King Saud University

Arabian Journal of Chemistry

REVIEW ARTICLE

A review on non-noble metal based electrocatalysis for the oxygen evolution reaction

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Abstract   In order to find a clean, efficient and sustainable new energy source that can replace fossil fuels, hydrogen energy is considered to be the most ideal choice. Electrocatalytic oxygen evolution plays a vital role in the development of hydrogen energy, promotes the research of new electrocatalysts, and is dedicated to find materials with high electrocatalytic efficiency. This article discusses in detail the major developments in OER electrocatalysts, including recently reported metal and non-metal based materials. Metal-based catalysts, although having the advantages of high catalytic activity, have disadvantages such as poor stability and low selectivity, which hinder the further application of such materials. Non-metallic based materials avoid such disadvantages and exhibit very substantial performance in overall water decomposition. This review provides useful knowledge of a well-designed OER electrocatalyst and a possible strategy for OER/HER dual-function catalytic performance for future development.

Contents

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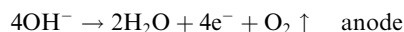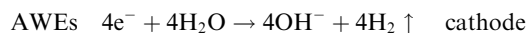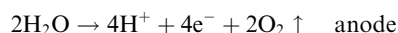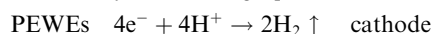
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1. Introduction

In the era of increasing energy consumption and the depletion of fossil fuels, carbon-based coal, gas fuels, and petroleum commonly used in various industrial technologies can cause serious air pollution. So, to find the efficient, clean and environmentally friendly energy has become an urgent problem. Due to the process of energy conversion releasing no carbon dioxide, hydrogen (H_2) is a green energy with high energy density, which has attracted much attention. In order to achieve more efficient energy conversion or storage systems such as alkaline water electrolysis, fuel cells (FC), and metal-air batteries, numerous innovative ideas have been proposed (Suen et al., 2017; Jamesh, 2016; Li et al., 2016a; Li et al., 2019). Hydrolysis technology, as a typical hydrogen evolution technology, has been widely studied. In the past few years, noble-metal-free HER electrocatalysts have rapidly increased. Among them, transition metal carbides (TMCs) are attracted much attention due to their high conductivity, metallic band states, tunable surface/bulk architectures (Gao et al., 2019). Carbon materials are as conductive substrates and highly-dispersed support materials ; which can improve their catalytic activity by heteroatom doping (You and Sun, 2018). Carbon-based catalysts in some report have excellent HER performance even close to that of Pt. In addition, fuel cells as one of the most promising technologies gain great expectations for the commercial application in sustainable energy conversion systems. Cathode oxygen reduction reaction (ORR) kinetics of fuel cells is very slow, which lead to require a large overpotential reaction to occur, greatly limiting the energy output of fuel cell. Currently, Pt-based catalysts are the widely used cathode electrode materials to catalyze the sluggish ORR due to the best catalytic activity of the metal and oxygen binding energy (Nie et al., 2015). Carbon-based materials obtained active sites by doping are considered to be the most promising alternatives of the high-cost and scarce Pt-based catalysts for oxygen reduction reactions (ORR) (Wang et al., 2018a). Oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) are two half-reactions of the water electrolysis. Oxygen evolution reaction (OER) involves the transfer of four electrons, and the mechanism is relatively complex, which owns a slow kinetic reaction and a high overpotential. Therefore, it is the main reason to limit the water electrolysis efficiency, which has also become the focus of research.
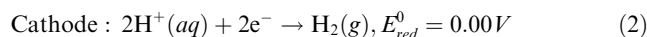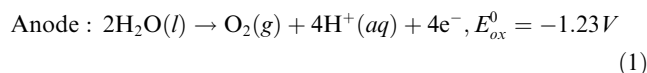
Water electrolysis has been studied in depth since it was first proposed in 1789 (Trasatti, 1999). In fact, water electrolysis still needs to be improved in terms of efficiency and durability to become economically attractive, even though it has the advantages of flexibility, virtually zero-emissions, and production of high purity gas (Ibrahim et al., 2008). The electrodes include cathodes for the hydrogen evolution reaction (HER) and anodes for the oxygen evolution reaction (OER). According to the operating temperature of water electrolysers, low temperature electrolysers can be divided into (acidic) polymer electrolyte water electrolysers (PEWEs) and alkaline water electrolysers (AWEs). PEWE water electrolysis is one of the water electrolysis technologies available on the market. During PEWE water electrolysis, the PEWEs use a solid polymer electrolyte which selectively conducts positive ions such as protons and creates a local acidic environment. The main advantage of PEWEs is can produce pure hydrogen at high current densities (capable of achieving values above 2 A cm^{-2}) and high pressures (over 150 bar) (Carmo et al., 2013; Wang et al., 2018b), which reduces the operational cost. However, under the typical operation conditions of a PEWE only a few electrode materials can exhibit adequate stability (Fabbri et al., 2014; Zhao et al., 2018). Therefore,

the anodic and cathodic reaction is generally catalysed by noble metal based catalysts such as Pt, Ru, Ir and their oxides. On the other hand, the main advantage of AWEs is that it can show sufficient stability when the noble metals are replaced by the alternative catalysts. In addition, in the alkaline medium, it is more favorable oxygen electrocatalysis at the anode side than the acidic medium (Ramaswamy and Mukerjee, 2012; Jiang et al., 2015). Recently, Various non-noble metal catalysts have been found to have similar properties to noble metals, and some of them even show higher catalytic activity than commercial noble metal electrodes (Wang et al., 2016; Liu et al., 2017b; Tian et al., 2014a).

Cathodic HER and anodic OER are two crucial half-cell reactions of electrochemical water splitting. In general, the cathodic and anodic reactions occurring at the PEWE and AWE electrodes can be described by the following equations:

PEWEs $\quad 4e^- + 4H^+ \rightarrow 2H_2 \uparrow \quad$ cathode

$2H_2O \rightarrow 4H^+ + 4e^- + 2O_2 \uparrow \quad$ anode

AWEs $\quad 4e^- + 4H_2O \rightarrow 4OH^- + 4H_2 \uparrow \quad$ cathode

$4OH^- \rightarrow 2H_2O + 4e^- + O_2 \uparrow \quad$ anode

PEWEs and AWEs share a significant overpotential on the anode side of the oxygen evolution reaction (OER), as described by the following equations:

$$\text{Anode}: 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-, E_{ox}^0 = -1.23 V \tag{1}$$

$$\text{Cathode}: 2H^+(aq) + 2e^- \rightarrow H_2(g), E_{red}^0 = 0.00 V \tag{2}$$

The standard oxidization potential of the OER is defined as 1.23 V related to a relative hydrogen electrode (RHE) and the standard reduction potential of HER is 0 V (vs. RHE) at standard temperature and pressure (25 °C, 1 atm). However, in the actual water electrolysis process, a larger applied potential is always required due to the involvement of complex electron and ion transfer processes, which result in sluggish kinetics and low energy efficiency (Bajdich, 2013; Zhu et al., 2018). For this reason, the OER has been studied intensively for decades to elucidate the reaction mechanism and minimize energy loss during water electrolysis. Therefore, the assistance of a suitable electrocatalyst can be sought which can greatly reduce the overpotential and increase the reaction rate. Initially, the catalyst IrO$_2$ exhibited excellent catalytic activity and stability in both acidic and alkaline environments. However, due to the high price and limited resources of Ir, many research efforts have been directed towards the development of OER catalysts based on transition metal oxides and non-metal materials.

Currently, numerous alternative OER electrocatalysts have been exploited to improve electrode kinetics and stability under different electrolyte media. Many researchers show great interest in metal-based materials for OER since these metal-based electrocatalysts generally exhibit excellent catalytic abilities for oxygen evolution. Ru-, Ir-, and Rh-based nanomaterials catalysts (Zhao et al., 2019a, 2019b; Bai et al., 2017) exhibit most outstanding OER catalytic activity, which includes high conductivity, chemical and thermodynamic stability (Lee et al., 2015), but the disadvantages of resource shortages, high prices and poor stability limit the application of these catalysts

(Fabbri et al., 2014; Li et al., 2016b; Hu et al., 2012; Xiang et al., 2016). Transition metal based OER catalysts have become the promising alternatives because of the structural and compositional active sites during the oxygen evolving complex. Such as transition-metal oxides (Lu et al., 2014; Sun et al., 2014; Kleiman-Shwarsctein et al., 2009; Han et al., 2015), hydro(oxy)oxides (Gao et al., 2014b; Zhao et al., 2014; Wu et al., 2016; Ping et al., 2016; Wang et al., 2017b), perovskites (Jung et al., 2014; Risch et al., 2014; Guo et al., 2016; Kim et al., 2015; Zhu et al., 2015b), spinels (Ponce et al., 2002; Godinho et al., 2003; Chi et al., 2005; Jin et al., 2013; Pendashteh et al., 2017). However, the main drawback of metal oxide electrocatalysts is their poor electroconductivity, which hinders the further application of materials. Metal nonoxide systems with superior conductivity such as transition-metal dichalcogenides (TMDs) (Xia et al., 2016; Ganesan et al., 2015; Tang et al., 2016; Cao et al., 2016; Liu et al., 2015b), transition-metal nitrides (TMNs) and phosphides (TMPs) (Xu et al., 2015; Chen et al., 2016b; Zhang et al., 2016; Liu and Li, 2016; Chang et al., 2015; Yu et al., 2016), have been employed and showed excellent activities for both HER and OER, which exhibits the promising potentials for bifunctional electrocatalysts toward the overall water-splitting reaction. Currently, the development bottlenecks of fuel cell and water splitting depend on the slow kinetics of oxygen electrode reactions, the high over potential and the large use of metal electrode catalysts. So, it is of great significance to develop mental-free electrocatalysts for OER with low cost, high electrocatalytic activity and outstanding durability. In particular, various mental-free electrocatalysts, such as carbon-based materials and black phosphorus, have been extensively studied because of their unique catalytic advantages (Wang et al., 2014; Lu et al., 2015b; Cai et al., 2017; Chen et al., 2014; Jiang et al., 2016; Ren et al., 2017; Zhang et al., 2015b). Naturally, non-metallic compounds have attracted the attention of researchers. Early before, Mirzakulova and co-works reported a molecule catalyst of N(5)-ethylflavinium ion (Et-Fl$^+$) for OER and it may be the first proofed that non-metallic compounds have the ability to perform oxygen evolution reactions (Mirzakulova et al., 2012), which provides a non-metallic compounds replacement for traditional transition metal-based water oxidation catalysts. In addition, non-metallic materials show great potential in electrocatalysis for the oxygen evolution reaction in practice since no metal is needed in this kind of materials.

Here, we demonstrate the development and applications of lower overpotential and longterm stability OER electrocatalysts in recent years and list them. The corresponding electrocatalytic parameters of these selected electrocatalysts mentioned in this article are listed in Table 1. Firstly, the reaction mechanism of OER are introduced simply, then, various metal and non-metal based OER electrocatalysts are reviewed, mainly transition metal oxides, chalcogenides, pnictides and non-metal compounds such as carbon-based materials, black phosphorus, and the like. Most of the OER electrocatalysts shows the remarkable OER catalytic performance with lower overpotential and longtime stability, also exhibits better or well comparable with commercial IrO$_2$/RuO$_2$ electrocatalysts. For these electrocatalysts, non-metallic catalyst shows the higher efficiency and stable performance towards both the HER and OER under alkaline conditions, which can used as a highly active electrocatalyst towards both the OER and HER. With the development study of researchers from various country and field, a new type bifunctional OER/HER electrocatalysts with novel material showing high performance will be realized to meet our requirements of practical applications in the near future.

2. Fundamentals of the OER

Water molecules are decomposed into hydrogen and oxygen at external potential. To accelerate water splitting reaction, hydrogen and oxygen evolving catalysts are applied to the surface of cathode and anode, respectively. The reaction pathway of OER depends on the pH of the solution. In acidic medium, OER takes place by converting two water molecules into protons and oxygen molecule. However, in alkaline and neutral solutions, OER involves oxidation of four hydroxide ions to water and dioxygen.

Oxygen evolution reaction is an anodic reaction of the water splitting reaction and it is the most energy-intensive step in the electrolysis reaction because the anode reaction involve four-electron transfer. Many research groups have proposed possible mechanisms for oxygen release reactions in acidic or alkaline conditions at anode electrodes. A brief overview of OER process on the surface of transition metal oxide can help to understand the activity trends observed (Bandal et al., 2018). Oxygen evolution reactions involve the adsorption and desorption of metal active sites on a variety of oxygen containing intermediate species (Kleiman-Shwarsctein et al., 2009; Strasser et al., 2010). As can be seen in Fig. 1a, there are two different ways of producing oxygen from the MO intermediate product. One is the green route, in which oxygen is produced by the direct combination of two M-Os; the other is the generation of oxygen by the formation of MOOH intermediates followed by decomposition, including acidic and basic mechanisms (Suen et al., 2017). Despite these differences, OER's general mechanism for oxides in acidic and alkaline solutions can be summarized as follows (Fig. 1b). Generally, the OER intermediates are stabilized by the catalyst such as surface-bound peroxo- or oxo-species. The relative stabilities of these intermediates and the activation barriers between them dictate the determined step to the rate and further to the overall rate of water oxidation. The properties of the surface intermediates depend on the reaction conditions (e.g. pH) and the catalyst materials (Trotochaud and Boettcher, 2014).

Electrocatalysis is a catalytic action accelerating the charge transfer at the interface between the electrode and the electrolyte, and also can be used as a catalyst to promote the electrochemical reaction. Electrocatalytic kinetics is a measure of electrocatalytic activity. Based on some key parameters such as overpotential, Tafel slope, stability, Faraday efficiency and Turnover frequency (TOF), it is often used to measure the catalytic activity of OER electrocatalysts. Tafel equation: $\eta = a + b \log |j|$, where η is the overpotential, b is the Tafel slope, and j is the current density, which are effectively evaluate the performance of electrocatalysts. Overpotential(η) is one of the most important indicators to measure the performance of electrocatalysts. In electrochemistry, overpotential is the potential difference (voltage) between the reduction potential of the semi-reaction thermodynamic and the potential of the redox reaction observed by the experiment. Generally speaking, it is necessary to achieve the value of the specified density (10 mA cm^{-2}), and the lower the overpotential of the electrocatalyst the better the electrocatalytic power. Exchange current density (j) is another important parameter for electrocatalytic kinetics. The exchange current density can be used to describe the ability of an electrode to react to lose electrons and to reflect the ease with which an electrode reaction can proceed. Higher exchange current density indicates better electrocatalytic capability. Tafel slope (b) is also an important indicator of the electrocatalytic kinetics. Usually smaller Tafel slope (b) indicates that the current density can increase more rapidly with a smaller overpotential (η), which illustrates good electrocatalytic kinetics. Furthermore, catalyst stability refers to the ability of

Table 1 Important measurement and kinetic parameters for mentioned electrocatalysts for OER.

| Catalysts	Electrolytes	Substrate	Overpotential (mV) at specific current density	Current density (mA cm^{-2}) at specific overpotential	Tafel slope (mV dec^{-1})	Ref.
Metal-based electrocatalysts						
RuO$_2$	0.1 M HClO$_4$	GCE	—	~0.01/~0.003@ 250 mV	—	25
IrO 2	0.1 M HClO$_4$	GCE	—	~0.004/~0.002@ 250 mV	—	25
PNC/Co	1.0 M KOH	MOF	410@10 mA cm^{-2}	—	131	26
bulk Ru	0.1 M HClO$_4$	GCE	219@0.5 mAmol^{-1}10^9	—	44	74
Bulk Ir	0.05 M H$_2$SO$_4$	GCE	321@0.5 mAmol^{-1}10^9	—	63	74
Bulk Pt	0.1 M HClO$_4$	GCE	536@0.5 mAmol^{-1}10^9	—	145	74
Ru NPs	0.1 M HClO$_4$	GCE	274@0.5 mAmol^{-1}10^9	—	—	74
Ir NPs	0.05 M H$_2$SO$_4$	GCE	333@0.5 mAmol^{-1}10^9	—	64	74
Pt NPs	0.1 M HClO$_4$	GCE	240@0.5 mAmol^{-1}10^9	—	210	74
Co/N-CNTs	0.1 M KOH	GCE	390@10 mA cm^{-2}	—	67	75
Fe/N-CNTs	0.1 M KOH	GCE	520@10 mA cm^{-2}	—	76	75
Ni/N-CNTs	0.1 M KOH	GCE	590@10 mA cm^{-2}	—	138	75
CoOx NPs/BNG	0.1 M KOH	GCE	295@10 mA cm^{-2}	—	57	77
Co-Bi/G	0.1 M KOH	GCE	320@10 mA cm^{-2}	—	70	77
CoOx@CN	1 M KOH	Ni foam	260@10 mA cm^{-2}	—	—	81
Co-Fe-O/rGO	1 M KOH	GCE	340@10 mA cm^{-2}	—	31	84
CoFe$_2$O$_4$/rGO	0.1 M KOH	GCE	540@29.5 mA cm^{-2}	—	—	85
Ni$_{0.4}$Co$_{2.6}$O$_4$	0.1 M KOH	Ni foil	520@10 mA cm^{-2}	—	—	86
Ni$_{0.6}$Co$_{2.4}$O$_4$	0.1 M KOH	Ni foil	530@10 mA cm^{-2}	—	—	86
Ni$_{0.9}$Co$_{2.6}$O$_4$	0.1 M KOH	Ni foil	530@10 mA cm^{-2}	—	—	86
NiCo$_2$O$_4$	0.1 M KOH	GCE	490@10 mA cm^{-2}	—	—	86
Ni-Fe oxide/Ni:Fe = 3:7	0.1 M KOH	FTO	329@2 mA cm^{-2}	—	120	87
Ti/Co$_3$O$_4$	2 M KOH	Ti	—	~0.018/~0.02@660 mV	50	89
Ti/NiCo$_2$O$_4$	2 M KOH	Ti	—	~0.44/~0.008@660 mV	64	89
NiCo$_2$O$_4$	2 M NaOH	GCE	—	—	51	90
NiCo$_2$O$_4$(TD)	1 M KOH	Ni	453@100 mA cm^{-2}	—		91
NiCo$_2$O$_4$(EPD)	1 M KOH	Ni	471@100 mA cm^{-2}	—		91
NiCo$_2$O$_4$(AO)	1 M KOH	Ni	567@100 mA cm^{-2}	—		91
NiCo$_2$O$_4$-G	0.1 M KOH	GCE	950@35.4 mA cm^{-2}	—	164	92
CuCo$_2$O$_4$	1 M NaOH	Ti	—	—	—	94
CuCo$_2$O$_4$/NrGO	1 M NaOH	GCE	360@10 mA cm^{-2}	—	64	96
CuCo$_2$O$_4$/NrGO	0.1 M KOH	GCE	410@10 mA cm^{-2}	—	—	96
CuCo$_2$O$_4$/NrGO	0.1 M PBS	GCE	1150@10 mA cm^{-2}	—	—	96
MnFe$_2$O$_4$	0.1 M KOH	GCE	470@10 mA cm^{-2}	—	114	99
CoFe$_2$O$_4$	0.1 M KOH	GCE	370@10 mA cm^{-2}	—	82	99
NiFe$_2$O$_4$	0.1 M KOH	GCE	440@10 mA cm^{-2}	—	98	99
CuFe$_2$O$_4$	0.1 M KOH	GCE	410@10 mA cm^{-2}	—	94	99
NiS	0.1 M KOH	SLS	297@11 mA cm^{-2}	—	47	101
CoSe	1 M KOH	GCE	295@10 mA cm^{-2}	—	40	102
Ni$_3$S$_2$	1 M NaOH	Ni foam	260@10 mA cm^{-2}	—	—	104
Fe$_3$O$_4$@Co$_9$S$_8$/rGO	1 M KOH	GCE	340@10 mA cm^{-2}	—	54.5	105
Co$_2$N	1 M KOH	GCE	430@10 mA cm^{-2}	—	80	54
Co$_3$N	1 M KOH	GCE	410@10 mA cm^{-2}	—	72	54
Co$_4$N	1 M KOH	GCE	330@10 mA cm^{-2}	—	58	54
Ni$_2$P	1 M KOH	GCE	339@10 mA cm^{-2}	—	—	107
Co$_2$P	1 M KOH	GCE	367@10 mA cm^{-2}	—	—	107
Fe$_2$P	1 M KOH	GCE	390@10 mA cm^{-2}	—	—	107
NiFeP	1 M KOH	GCE	277@10 mA cm^{-2}	—	—	107
Ni$_2$P	1 M KOH	Ni foam	200@10 mA cm^{-2}	—	72	109
CoNiP	1 M KOH	GCE	280@10 mA cm^{-2}	—	66.5	110
Ni$_3$N bulk	1 M KOH	GCE	490@10 mA cm^{-2}	—	45	53
Ni$_3$N NSs	1 M KOH	GCE	350@10 mA cm^{-2}	—	85	53
Ni$_3$N NSs	1 M KOH	GC	350@52 mA cm^{-2}	—	41	53
NiSe$_2$-DO	1 M KOH	Ni foam	241@10 mA cm^{-2}	—	32	28
Ni$_x$Fe$_{1-x}$Se$_2$-DO	1 M KOH	Ni foam	195@10 mA cm^{-2}	—	28	28
Carbon-based electrocatalysts						
NG	0.1 M KOH	GC	700@10 mA cm^{-2}	—	—	59
N-CNT/GNR	0.1 M KOH	GC	360@10 mA cm^{-2}	—	—	60
G-CNT	0.1 M KOH	GCE	498@5 mA cm^{-2}	—	231	62
NG-CNT	0.1 M KOH	GCE	368@5 mA cm^{-2}	—	141	62

Table 1 (*continued*)

Catalysts	Electrolytes	Substrate	Overpotential (mV) at specific current density	Current density (mA cm^{-2}) at specific overpotential	Tafel slope (mV dec^{-1})	Ref.
NPMC[a]	0.1 M KOH	GCE	395@10 mA cm^{-2}	—	—	65
N/C	0.1 M KOH	GCE	380@10 mA cm^{-2}	—	—	115
o-MWCNTs[b]	0.1 M KOH	GCE	300@10 mA cm^{-2}	—	—	118
CNT/BN[c]	0.1 M KOH	GCE	580@10 mA cm^{-2}	—	122	120
N-CNTs	0.1 M KOH	GCE	390@10 mA cm^{-2}	—	—	121
N-MWNT	1.0 M NaOH	GC	320@10 mA cm^{-2}	—	68	122
N-G	0.1 M KOH	GC	434@10 mA cm^{-2}	—	—	123
N-G/CNT	0.1 M KOH	GCE	400@10 mA cm^{-2}	—	83	124
S,S-CNT	1 M KOH	GCE	350@10 mA cm^{-2}	—	95	126
NS-GR/CNT	0.1 M KOH	GCE	560@10 mA cm^{-2}	—	103	127
g-C$_3$N$_4$[d]	0.1 M KOH	GCE	734@10 mA cm^{-2}	—	120.9	128
g-C$_3$N$_4$/G	0.1 M KOH	GCE	539@10 mA cm^{-2}	—	68.5	128
Black phosphorous materials						
BP	0.1 M KOH	Ti	370@10 mA cm^{-2}	—	72.9	63
Few-layer BP	1 M KOH	GCE	220@10 mA cm^{-2}	—	88	64

[a] N and P co-doped mesoporous nanocarbon.
[b] Oxidized Multiwall Carbon Nanotubes.
[c] carbon nanotube-boron nitride nanocomposites.
[d] Graphitic carbon nitride.
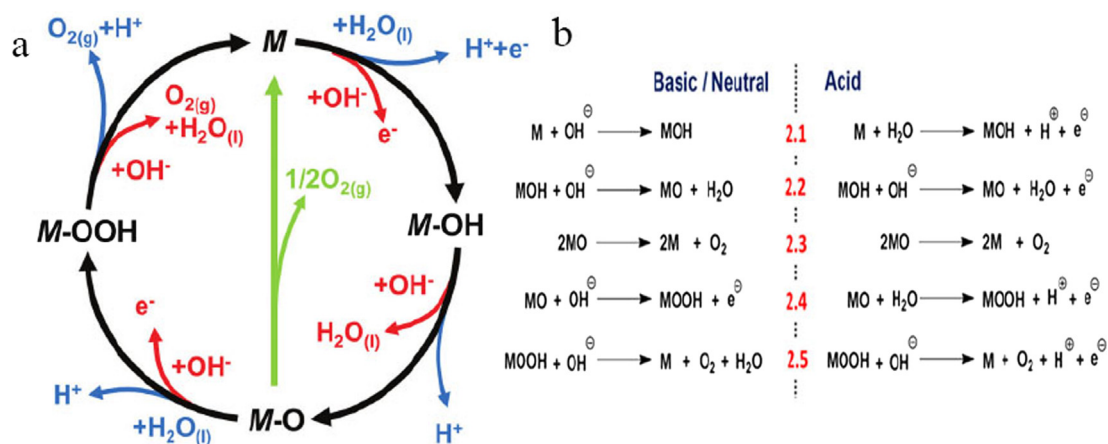
Fig. 1 (a) The OER mechanism for acid (blue line) and alkaline (red line) conditions. The black line indicates that the oxygen evolution involves the formation of a peroxide (M-OOH) intermediate (black line). Reprinted with permission from Suen et al. (2017) copyright 2017, The Royal Society of Chemistry. (b) The scheme of proposed mechanism for OER. Reprinted with permission from Bandal et al. (2018) copyright 2018, Elsevier.

a catalyst to maintain its activity, thermal stability and structure unchanged during the catalytic reaction. Faraday efficiency refers to the percentage of actual and theoretical products, which is affected by temperature, electrolyte concentration, applied voltage, solution acidity and even the purity of electrode material. Turnover frequency (TOF), is the number of transformations at a single active site per unit time, measuring the rate of a catalyst's catalytic reaction and represents the intrinsic activity of the catalyst (Liang et al., 2014). Besides, the electrocatalytic properties of the tests are mainly measured for its elemental composition, surface area, faradaic efficiency, catalytic activity, stability and so on. McCrory et al. (2013) proposes a general test method for electrocatalysts for oxygen evolution reaction including morphology test, composition test, specific surface area test, and electrochemical test in Fig. 2,

which provides convenience for the evaluation of electrocatalytic performance and the assistance for the development of electrocatalysts. In recent years, relevant researchers have suggested that the phase change of the electrocatalyst during the oxygen evolution reaction will result in a different catalytic active site from the original sample preparation (Liu et al., 2015a; Seitz et al., 2016). Therefore, we should pay close attention to the structural evolution of the electrocatalyst during the oxygen evolution reaction, and develop an electrocatalyst with outstanding performance.

3. Noble-metal-free based electrocatalysts for OER

Among the available metal based catalysts, Ru-, Ir-, and Rh-based catalysts exhibit most outstanding OER catalytic
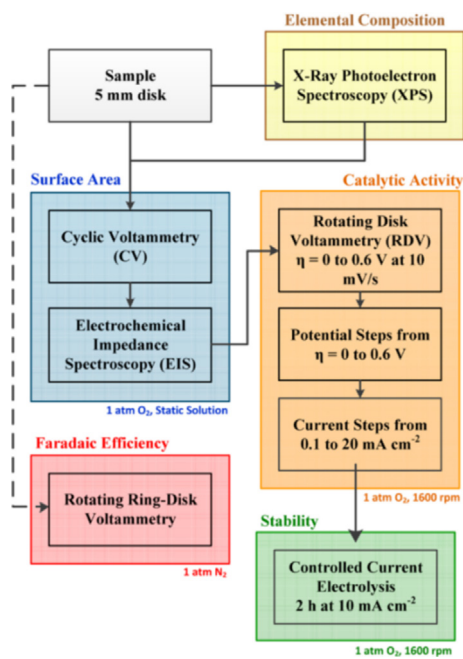
Fig. 2 General test method for OER or ORR. Reprinted with permission from Mccrory et al. (2013) copyright © 2013, American Chemical Society.

activity, and the OER activity catalysts decreases as Ru > Ir > Rh (Li et al., 2016a; Fabbri et al., 2014; Reier et al., 2012). Resource shortages, high prices and poor stability limit the use of these catalysts despite noble-metal materials being the best catalysts for OER. So, it is a challenge that to reduce the use of a large number of noble metal catalysts and to find alternative non-noble material with excellent performance. Transition metal based OER catalysts have become promising alternatives because of the structural and compositional active sites of the oxygen evolving complex (Liu et al., 2016), such as spinel, transition-metal oxides, sulfides, nitrides and phosphides and so on. Meanwhile, transition-metal elements have low cost, high activity and long-term stability under low oxidation conditions, which makes the whole water splitting more feasible. Among the excellent transition-metal based catalysts, cobalt oxides is one of the earlier used oxides as an oxygen evolution catalyst in an alkaline medium due to its high stability and special 3d electronic configurations (Krishtalik, 1981; Tong et al., 2017; Li et al., 2018b). With the deepening of research, it has been found that it is still inferior to noble metal oxides, although cobalt oxides has good stability and good catalytic activity. Then, it is found that doped or mixed oxides can produce synergistic effects through intra-component electronic interactions, which can effectively regulate the physicochemical properties of oxides and further improve the catalytic performance of oxides (Li et al., 2018a; Huang et al., 2017). Jin et al. (2015) have synthesized cobalt/-cobalt oxide/N-doped carbon hybrids (CoOₓ@CN) by simple one-pot thermal treatment method, and it exhibited the better catalytic activity than cobalt oxides for both oxygen evolution and oxygen reduction reactions, reaching a current density of 20 mA cm^{-2} at 1.55 V.

The transition metal oxides owns the surface active sites, which can catalyze the oxygen evolution reaction (Burke et al., 2016). The process of the oxygen evolution mechanism is the continuous oxidation of the active site of the metal. However, metal cation forms the hydroxyl peroxide, leading to limit the rate of oxygen evolution (Chi et al., 2005; Strasser et al., 2010), which reflects the prosperity of transition metal oxides. Numerous kinds of transition metal oxides catalysts can be used as superior OER electrocatalysts, such as TMOs/N-doped carbon hybrids (Tong et al., 2017; Rossmeisl et al., 2007), Co-Fe-O/rGO (Geng et al., 2015; Bian et al., 2014), $Ni_xCo_{3-x}O_4$ (Lambert et al., 2015); Ni-Fe oxide (Zhang et al., 2015a), $M_xMn_{3-x}O_4$ (M = divalent metals) (Chinnusamy et al., 2011) and so on. At present, spinel-type oxides include MCo_2O_4, MFe_2O_4, MMn_2O_4, etc., among them, cobalt-based spinel oxides (MCo_2O_4, M = Ni, Zn, Cu, Mn, etc.) have high stability and activity in alkaline solution, and low price of transition metals, which makes this type of oxide electrode become one of the most potential OER the electrocatalysts. Singh et al. (1990) and Chialvo and Chialvo (2010) early studies found that the spinel $NiCo_2O_4$ with cobalt-based nickel exhibited the best catalytic activity for both oxygen evolution and oxygen reduction reactions. The effects of three preparation methods including pyrolysis, electrophoretic deposition and Ni-Co alloy oxidation on the catalytic performance of $NiCo_2O_4$ electrode were compared, which shows that the oxide catalyst prepared by pyrolysis has the best apparent catalytic activity, the catalyst prepared by electrophoretic deposition has the best stability, and the alloy oxidation method has no obvious effect on improving the performance of the catalyst. Chi et al. (2006) Besides, Dong et al. (2013) reported that a novel hybrid material composed of mesoporous $NiCo_2O_4$ nanoplatelets and graphene ($NiCo_2O_4$-G) as an active bi-functional electrocatalyst for both ORR and OER synthesized by a one-pot method. They investigated the hybrid effect of combining $NiCo_2O_4$ nanoplatelets with graphene sheets by comparing its performance to that of $NiCo_2O_4$ itself without graphene sheets, which shows that graphene sheets as a support material can facilitate charge transfer much fast. Lastly, compared with Co_2O_4-G, the electrocatalytic activities of $NiCo_2O_4$-G shows that Ni incorporation into the octahedral sites of the spinel crystal structure can improve electrical conductivity and generate new active sites. Meanwhile, a facile template-free co-precipitation route for the design and fabrication of well-ordered $NiCo_2O_4$ (NCO) spinel nanowire owns high specific surface area (124 m^2 g^{-1}) and good catalytic activity for the OER (Jin et al., 2013), which is higher than that of the previously reported $NiCo_2O_4$ nanoplatelet/graphene hybrid catalyst (77 m^2 g^{-1}) (in Fig. 3a, b) (Dong et al., 2013). Taking into consideration of the price and performance advantages with copper ion doping, spinel structure $CuCo_2O_4$ has become a hot spot for doped oxide catalysts. $Cu_xCo_{3-x}O_4$ prepared by pyrolysis and sol-gel method revealed that the copper ions not only selectively enter the octahedral active sites during the doping process, but also facilitate the refinement of the crystalline grains. It is also pointed out that the sol-gel method is easier to prepare pure spinel structure $CuCo_2O_4$, which has the best catalytic activity and does not contain the CuO phase (Koninck et al., 2006). It can be seen from the preparation of spinel $Cu_xCo_{3-x}O_4$ film (Berenguer et al., 2008; Rosatoro et al., 2006) that, when the stability content of Cu reaches a certain amount, the electrode will corrode, which is caused by the damage degree of the spinel surface on the degree of sharpening of Cu grain, and it is also the main causes of poor stability potential Cu in binary
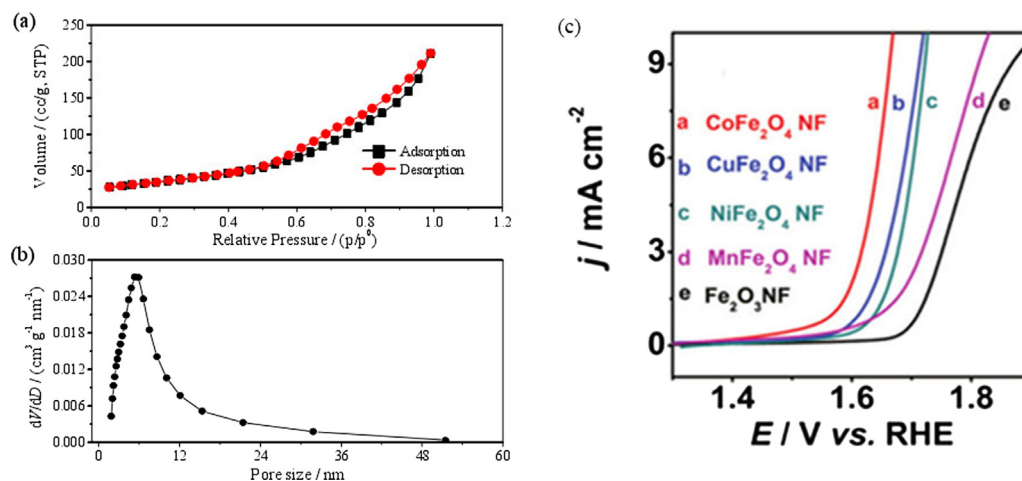
Fig. 3 N$_2$ adsorption-desorption isotherm (a) and pore distribution plot (b) of NCO spinel nanowire arrays. Reprinted with permission from Dong et al. (2013) copyright © 2013, The Royal Society of Chemistry. (c) Polarization curves for OER on Fe$_2$O$_3$, CoFe$_2$O$_4$, NiFe$_2$O$_4$, CuFe$_2$O$_4$, and MnFe$_2$O$_4$ NFs. Reprinted with permission from Li et al. (2015) copyright © 2015, The Royal Society of Chemistry.

oxide dissolution of electrode under high anode. In order to improve the OER catalytic performance of CuCo$_2$O$_4$, a composite material (CuCo$_2$O$_4$/NrGO) consisting of CuCo$_2$O$_4$ nanoparticles anchored on nitrogenated reduced graphene oxide had been reported (Bikkarolla and Papakonstantinou, 2015), which greatly improves its catalytic activity. The study of Mn$_x$Co$_{3-x}$O$_4$ binary oxides shows that doping of Mn ions is not conducive to the improvement of oxygen evolution activity of oxides, but it is beneficial to the improvement of catalytic oxygen reduction activity (Restovic, 2002; Hirai et al., 2016). In addition, Li et al. (2015) have designed a series of porous M-substituted magnetite MFe$_2$O$_4$ nanofibers (MFe$_2$-O$_4$NFs) with M = Co, Ni, Cu, and Mn, and also reported a trend of the OER electrocatalytic activities with CoFe$_2$O$_4$ > CuFe$_2$O$_4$ > NiFe$_2$O$_4$ > MnFe$_2$O$_4$ for MFe$_2$O$_4$ samples (as Fig. 3c).

The above-mentioned metal oxides show excellent electrocatalytic abilities for OER, but there is a problem of phase transformation of spinel during oxygen evolution. The replacement of oxides with chalcogenides (sulfides, selenides or tellurides) will increase the intrinsic conductivity of the material. It is well known that transition-metal chalcogenides have prominent electronic structures and physical appearance, for instance, excellent conductivity, magnetic property and halfmetallicity (Xiang et al., 2016; Xia et al., 2016; Ganesan et al., 2015; Tang et al., 2016; Cao et al., 2016; Liu et al., 2015b; Kakade et al., 2016; Chen et al., 2016a; Liao et al., 2016; Gao et al., 2014a; Feng et al., 2015; Yang et al., 2016). Fe doped NiSe$_2$ derived oxide catalysts (Ni$_x$Fe$_{1-x}$Se$_2$-DO) with an overpotential of ~195 mV, a Tafel slope of 28 mV dec^{-1} (as Fig. 4), and the derived oxide (Ni$_x$Fe$_{1-x}$Se$_2$-DO) exhibits much better OER activity than that of NiFe-LDH (Xiang et al., 2016). Due to their distinct electronic structure especially in as electrocatalysts, similar to metal chalcogenides, transition metal nitrides (TMNs) also show excellent catalytic activities in many fields (Xu et al., 2015; Chen et al., 2016b; Zhang et al., 2016; Liu and Li, 2016). A series of metallic cobalt nitrides (Co$_2$N, Co$_3$N and Co$_4$N) arising from electron
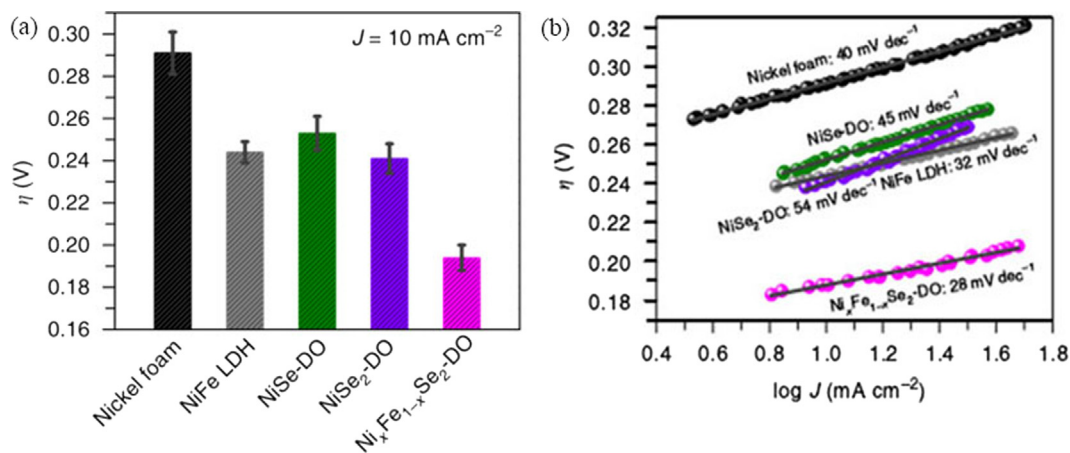

Fig. 4 (a) Overpotential (η) at 10 mA cm^{-2} and (b) Tafel plots for Ni foam, NiFe LHD, NiSe-DO, NiSe$_2$-DO and Ni$_x$Fe$_{1-x}$Se$_2$-DO. Reprinted with permission from Xiang et al. (2016) copyright © 2016, Nature Communications.

delocalization modulation indicated that the materials with higher amounts of cobalt are more conductive and more active for OER (Chen et al., 2016b). Likewise, Xu et al. (2015) pointed that the electroconductivity of Ni_3N sheet is higher than that of bulk Ni_3N. The calculated density of states (DOS) of Ni_3N sheet (Fig. 5a) nearing the Fermi level is more intense than bulk Ni_3N, which improves the OER activity greatly. Recently, transition metal phosphides (TMPs) have been extensively identified as new promising earth-abundant and highly active catalysts for hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) (Liu and Li, 2016; Chang et al., 2015; Yu et al., 2016; Read et al., 2016; Ryu et al., 2015; You et al., 2016; Fu et al., 2016). A series of transition metal phosphide electrodes as electrocatalysts for the HER and OER are fabricated by thin film phosphidation strategy, which have highly actives and excellent electrocatalytic performance (as Fig. 5b) (Read et al., 2016). In a word, metal phosphides have shown great potential in both HER and OER (Liu et al., 2017a). The combination of transition metals and metal phosphides catalysts can improve their

OER activity, but their performance will deteriorate rapidly after long-term use, which is worthy of our consideration.

4. Carbon-based electrocatalysts for OER

Metal-based catalysts suffer from many drawbacks, such as impurity interference, low selectivity, poor stability, unclear active sites and so on (Frydendal et al., 2015. Therefore, it is will be a particularly challenge to find a category of OER catalyst, which has a sufficiently high activity, with more electrocatalytic active sites, larger specific surface area and stable lifetime. Since Mirzakulova et al. (2012) proved that the non-metallic compounds has the ability to perform oxygen evolution reactions, carbon-based materials such as carbon black, carbon nanotubes and graphene with N, P, B and S doped as good conductive material and in acidic or alkaline electrolyte showing chemical inertness, have been studied and widely used in electric catalytic. Carbon-based materials can be used as promising electrocatalysts, and doping mixed atoms such as nitrogen or boron can effectively improve their
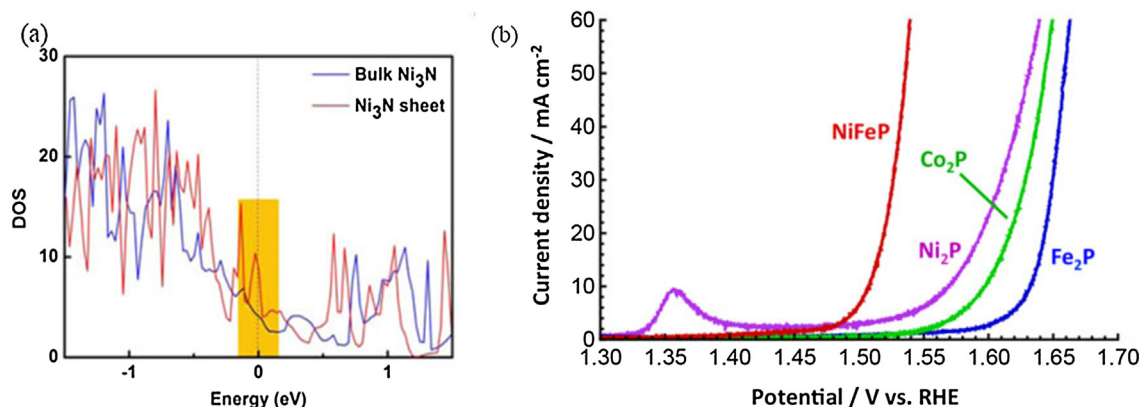
Fig. 5 (a) Calculated density of states for bulk Ni_3N and Ni_3N sheet. The Fermi level is set at 0 eV. Reprinted with permission from Xu et al. (2015) copyright © 2015, American Chemical Society. (b) Polarization data of NiFeP, Co_2P, Ni_2P, Fe_2P films for the OER in 1 M KOH. Reprinted with permission from Read et al. (2016) copyright © 2016, American Chemical Society.
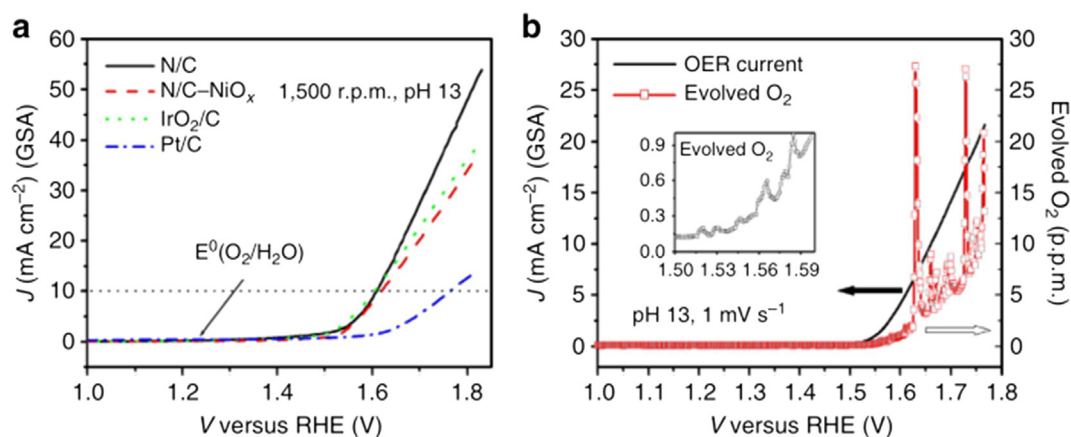
Fig. 6 (a) Oxygen evolution activities of the N/C electrodes with KOH electrolyte (pH 13) analyzed from RRDE system (b) The amount of evolved O_2 (curve 1) and current density on the N/C electrode (curve 2) during the positive potential sweep with the electrochemical cell (inset: the evolved O_2 in the potential range from 1.5 to 1.6 V). Reprinted with permission from Zhao et al. (2013) copyright © 2013, 2013 Macmillan Publishers Limited.

catalytic activity. Moreover, the presence of N in N-doped carbon results in more chemically active sites, high density defects and high electrochemical activity (Chi et al., 2018). Due to these enhanced electronic properties, N-doped catalysts in the Carbon network are attractive for a wide range of applications, as non-metallic catalysts for OER/ORR in fuel cell systems (Yang et al., 2017) For example, Nitrogen-doped carbon nanomaterials as non-metal electrocatalysts for OER with a current density reached to 10 mA cm^{-2} at 0.38 V in alkaline media (Fig. 6a), this value is equivalent to iridium and cobalt oxide catalysts and is the best among non-metal oxygen evolution catalysts. The evolved O$_2$ gas was detected at an onset potential (Fig. 6b), clearly showing that the N/C catalyst has OER activity (Zhao et al., 2013).

The original features of carbon nanotubes (single wall and multiple walls, SWNTs and MWNTs) and the correlation between the numbers of the walls and their corresponding OER activities, in which the outer wall was responsible for OER and the function of the inner wall is to increase the electron transfer rate, thus the OER activity will be enhanced with the numbers of walls increased. Recently, the increased number of walls has a lower OER activity due to the diminishment of dc bias influence (Cheng et al., 2015). Later, some people successfully used MWCNT without any treatment as a high-efficiency electrocatalyst in OER, and proposed the dual function of MWCNT with outer wall and inner wall (Ali et al.,

2018). At the same time, the surface oxidation of MWCNTs to generate oxygen-containing groups and defect sites to dope the heteroatoms to achieve unexpectedly high OER catalytic activity was also firstly proposed (Lu et al., 2015a). In addition, the composite of carbon nanotubes with other nanomaterials has also proven to be an important catalyst (Patil et al., 2016; Zhu et al., 2015a). Particularly, due to the unique graphene-like structure of hexagonal boron nitride (h-BN) and its synergy with carbon nanotubes, the composites exhibits an excellent OER electrocatalytic activity towards, which owns better stability than that of the state-of-the-art Pt/C catalyst (as Fig. 7) (Patil et al., 2016). In the research field of carbon nanotubes, large surface area N-doped porous carbon nanotubes (NCNT) obtained by nitrogen doping have in situ N-doped graded porous structures, which can promote the transport of gas molecules, and N-doping can provide abundant active sites to enhance catalytic activity, which was proved by Pan et al. (2016). Nitrogen-doped multi-walled carbon nanotubes (N-MWNTs) are controlling the nitrogen active sites, in which shows remarkable OER activity, owing the most superior active non-metallic OER electrocatalyst (Davodi et al., 2017).

Except that, graphene-based materials such as graphene, graphene-doped or graphene-like materials also have the excellent OER activity (Chen et al., 2014; Chi et al., 2018; Wang et al., 2017a; Tian et al., 2014b, 2015a, 2015b; El-Sawy et al.,
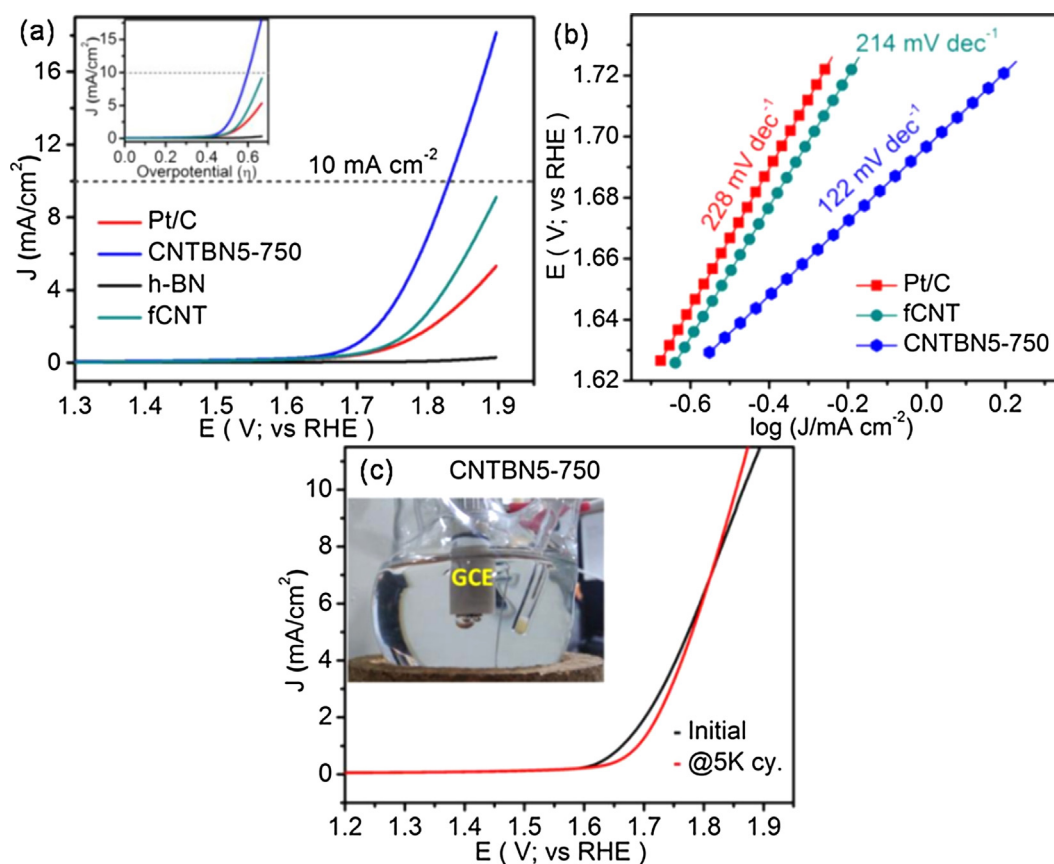
Fig. 7 (a) OER voltammograms of CNTBN5-750, bare h-BN, fCNT and Pt/C catalyst; inset shows plot of standard thermodynamic potential for OER; (b) Tafel plots of CNTBN5-750, fCNT and Pt/C. (c) Comparison of durability of CNTBN5-750; inset shows a picture of the oxygen bubbles generated on the CNTBN5-750 modified electrode during OER. Reprinted with permission from Patil et al. (2016) copyright © 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

2016; Zhao et al., 2016). Chen et al. (2014) reported a N,O-dual doped graphene-CNT hydrogel film with excellent electrochemical durability because of the higher surface area and more active sites. While the Tafel slope was around 141 mV dec^{-1}, the slightly higher Tafel slope indicates that OER dynamics need to be improved, and a more active site may improve OER dynamics. In order to develop an effective catalyst with abundant highly active sites and full exposure to reactants, a nitrogen-doped mesoporous graphene framework (NMGF) was synthesized by a CVD method on 3D MgO templates (in Fig. 8a). The as-obtained NMGF has unique structural features with plentiful active centers due to defects and heteroatoms, a large specific surface area and a high electrical conductivity, which improves utilization efficiency due to the high electrochemically active surface area and hydrophilic surface (as Fig. 8c), thereby leading to superior ORR and OER bifunctional activities (as Fig. 8b) (Wang et al., 2017a). Meanwhile, a new N-doped graphene/single-walled carbon nanotube (SWCNT) hybrids is synthesized by one-step CVD method as a bifunctional electrocatalyst, which forms a three-dimensional interconnect network of graphene and SWCNT. Meanwhile, the NGSHs have a large specific surface area of 812.9 m^2 g^{-1} and a high conductivity of 53.8 S cm^{-1} (Tian et al., 2014b). Controlling active sites of metal-free catalysts is an important method to improve activity of the oxygen evolution reaction (OER) (Tian et al., 2015b). El-Sawy et al.
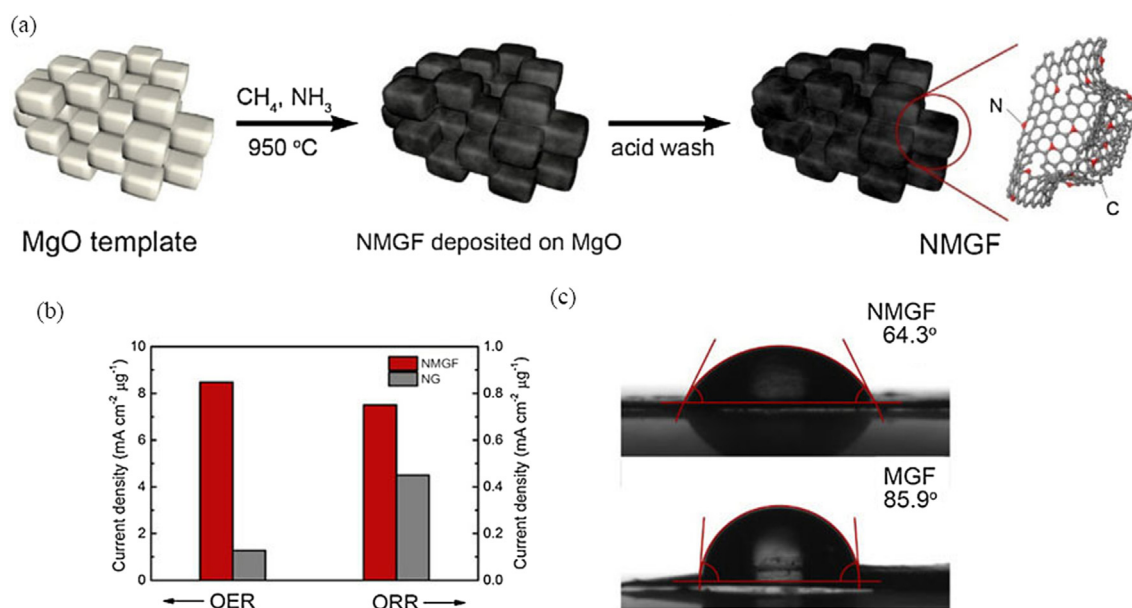
Fig. 8 (a) Schematic illustration of NMGF formation on porous MgO template. (b) The specific current density of NMGF and NG. (c) The contact angles of NMGF and MGF, With the introduction of N heteroatoms, contact Angle from 85.9° greatly reduced to 64.3°, show that the surface wettability significantly increased, thus improve the permeability of the electrolyte and affinity. Reprinted with permission from Wang et al. (2017a) copyright © 2017, Elsevier.
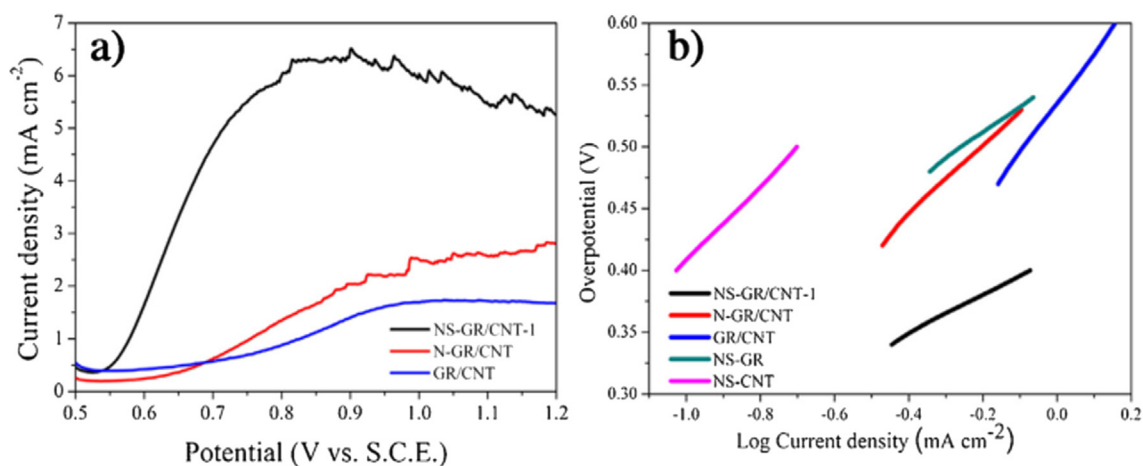
Fig. 9 (a) Linear sweep voltammograms of NS-GR/CNT-1, N-GR/CNT and GR/CNT. (b) The Tafel plots of NS-GR/CNT-1, N-GR/CNT, GR/CNT-NS-GR and NS-CNT. Reprinted with permission from Zhao et al. (2016) copyright © 2016, Elsevier.
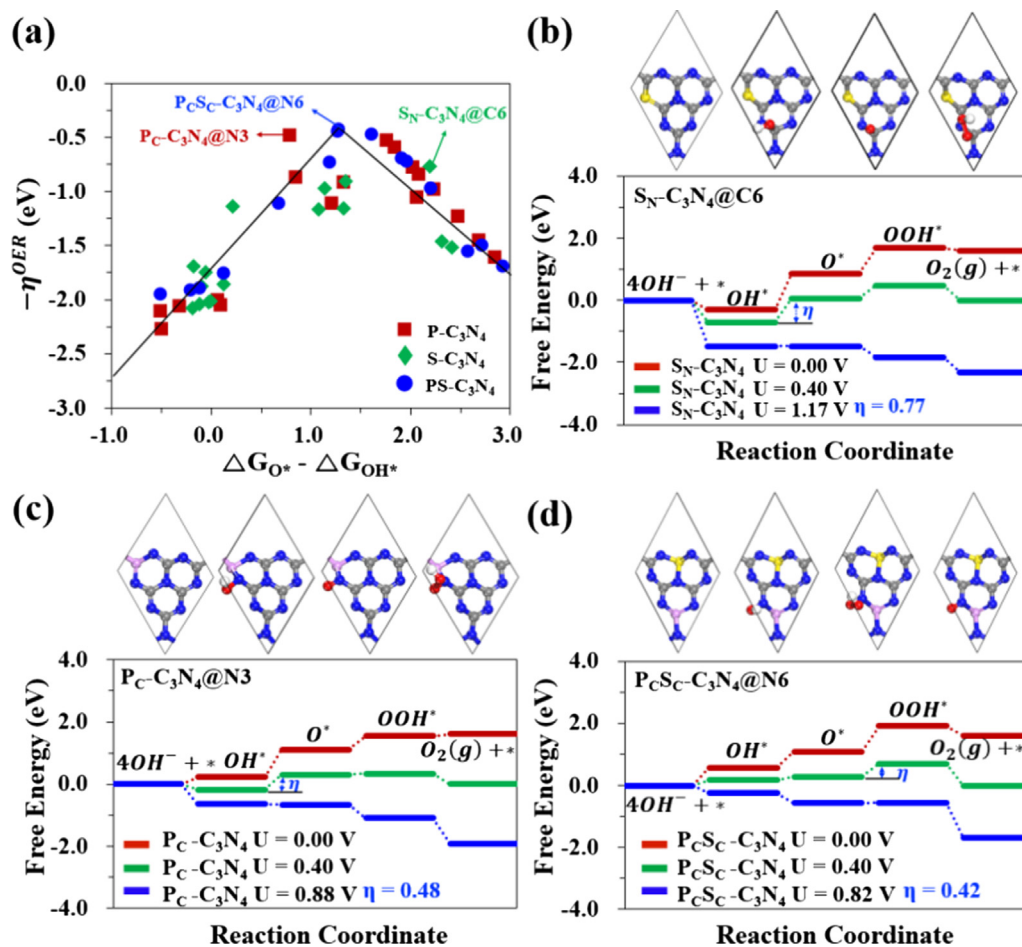
Fig. 10 (a) The volcano plots of OER at all possible active sites on X_Y-C_3N_4. (b)–(d) The free energy diagrams (FEDs) of S_N-C_3N_4, P_C-C_3N_4 and P_CS_C-C_3N_4 structures having the best catalytic activity. (The order of OER activity is P_S-$C_3N_4 > P$-$C_3N_4 > S$-C_3N_4.) Reprinted with permission from Chi et al. (2018) copyright © 2018, American Chemical Society.

(2016) developed a sequential two-step strategy to dope sulfur into carbon nanotube-graphene nanolobes and the strategy introduces stable sulfur-carbon active-sites and enhances catalytic activity of bidoped carbon nanotubes. Moreover, compared the 3D structure of nitrogen and sulfur co-doped graphene/carbon nanotube (NS-GR/CNT) with single N-doped graphene/carbon nanotubes (N-GR/CNT), NS-GR/CNT has more negative onset potential and lower Tafel slope (in Fig. 9), which indicates S doping provides more active site and further significantly improves OER performance (Zhao et al., 2016).

Considering the excellent chemical and thermal stability, graphite C_3N_4 (g-C_3N_4) owing high nitrogen content has attracted much attention. Tian et al. (2015a further demonstrated that g-C_3N_4 nanosheets/graphene composites are synthesized by the integration of ultrathin g-C_3N_4 nanosheets and graphene, which can be used as an efficient OER catalyst with good durability. It is the first demonstration of the use of g-C_3N_4 as a metal-free OER electrocatalyst. In addition, g-C_3N_4 as a good composite material can be doped with P or S, which has shown promising catalytic activities in OER. Recently, P and S co-doped C_3N_4 (P_CS_C-C_3N_4, C_3N_4 with P and S co-doped at the carbon site) shows superior OER/ORR activity due to the synergistic effects between electronic

and geometric factors, which improves electrical conductance by modulating the electronic structure with extra electrons from dopants (in Fig. 10) (Chi et al., 2018).

As mentioned above, carbon-based materials not only provide higher electron conductivity and improve the electrochemical performance of the catalysts compared with metal oxide-based OER catalysts, but also can be mass produced due to lower manufacturing costs. Moreover, such metal-free catalysts can avoid the release of metal ions, thereby reducing the environmental impact.

5. Black phosphorus materials

Recently, black phosphorus as a new 2D material with 2D puckered layer structure, which can be regulated its electroconductivity by adjusting the film thickness. The black phosphorus layers have an anisotropic structure, which is unique among layered materials (Churchill and Jarilloherrero, 2014; Li et al., 2014). In the recent work of Jiang et al. (2016), black phosphorus (BP) prepared by the thermal-vaporization transformation (TVT) method exhibits a highly efficient OER activity with an onset potential of about 1.48 V (vs. RHE) and a current density of 10 mA cm^{-2} at an applied voltage of around 1.6 V. The stability performance of BP grown on carbon
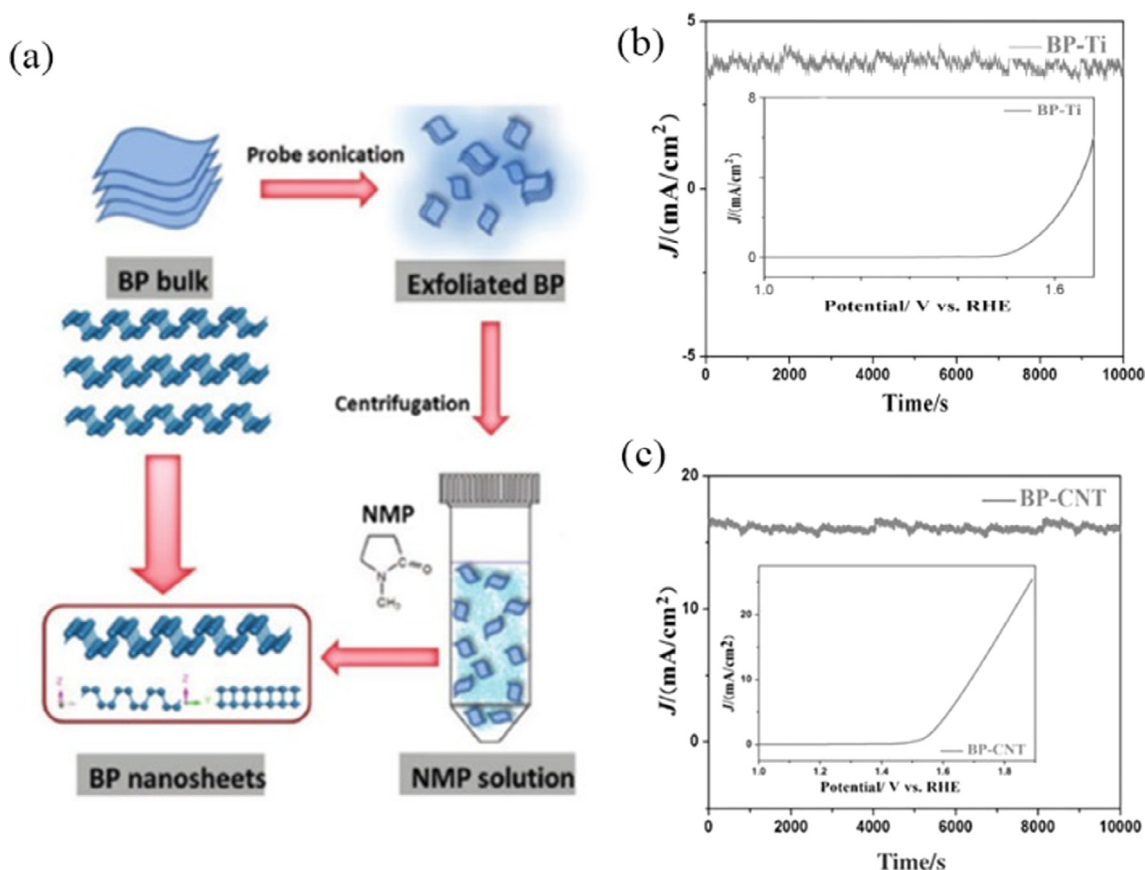
Fig. 11 (a) Schematic illustration of solution-phase exfoliation route to prepare few-layer BP nanosheets. Reprinted with permission from Ren et al. (2017) copyright © 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b and c) Chronoamperometric response at 1.65 V and 1.77 V (E j = 16.5), insert shows polarization curves of BP-Ti and BP-CNT before chronoamperometric response. Reprinted with permission from Jiang et al. (2016) copyright © 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

nanotube network (BP-CNT) is better than that of BP supported on Ti foil (BP-Ti) (as Fig. 11b, c), which is the first time the application of BP in electrocatalysis has been proposed. However, the crystal structure of bulk BP owns little active sites, which leads to the inferior OER catalytic performances, thus few-layer BP nanosheets prepared by facile liquid exfoliation (Fig. 11a) with excellent OER catalytic performance compared with that of bulk BP (Ren et al., 2017). The synergy of few-layered exfoliated black phosphorus (EBP) and N-doped graphene (NG) is fully exploited by interface engineering, which not only improves the stability of EBP, but also effectively boosts their intrinsic activities. EBP@NG as an efficient bifunctional catalysts towards hydrogen evolution and oxygen evolution reactions (HER/OER) achieves significant catalytic performance and an excellent durability (Yuan et al., 2019). At present, there are few studies on BP, it is both an opportunity and a challenge for us to continue to the study based on black phosphorus.

6. Conclusion and outlook

Water electrolysis to hydrogen and fuel cells are two key technologies in the field of hydrogen energy, the development of highly efficient materials to electrocatalyze water splitting plays a crucial role in realizing high energy conversion efficiency. However, the use of rare precious metal catalysts has hindered the smooth development with

these two technologies because of their high price and scarce resources. Therefore, the development of efficient and low-cost non-noble metal catalysts and non-metallic catalysts are become the key problem to solve. For many catalyst materials proposed in the present review have their advantages and disadvantages. For example, the drawback of metal oxide electrocatalysts is the poor electroconductivity. Non-metallic oxide systems with excellent conductivity such as metal chalcogenides and pnictides have been employed and have exhibited excellent activities for both HER and OER, which makes it promise potentials for bifunctional electrocatalysts toward the overall water-splitting reaction. In addition, non-metal compounds and black phosphorus electrocatalysts have demonstrated excellent oxygen evolution catalytic capabilities.

Many researchers initially were very interested in metal-based electrocatalysts, because these metal-based electrocatalysts exhibit excellent electrocatalytic effects and the catalyst is of great practical value based on inexpensive transition metals such as nickel, iron, and cobalt. For such transition metal oxide catalysts, including spinel structures, perovskite structures, and pyrochlore structures, the most widely studied are spinel electrocatalysts. But some literature indicates that there are some problems with such catalysts. For example, the effects of the preparation methods, the doping of excess elements in the spinel material results in structural instability and the poor conductivity of ubiquitous metal oxides. Therefore, it is especially important to find new types of doped oxide electrocatalysts to break the limitations. While, for non-metal oxide systems, such as metal chalcogenides and pnictides, have excellent electrical conductivity and exhibit excellent activity for both HER and OER. This bifunctional electrocatalyst becomes

a potential share of the overall hydrolysis reaction. The catalytic mechanism of this catalyst is that the thin oxide layer formed in situ on the surface is responsible for performing the OER, while the material itself acts as a conductive support. Similarly, designing a non-metallic compounds catalyst requires only a large number of active sites to increase its catalytic activity, which can avoid impurities introduced by metal doping.

In summary, future efforts to design high-activity OER catalysts should pay much attention on the material composition, dynamic structures of the catalysts and purity materials during the synthesis process. Therefore, designing an efficient, stable, economic and environmental electrocatalyst is a urgent challenge to be faced. In this case, the electrocatalyst can be designed with high efficiency by introducing foreign elements, doping conductive materials, and changing the morphology, which can improve its electrocatalytic ability. Most importantly, most works in the design of nonprecious electrocatalysts have focused on developing HER catalysts for acidic conditions. But for OER catalysts, due to their thermodynamic convenience are used for alkaline conditions, which may lead to incompatible integration of the two types of catalysts and resulting in poor overall performance. Thus, in order to develop more mature cathode and anode catalysts with excellent electrocatalytic performance, more and more research on combination of HER and OER catalyst should be done, which will satisfy the need of practical application requirements in the future.

Acknowledgements

Declaration of Competing Interest

The authors declare no conflict of interest.

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