the catalytic rate from 6 to 128 s^{-1}.

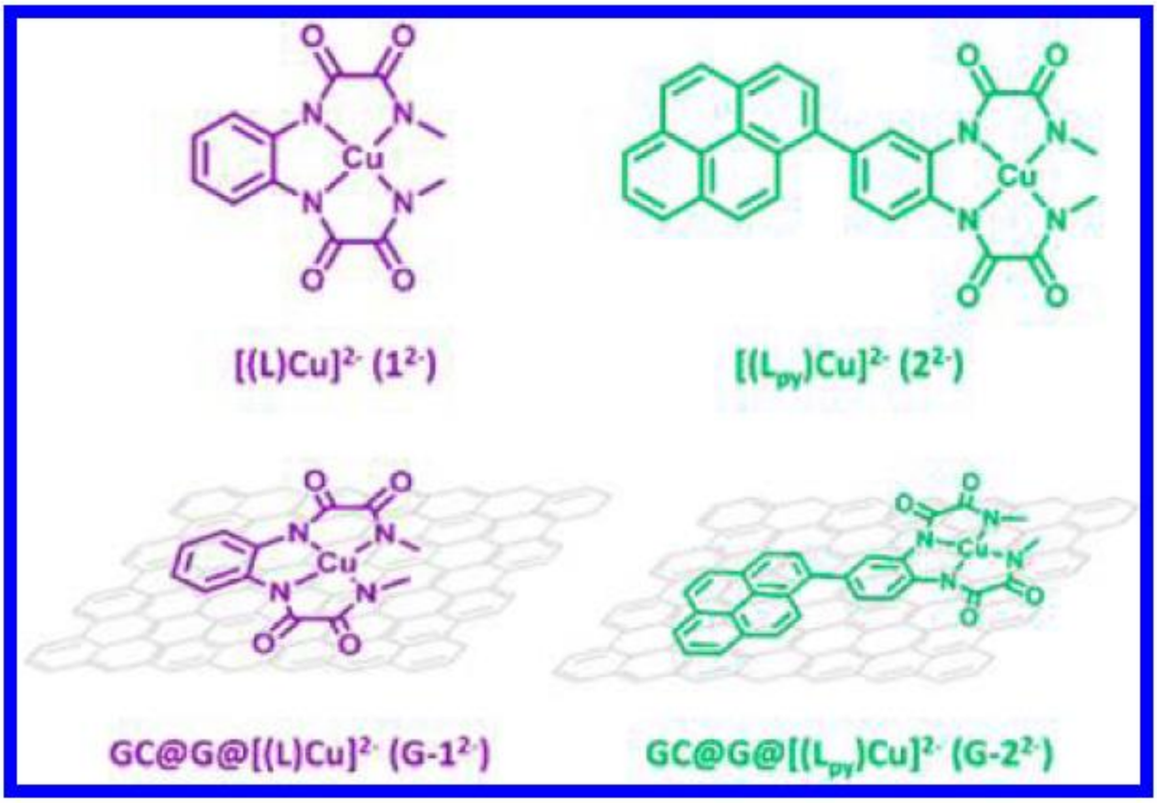

Figure 4. Structural representation and labeling code of the complexes and the hybrid materials used in this work. Reprinted with permission from reference [27]. Copyright 2017 American Chemical Society.

Additionally, Crabtree and Brudvig discovered a homogeneous N_2O_2-copper water oxidation electrocatalyst (Cu(pyalk)$_2$, pyalk = 2-pyridyl-2-propanoate) (Figure 5) [29], which operated at pH > 10.4 with a turnover frequency of ~0.7 s^{-1} and exhibited a low overpotential (520 ~ 580 mV). Controlled potential electrolysis experiment (> 12 h) at 1.1 V vs. NHE led to the formation of >30 catalytic turnovers of oxygen with only ~20% catalyst degradation. Under optimized conditions, simple Cu(II) ions are also highly active for electrocatalytic water oxidation in weak basic or near neutral buffer solutions (e.g. carbonate, phosphate, acetate and fluoride) [30,31]. However, the Cu(II) ions readily precipitate on the electrode. The resulting copper oxide film is bad for the practical homogeneous catalytic application. Recently, Lu and co-workers demonstrated that Cu(II) can act as an excellent homogeneous catalyst for water oxidation in a neutral borate buffer, which was studied by experimental and theoretical methods [32]. In this system, the borate anion is an oxygen donor playing a decisive role in the rate-limiting step of O–O bond formation. This reduces the reaction energy barrier and improves the catalytic efficiency. With copper complexes as the procursors, $CuO/Cu(OH)_2$ could be formed on electrode surface as heterogeneous electrocatalysts. For example. Chen's group demonstrated that electrolysis of Cu(II)-glycine complexes resulted in the formation of $CuO/Cu(OH)_2$ which can electrocatalyze water oxidation with an overpotential of 0.45 V for a current density of 1 mA/cm^2 [33].

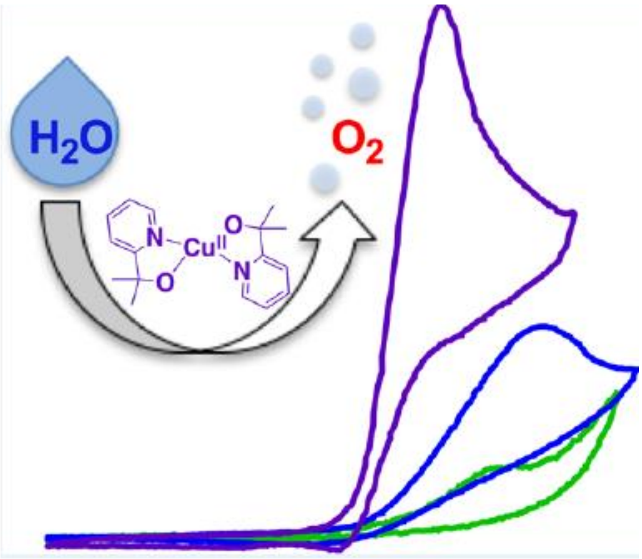

Figure 5. Reprinted with permission from reference [29]. Copyright 2017 American Chemical Society.

Table 1. Electrocatalytic performances of the reported copper complexes.

Complex	Overpotential/V vs. NHE	Turnover frequency/s^{-1}	pH	Refs.
1	0.75	100	11.8	[8]
2	0.64	0.4	12	[11]
3	1.0	33	12.5	[14]
4	0.61	0.158	9.5	[10]
5	0.52	33	11	[21]
7	0.52	0.7	10.4	[29]
11	0.689	6.7	7	[24]
12	0.85	35	12	[20]
13	0.7	3.6	11.5	[34]
14	0.639	1.13	7	[35]
15	0.76	0.38	8	[12]
16	0.5	100	7	[9]
17	0.57	0.063	9.5	[36]
18	0.8	–	7	[13]

3. IRON COMPLEXES

For iron-based water oxidation electrocatalysts, Collins and Bernhard first reported their precedent in 2010, in which iron(III) was coordinated with a tetraamido macrocyclic ligand (TAMLs) [37]. However, the catalytic activity of Fe-TAML vanishes after a few seconds. To resolve this problem, Fillol's group reported several iron complexes as homogeneous water oxidation to release oxygen with high efficiency during a period of hours [38, 39]. For electrocatalytic water oxidation, Meyer's group is the first to report single-site Fe complexes, $[Fe^{III}(dpag)(H_2O)](ClO_4)_2$ (dpag = 2-[bis(pyridine-2-ylmethyl)]amino-N-quinolin-8-yl-acetamido) (Figure 6) [40]. The electrocatalyst operates in a propylene carbonate-water mixture at electrode surface to release oxygen through >29 turnovers over 15-h electrolysis period. The Faradaic yield is 45% and no decomposition was observed. TAML activator is a fast homogeneous water oxidation catalyst in the presence of a chemical oxidant. However, the homogeneous system shows low turnover number. Kitchin and co-workers demonstrated that the TAML activator immobilized on electrode exhibited high electrocatalytic property for water oxidation [41]. This system facilitated the generation of oxygen with much higher turnover number than the homogeneous predecessor. Moreover, covalent immobilization of 2,2′-bipyridine to a graphene-modified electrode and follow-up incubation of the electrode with a metal salt solution (Fe^{3+}, Co^{2+}, Ni^{2+}, or Cu^{2+}) led to the formation of surface-bound electrocatalysts (Figure 7) [42]. The modified electrode showed high redox activity in neutral water. This work is valuable for studying the electrocatalytic activity of different metal complexes for water oxidation.

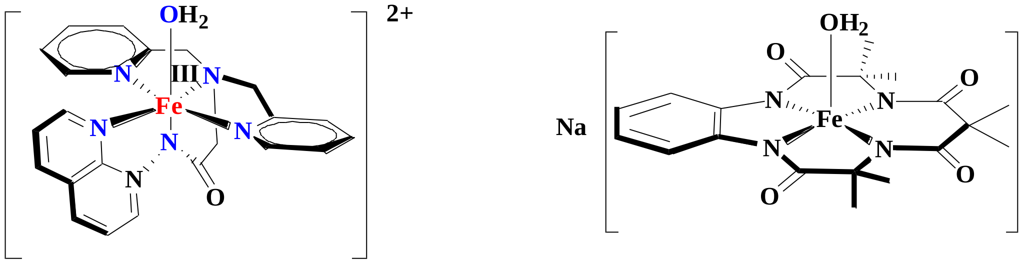

Figure 6. Structure of $[FeIII(dpaq)(H_2O)]^{2+}$ (left) and TAML activator (right).

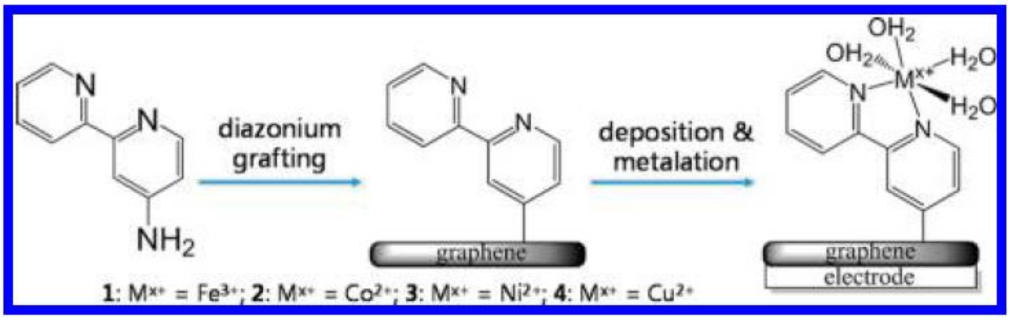

Figure 7. Method for covalent attachment of 1st row transition metal WOCs to graphene-modified ITO electrodes. Reprinted with permission from reference [42]. Copyright 2017 American Chemical Society.

4. COBALT COMPLEXES

From the standard potential of the M^{3+}/M^{2+} redox couple in the first-row transition-metal system, cobalt provides the most oxidization system (E^0 = 1.84 V vs NHE), which is higher than that of manganese and iron. Thus, it is unfavorable to oxidize Co^{II} without a ligand to stabilize Co^{III}. Nocera demonstrated that a cobalt catalyst can be formed by oxidative polarization of an ITO electrode in the cobalt (II)-containing phosphate buffer with a 1:2 ratio (phosphate/cobalt) [43]. The hydrogen phosphate ion acts as the proton acceptor in the oxygen evolution reaction. Therefore, complexation of cobalt ion by a ligand may facilitate the water oxidation. In this part, the reported cobalt complexes as electrocatalysts for water oxidation to oxygen are reviewed.

Using a mononuclear cobalt pentapyridine complex, Berlinguette and co-workers first suggested that $[Co^{IV}]O]^{2+}$ is an intermediate for the O-O bond formation during electrocatalytic water oxidation [44]. Recently, Gupta's group demonstrated that the biuret-modified tetraamidomacrocyclic cobalt complex [Co^{III}-bTAML] shows electrocatalytic ability toward to water oxidation basic conditions [45]. The electrochemical and spectroscopic results confirmed that $Co^V(O)$ is the decisive intermediate responsible for O-O bond formation. Verpoort and co-workers reported a photo and electrochemical cobalt water oxidation catalyst, $[Co^{II}(TCA)_2(H_2O)_2]$ (TCA = 1-mesityl-1,2,3-1H-triazole-4-carboxylate) [46]. The in situ generated catalyst by incorporating the ligand to cobalt ion can assemble into a film during electrochemical oxidation. The catalytic film exhibited a low overpotential toward electrocatalytic water oxidation (0.36 V) and high oxygen evolution peak current at neutral pH. No catalyst decomposition or nanoparticle formation was found in this process. Moreover, Du's group reported that the cobalt-salen complex can serve as a precursor for the deposition of nanostructured amorphous catalytic film for electrochemical water oxidation, which is characterized by SEM, EDX and XPS (Figure 8) [47]. The cobalt-based film electrode exhibited a high catalytic current in 0.1 M KBi solution at pH 9.2. Its onset catalytic potential is about 0.85 V (vs. Ag/AgCl). The catalytic current started at η = 0.29 V with a current density of 0.01 mA/cm^2. This is accompanied by a Faradaic efficiency > 93% at 1.2 V.

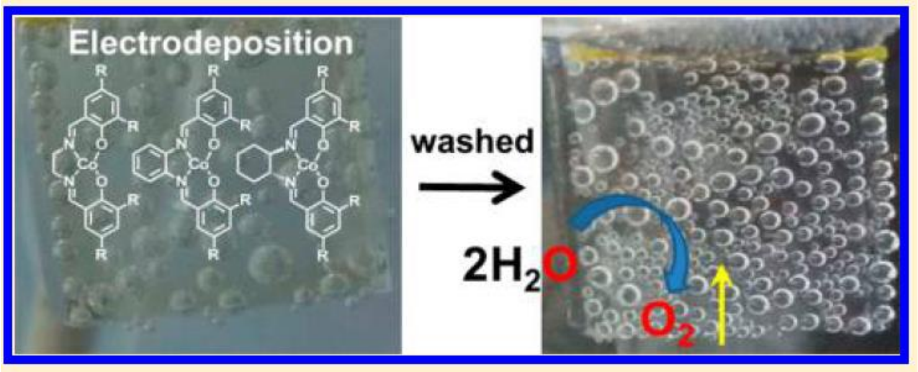

Figure 8. Graphical abstract of the cobalt-salen complex and the cobalt-based film for water oxidation. Reprinted with permission from reference [47]. Copyright 2017 American Chemical Society.

Zheng and co-workers demonstrated that modification of a pyrene-containing cobalt Schiff base complex on the surface of multiwalled carbon nanotubes (MWCNTs) through π-stacking interaction led to a hybrid electrode for electrocatalytic water oxidation [48]. The electrode displayed excellent electrocatalytic capability and durability under neutral conditions with an overpotential of 0.33 V. The catalytic current density at 1.15 V vs. NHE was found to be 1.0 mA cm^{-2}.

Metal-organic frameworks (MOFs) can encapsulating an active guest. Das and co-workers indicated that the cobalt-based MOF $[Co_3(m3\text{-}OH)(BTB)_2(dpe)_2Co(H_2O)_4(DMF)_2 0.5]n{\cdot}nH_2O$ [H_3BTB = 1,3,5-benzenetribenzoic acid; dpe = 1,2-di(4-pyridyl)ethylene] works as an efficient water oxidation catalyst [49]. Being coated on electrode surface, the MOF exhibits electrocatalytic ability towards water oxidation in 0.1 M KOH with a turnover frequency of 0.05 s^{-1} and an overpotential of 0.39 mV (NHE).

5. NICKEL COMPLEXES

With the discovery of homogeneous water oxidation catalysts of first row transition metals including Cu, Fe, and Co, a few nickel complexes-based electrocatalysts have also been found [50-53]. Typically, Ke and Lu found that the nickel complex, $[Ni(meso\text{-}L)](ClO_4)_2$ (L=5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) that can electrocatalyze H_2 production from water, can also catalyze water oxidation at neutral pH 7 (Figure 9) [51]. Cis-Ni-3_O generated by isomerization from trans-Ni-3_O is active intermediate. Its presence is a key factor for the O-O bond formation during water oxidation. At the same time, Allen's group found that the nickel complex with glycine ligands exhibited electrocatalytic ability toward water oxidation with an overpotential of 0.475 V at a current density of 1 mA/cm^2 at pH 11 [52]. Ni(II) is likely coordinated with the amine group within the glycine in a 1:4 molar ratio. The oxygen evolution yielded a Faradaic efficiency of ~ 60%. The catalytic mechanism is an electron-proton coupled process by monitoring the pH dependence of the current amplitude and redox peak. As discussed above, metalloporphyrins have been explored as electrocatalysts for water oxidation. Recently, Lai and Gao demonstrated that the water-soluble cationic nickel complex with meso-tetrakis(4-N-methylpyridyl)porphyrin can electrocatalyze water oxidation for oxygen evolution at neutral pH (Figure 10) [50]. Mechanism investigation suggested that water is oxidized by a two-electron raction. The onset of catalytic wave (~1.0 V vs. NHE) wave is 0.2 V lower in contrast to its cobalt porphyrin analogues.

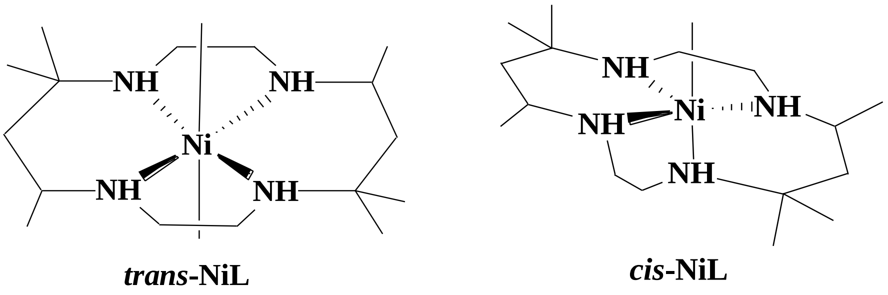

Figure 9. Structure of the *trans*-NiL and *cis*-NiL complexes.

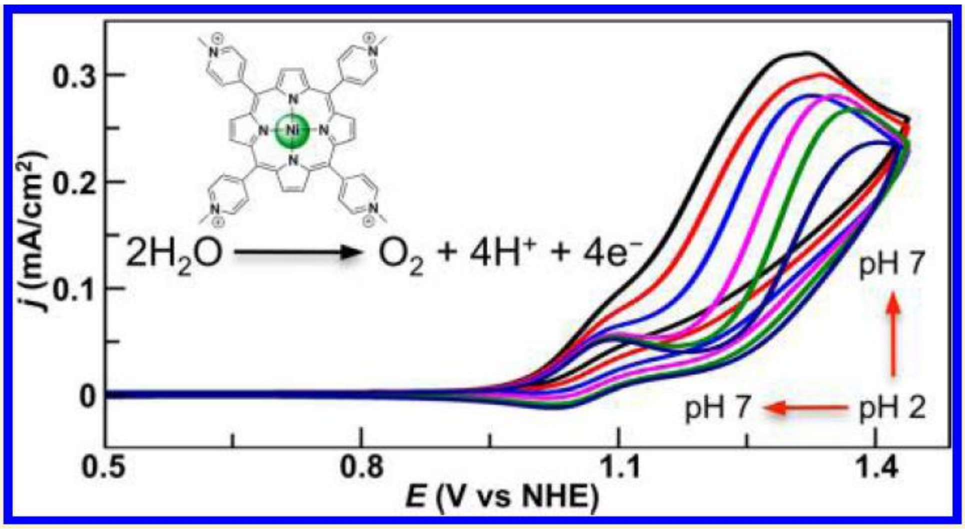

Figure 10. Graphical abstract of the nickel complex with meso-tetrakis(4-N-methylpyridyl)porphyrin. Reprinted with permission from reference [50]. Copyright 2014 American Chemical Society.

6. CONCLUSION

In summary, metal complexes as the electrocatalysts for water oxidation have been widely studied in recent years. However, further understanding the mechanism is required for their roles in the catalytic cycle. Additionally, for the practical applications of electrocatalysts, attention should be paid to their electroconductivity and stability at high anodic potential. Attaching meal complexes on the conductive materials such as graphene and carbon nanotubes may be an effective strategy to improve the electron transfer.

ACKOWLEDGMENTS
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