

Recent Progress on Two-dimensional Electrocatalysis

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Abstract Due to their unique electronic and structural properties triggered by high atomic utilization and easy surface modification, two-dimensional(2D) materials have prodigious potential in electrocatalysis for energy conversion technology in recent years. In this review, we discuss the recent progress on two-dimensional nanomaterials for electrocatalysis. Five categories including metals, transition metal compounds, non-metal, metal-organic framework and other emerging 2D nanomaterials are successively introduced. Finally, the challenges and future development directions of 2D materials for electrocatalysis are also prospected. We hope this review may be helpful for guiding the design and application of 2D nanomaterials in energy conversion technologies.

Keywords Two-dimensional material; Electrocatalysis; Electrochemical reaction; Water electrolysis; Fuel cell

1 Introduction

The recent development of society embosses a widespread concern among scientists regarding the environmental impact of traditional fossil fuel combustion(ocean acidification, global warming, sea-level rise, etc.)^[1–3]. The use of renewable and clean energy(water, wind, tidal, solar, etc.) is of great strategic significance to replace traditional fossil fuels. This can not only solve the energy crisis caused by the shortage of fossil fuels but also effectively meet the requirements of sustainable ecology. Electrocatalysis is one of the most effective strategies in the clean energy conversion technology^[4–7], converting intermittently renewable electrical energy into chemicals, usually including hydrogen evolution reaction(HER)^[8,9], carbon dioxide reduction reaction(CRR)^[10], nitrogen reduction reaction(NRR) and oxygen evolution reaction(OER)^[11] in the hybrid water electrolysis^[12], while converting chemical fuels into electric power through formic acid oxidation(FAOR)^[13], and oxygen reduction reaction(ORR) in fuel cells technologies(Fig.1)^[14].

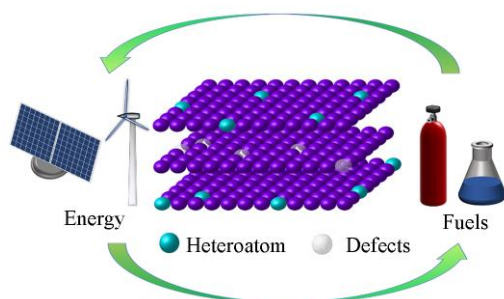


Fig.1 Schematic diagram of 2D electrocatalysis in the interconversion of energy and fuels

Since the kinetics of thermodynamically feasible reactions are very sluggish, these electrochemical reactions often need efficient electrocatalysts to overcome high energy barriers. In addition to these problems, electrocatalysis usually involves a multiple electron transfer process. Most reactions complete with a mixture of products rather than a single product that leads to more complicated separation and purification at the end, therefore suitable catalysts are required for the selective formation of desired products^[15]. Excellent electrocatalysts can usually meet the following requirements at the same time^[3,16]: 1) high catalytic activity, the reaction can be carried out under low over-potential and energy efficiency will be improved; 2) high selectivity: due to the relatively complex catalytic system, many kinds of chemical products are often produced in the electrocatalysis process, and it is of considerable significance to choose a suitable catalyst to catalyze the production of a particular product; 3) good conductivity: the catalytic reactions involve the transfer of multiple electrons, therefore the mobility of electrons will affect the rate of catalytic reaction, and excellent conductivity would improve the rate of catalytic reaction; 4) excellent stability: the durability of catalyst is a key indicator that can promote electrocatalysis to the long-term operation; 5) and the final economic issues: the development of low-cost electrocatalysts is conducive to improve the economic benefits of chemical reactions for large-scale application.

Two-dimensional(2D) materials have abundant active sites due to their inherent characteristics in the high surface area, resulting in excellent conductivity and abundant active sites exposed. Simultaneously, 2D materials also own a

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characteristic that is easy to be modified. Researchers can control the electronic structure, size, and atomic exposed crystal surface of 2D materials by heteroatom doping, chemical modification, and even hybridizing with other nanostructures. Thus, 2D materials have huge application potential in the field of electrocatalysis. Besides, compared to their bulk counterparts, much better catalytic performance could be achieved by diverse design and preparation concepts of 2D nanomaterials. In this review, the recent research progress on 2D materials is reviewed mainly for electrocatalysis in electrochemical energy conversion. Followed the brief introduction of electrocatalytic reaction and 2D nanomaterials, five categories in form of metal, transition metal compounds, non-metal, metal-organic frameworks(MOFs), and other emerging 2D nanomaterials are successively introduced for their specific electrochemical reactions, especially in hybrid water splitting and fuel cells. Finally, we summarize the recent process on 2D nanomaterials for elec-

trocatalysis and some perspectives are also proposed. We hope this work might be helpful for research community in stimulating more interesting and fantastic 2D nanomaterials, in particular, for electrocatalysis in energy technologies.

2 Electrocatalytic Reaction

Catalysis is the chemical reaction carried out under the assistant of catalyst. In chemical reactions, some original chemical bonds of the reactive molecules dissociate and form new chemical bonds, which require a certain activation energy. In some systems, where chemical reactions are difficult to occur, the activation energies are high, which usually need the third substances(catalyst) to rearrange the chemical bonds of the reaction molecules and reduce the activation energy, and thus accelerate the chemical reaction and control the choice of products and stereo regularity[Fig.2(A)].

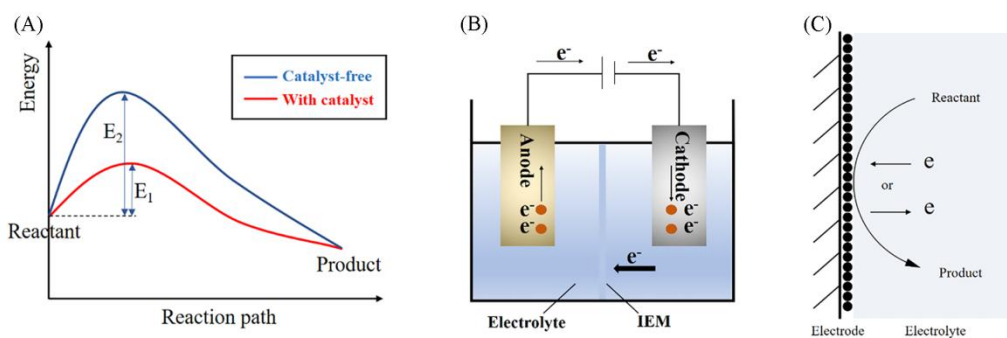
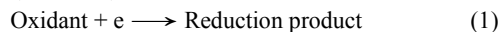


Fig.2 Schematic reaction routes(A), electrolytic cells(B), and reaction process occurring on the electrode surface(C)

Electrocatalytic reaction utilizes electrical energy as the driving force in the electrolytic cell. Since the electrocatalysis reactions usually have high activation energy and complex reaction products, it is necessary to select a suitable catalyst to promote the reaction. As shown in Fig.2(B), in the electrocatalytic reaction, the cathode(anode) reactant obtains(losses) electrons from(to) the electrode and undergoes a reduction reaction(oxidation reaction) to generate the target product [Eqs.(1) and (2)].

Cathode(reduction):



Anode(oxidation):



In the electrocatalytic reactions, current density, overpotential, and Faradaic efficiency(FE) are several important parameters. The overpotential usually represents the size of driving force required for the reaction to proceed. The higher overpotential, the higher energy required for the reaction and the more difficult reaction to be performed. On the contrary, the lower overpotential, the lower energy required to drive the reaction and the easier reaction to get on. Current density is a physical parameter that reflects the rate of electrochemical reaction. The larger current density, the faster reaction. Inversely, the smaller current density, the slower reaction. FE in electrocatalytic reaction is another parameter of reaction efficiency and selectivity. A higher FE means less energy loss during driving, and a lower FE means more energy loss. In summary, improving the current density and FE of the

electrochemical reaction, and reducing the overpotential are beneficial for the electrocatalytic reaction, but these three conditions are often not met at the same time in the electrocatalytic reaction. And the electrocatalysis is a complicated multistep electron transfer occurred at the three-phase of gas-solid-liquid interface[Fig.2(C)], it is thus a development direction to choose a suitable catalyst to increase the current density and the Faradaic efficiency(FE) while reducing the overpotential.

3 2D Nanomaterials

Based on the dimension, the materials could be zero-, one-, two-, and three-dimensional structures. Compared to other dimensional nanomaterials, 2D morphology possesses a long-range order in the plane and a disordered state in its normal direction, which usually exhibit a sheet structure^[17–19]. Since graphene has been reported by a mechanical peeling method, a wave of researches has been set off on 2D materials in the world^[20–22]. Contrary to other dimensional counterparts, 2D materials often have the thickness of single or multiple atoms with interatomic covalent bonds in the plane and the layers are concatenated by van der Waals force. The anisotropy and unique physicochemical properties of 2D materials endow them different diversified properties from bulk materials, which usually show a higher atomic exposure rate, larger specific surface area, excellent mechanical properties and flexible structure^[23,24]. Therefore, 2D counterparts have a promising potential in many fields, such as electrocatalysis^[25,26], photocatalysis^[27], biomedicine^[28], and optoelectronic devices^[29].

Similar to other applications, the unique electronic and structural properties, *e.g.*, rich surface atoms, high active center density, easy surface modification, and large-area volume ratio,

also endow 2D materials the excellent candidates for electrocatalysis^[5,6,23]. A variety of electrocatalytic reactions catalyzed by the 2D materials have achieved excellent results (Table 1)^[30,31].

Table 1 Some typical 2D materials in electrocatalysis

2D material	Composition	FE of product or overpotential or other parameter	Reaction	Ref.
Noble metal	Hexagonal Pd nanosheets	1380 mA/mg at 0.14 V	FAOR	[13]
	Pd nanosheets	94% for CO	CRR	[32]
	PdMo bimetallic/C	>95%	ORR	[25]
Non-noble metal	Ultrathin Bi nanosheets	86% for formate	CRR	[30]
	Triangular-shaped Cu nanosheets	70% for acetate	CRR	[33]
	Ultrathin Ni nanosheet array	94.9% for H ₂	HER	[34]
Transition metal compound	3DGN/CoAl-LDH	252 mV	OER	[35]
	NiFe-LDH/CNT	300 mV	OER	[36]
	MoS ₂ with sulfur vacancy	131 mV	HER	[37]
Nanocarbons	N-Graphene	<i>ca.</i> 200 mV	ORR	[38]
	Boron-doped graphene	10.8% for NH ₃	NRR	[12]
	Polymeric carbon nitride	11.59% for NH ₃	NRR	[39]
MOFs	NiCo-UMOFNs	250 mV	OER	[40]
Single-atoms	Single atom Ni-GO	96.5% for CO	CRR	[41]
	Mo ₂ TiC ₂ T _x -Pt _{SA}	30 mV	HER	[8]

3.1 2D Metallic Materials

3.1.1 Noble Metals

By the Sabatier principle, noble metals are often at the top position of the volcano diagram. In the electrocatalytic reactions, noble metals often have proper combination energy with *H or *OH intermediates and usually exhibit more excellent electrocatalytic performance and stability, they are therefore the hottest choice in the electrocatalysis^[42]. However, noble metals are not conducive to large-scale application because of their scarce reserve and high price. This problem can be solved by preparing precious metals with 2D nanosheet structure to a certain extent. Also, noble metal catalysts are often poisoned by CO and other intermediate species during the electrocatalysis process, which affects their operation stability. Consequently, improving the activity and stability of catalysts for specific electrochemical reactions is of great significance to promote electrochemical energy conversion technologies.

Palladium(Pd) shows excellent potential in electrocatalytic applications due to its unique electronic structure and physicochemical properties, but its high price hinders its application to some extent. Therefore, translating bulk Pd into 2D nanosheets can increase surface area and active sites and significantly improve the atom utilization, which is beneficial for excellent

performance in electrocatalysis. Zheng and coworkers^[13] used CO as a surface sealant to synthesize a hexagonal Pd nanosheet with a thickness of fewer than 10 layers for FAOR [Fig.3(A)], where the achieved catalytic activity was 2.5 times higher than that of commercial Pd black due to the unique structure of 2D Pd nanosheets [Fig.3(B)]. The active site density of Pd catalyst can be further improved by introducing porous structure into 2D nanosheets. Xu and coworkers^[43] prepared a Pd nanosheet with a porous structure by a polymer synergistic approach. Compared with commercial Pd black, Pd porous nanosheets endowed a higher electrochemical active area and active sites density, thereby improved the methanol oxidation and oxygen reduction performance by 2.7 and 5.9 times, respectively, as well as the pronounced stability improvement. Moreover, Pd nanosheets also exhibit excellent activities for CRR process. For example, Gong and coworkers^[32] reported a one-pot method to synthesize an ultrathin Pd nanosheet for CRR [Fig.3(C)]. The FE reached 94% for CO production at the potential of -0.5 V (vs. RHE). The theoretical and experimental results revealed that the high edge exposure ratio of ultrathin Pd nanosheets promoted CO₂ adsorption and CO desorption, and inhibited the HER, which synergistically improved the catalytic performance in the CRR process.

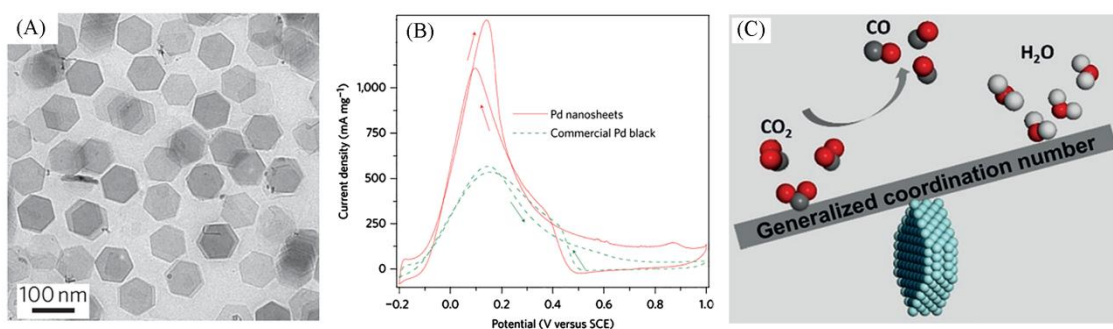


Fig.3 TEM image(A) and electrochemical performance(B) of Pd nanosheets(reproduced with permission from ref.[13], Copyright 2011, Nature Publishing Group) and schematic CRR diagram of ultrathin Pd nanosheet(C)(reproduced with permission from ref.[32], Copyright 2018, Wiley-VCH)

In particular, by constructing multi-metal complexes, the catalytic activity would be improved by the synergistic effect from the different metals. Mueller and coworkers^[44] prepared a Pd-Au bimetallic catalyst. Their density function theory (DFT) calculation results displayed that the 2D bimetallic catalyst has a lower CO₂ activation energy barrier in the CRR than the monometallic Au. Recently, Guo's group^[25] reported the

preparation of PdMo bimetallic nanosheets[Fig.4(A)—(C)]. Compared to commercial Pd/C and Pt/C, the mass activity for ORR reached 16.37 A/mg_{PdMo}, which was increased by 327 and 78 times, respectively[Fig.4(D)]. DFT results illustrated alloying, strain and quantum size effects regulated the internal electronic structure and optimized the oxygen binding of catalyst.

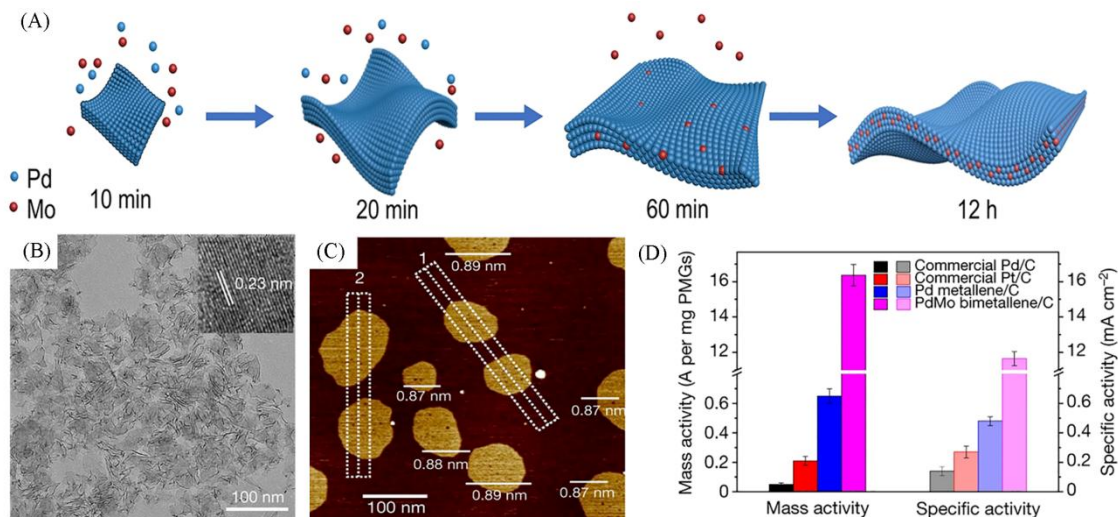


Fig.4 Synthetic scheme(A), TEM images(B), AFM image(C), and electrocatalytic activities of PdMo bimetallic/C(D)

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Besides, the bimetallic nanosheets by alloying or doping the second element will change their microchemical environment by adjusting the surface morphology and lattice structure, and their catalytic properties would be consequently improved compared to their monometallic nanosheets. Chen and coworkers^[45] reported an ultrathin Pt-Pd alloy nanosheet. Compared to Pd black, the electrochemically active area was increased nearly ten fold due to its 2D structure, which contributed to a lower overpotential, higher peak current and CO tolerance in FAOR. Another example showed the carbon-supported Pd₂B with a lamellar structure has an exciting overpotential of *ca.* 15.3 mV at 10 mA/cm² for HER^[46]. DFT results showed that the doping of B could reduce the potential barrier of the reaction and promote the coupling of H-H, making HER more likely to occur. Similarly, Au also has great potential in electrocatalysis^[47,48]. In 2011, Zhang and his colleague^[49] reported the synthesis of hexagonal close-packed(hcp) Au nanosheets with a thickness of only 2.4 nm, which provided a solid foundation for the development of Au in the electrocatalysis field. In addition to Pd and Au in 2D nanosheets structures, Pt, Ag and Ru have also been extensively studied in the 2D form for electrocatalysis^[50–53]. However, these nanosheets are often obtained by galvanic replacement method. Take Pt as the example, Huang and his colleague^[54] used Te substrates to synthesize Pt nanosheets by electrochemical corrosion. After removing Te, Pt nanosheets showed a highly distorted structure. Compared to commercial Pt/C catalyst, the porous Pt nanosheets achieved a current density of 3.1 mA/cm² at a potential of 0.9 V vs. RHE, and also maintained 30000 cycles stability test.

3.1.2 2D Transition Metals

Although precious metals are favored in electrocatalysis, the scarcity and high price will hamper their future development in large-scales application. Transition metals(Co, Ni, Fe, Cu, etc.) have also attracted much attention because of the abundant reserves, low prices and potential electrocatalytic properties in the energy conversion reactions^[11,55].

Generally, adjusting the surface or electronic structure of transition metals could enhance their electrochemical performance. Sun and coworkers^[34] prepared an ultrathin Ni nanosheets array(Ni-NSAs) by *in-situ* topology reduction method [Fig.5(A) and(B)]. This Ni nanosheets showed an incredible HER performance than Pt/C, which was mainly resulted from its abundant surface-active atoms and large electrochemically active area[Fig.5(C)]. Moreover, bismuth(Bi) with unique physical and chemical properties exhibits potential selectivity in the CRR for formic acid generation, and its active site density could be further improved by translating the bulk Bi into the 2D structure. Using the liquid-phase stripping method, Jin and coworkers^[30] obtained the ultrathin Bi nanosheets material [Fig.5(D)]. These Bi nanosheets could reach an FE of 86% and a current density of 16.5 mA/cm² at -1.1 V vs. RHE for the formate generation, which was far superior to the commercialized bulk Bi. DFT indicated a lower Gibbs free energy of *COOH intermediate at the active edge sites of 2D nanosheets was the critical factor for the enhanced catalytic activity.

In addition, introducing the porosity on the catalyst surface is another effective strategy for increasing the catalytic activity. Our group^[10] reported the ultrathin porous Cu nanosheets by a simple replacement method[Fig.6(A) and (B)].

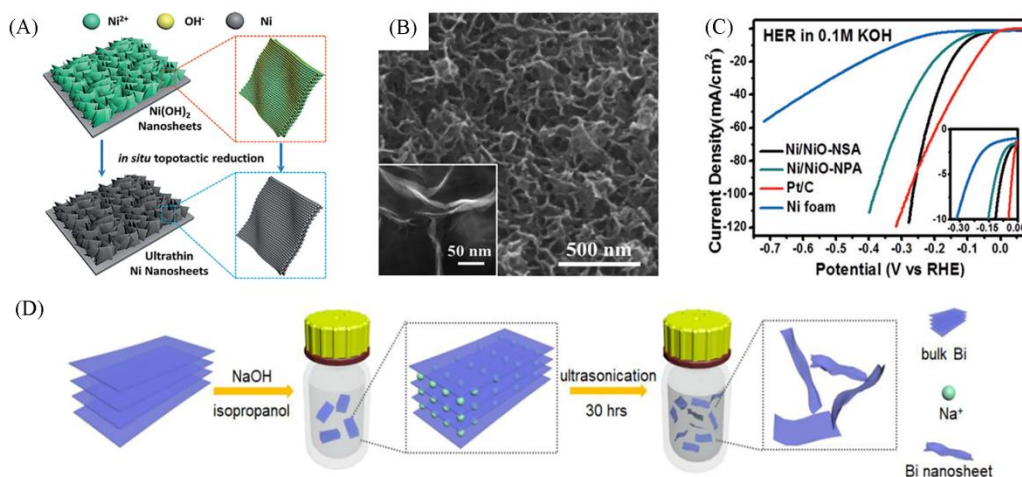


Fig.5 Synthetic process(A), SEM images(B), and HER performance of layered Ni nanosheet array(C) (reproduced with permission from ref.[34], Copyright 2016, Wiley-VCH) and synthetic process of ultrathin Bi nanosheets(D)(reproduced with permission from ref.[30], Copyright 2018, Elsevier)

This porous Cu nanosheet assembly could achieve an FE of 74.1% and a current density of 23.0 mA/cm² at -1.0 V vs. RHE for the CO generation[Fig.6(C)]. DFT studies revealed that the defects of porous Cu nanosheets were beneficial for accelerating the formation of CO intermediate, which led to an enhanced efficiency in the CRR.

Electrocatalytic reactions are often accompanied by several side reactions, which obstructs the selective generation of desirable products. 2D nanomaterials have the intrinsic advantages in adjusting the exposed crystal surface, which is effective to improve the selectivity of catalysts^[56,57]. For example, Kang and coworkers^[33] tuned the synthesis of triangular Cu nanosheets with specific crystal planes exposed. These triangular Cu nanosheets could selectively convert CO to acetate with an FE of 48% and a partial current density of 131 mA/cm². DFT investigations displayed that this phenomenon was related to the decreased Cu(100) and Cu(110), and the increased

Cu(111) crystal planes, which could suppress the formation of methane and ethylene, resulting in the selectivity improvement of acetate. Another work by Wang and coworkers^[58] demonstrated the preferentially controlled preparation of the exposed Cu(100) crystal plane, which significantly enhanced the catalytic activity and selectivity towards ethylene production, and the FE of ethylene reached 60% with a current density of 144 mA/cm².

In short, metal catalysts have received much attentions in the electrocatalysis because of their intrinsic active centers and good conductivity. The bulk structure could not be an excellent candidate due to the disadvantages of low atom utilization and poor intrinsic activity. These studies have shown that constructing 2D nanosheets structure from bulk catalysts or introducing porosity and defects on the catalyst surface is beneficial for increasing the active sites density and atom utilization, and achieve the enhanced catalytic activity.

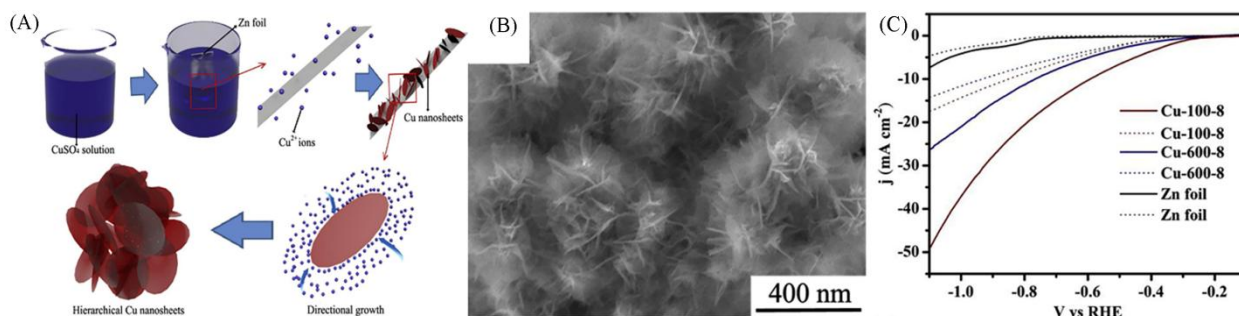


Fig.6 Schematic preparation(A), SEM image(B), and electroactivity curves of Cu nanosheet(dashed line-Ar and solid line-CO₂)(C)

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3.2 2D Transition Metal Compounds

Many studies have shown that the combination of non-metallic atoms with metal could obviously increase the intrinsic activity, and even be comparable to the precious metal catalysts. These catalysts usually include transition metal dichalcogenide/nitride/phosphide/carbide(TMD/TMN/TMP/TMC), and their transition metal hydroxides^[15].

Among them, transition metal hydroxides in the form of layered structure are considered as one of the ideal electrocatalysts due to their tunable compositions and structure. However, the superposition between layered double hydroxide(LDH) leads to the concealment of active sites and poor conductivity^[59]. Therefore, the catalyst morphology, interface, local environment, and composition of LDH materials are always considered in the synthesis^[59,60]. A good example is that the hybridization

of Ni-Fe LDH nanosheets with carbon nanotube(CNT) showed a higher OER activity and stability than commercial Ir-based catalysts^[36]. As mentioned above, due to the severe problems with superposition between multi-layers structures, design and synthesis of a single-layer structure is effective to maximize the utilization of active sites. Hu and coworkers^[61] reported a single-layer NiCo LDH material, which had a comparable electrochemical activity with the commercial IrO₂ in the aspect of water electrolysis. However, single-layer material is prone to agglomerate and inactivate even though their active sites are abundant. Therefore, employing substrates to support or separate the LDH materials would be more efficient to promote electrochemical reactions. For example, Zhang and coworkers^[35] reported the formation of CoAl LDH on the 3D graphene substrates[Fig.7(A)]. The *in-situ* formed 3D LDH/graphene hybrid(3DGN/CoAl-LDH) showed a significantly improved activity and stability, which could be an excellent electrocatalytic LDH material for OER process.

In addition, the introduction of defects into LDH materials is also effective to further increase the active sites. Wang and coworkers^[60] used nitrogen plasma to treat CoFe-LDHs and obtained a defect-rich OER catalyst. Compared with bulk counterpart, the plasma-treated CoFe-LDHs showed the modified adsorption and desorption of intermediates due to the existence of defects(oxygen vacancies) in material, which was conducive for improving catalytic capability. Besides that, the incorporation of noble metal with LDH would further change the local microenvironment of active sites. For example, Yang and coworkers^[62] reported the incorporation of Ru or Ir with Ni-V LDH. Their theoretical and experimental studies confirmed that the precious metals integrated in LDH would

change the local coordination environment of Ni and V, thus reduced the energy barrier of both the Volmer and Heyrovsky steps in HER and accelerated every step of OER, which in turn improved the bifunctional activity of HER and OER in overall water splitting.

Similarly, TMD materials have also attracted wide attention in electrocatalysis. Take MoS₂ as the representative example, which is often used in catalyzing HER. However, its limited intrinsic activity and poor conductivity limit the further development to some extent^[63–65]. Typically, heteroatoms doping, defects introduction, surface modifications, phase engineering, and conductive substrate hybridization are often developed to improve the activity of layered MoS₂. For example, Xie and coworkers^[66] used excessive thiourea to control the growth of incomplete crystal and obtained defect-rich MoS₂ nanosheets[Fig.7(B) and (C)]. Since the MoS₂ nanosheet with defect-rich showed a higher density of active sites than the normal one, its overpotential of HER was only 120 mV, and the current density could reach 13 mA/cm²[Fig.7(D)]. Moreover, the anions and cations doping methods were also employed to tune the electronic structure of MoS₂^[67]. By introducing sulfur vacancies in the 2D MoS₂ structure, the modified MoS₂ catalyst showed a considerable electrocatalytic activity with a Tafel slope of 48 mV/dec, and an overpotential 131 mV at 10 mA/cm² for HER[Fig.7(E)]. Experimental and simulation results revealed that the single S-vacancies in the 2D MoS₂ nanosheets caused hydrogen to be more easily adsorbed on the catalyst surface^[37].

Moreover, many pieces of researches about metal oxides, borides, phosphides materials and MXene have been studied in electrocatalysis^[15,68]. Their catalytic performance can also be

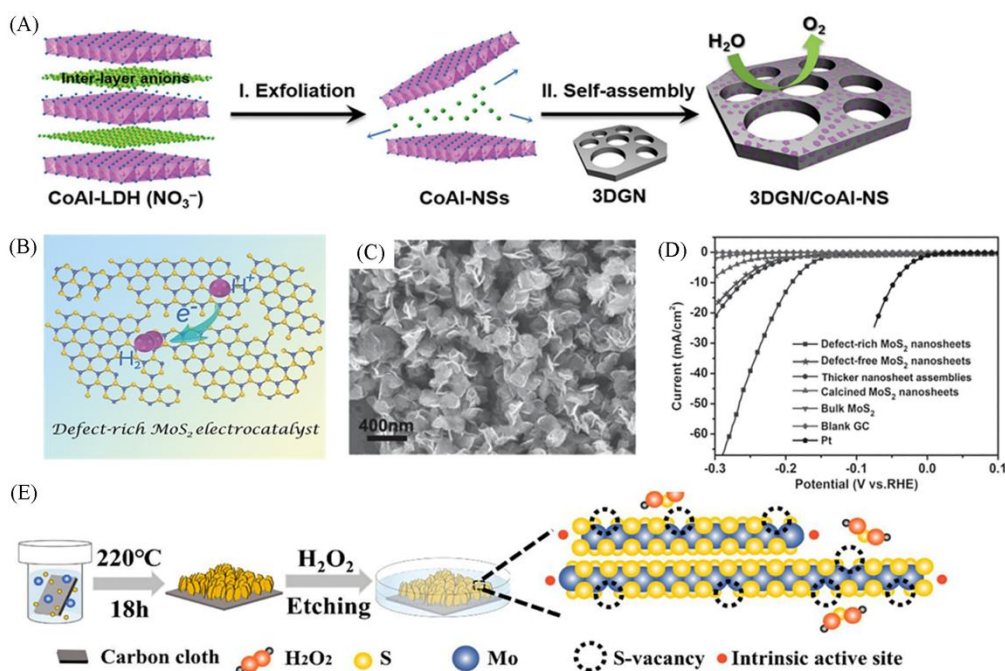


Fig.7 Synthetic process of 3DGN/CoAl-LDH(A)(reproduced with permission from ref.[35], Copyright 2016, Wiley-VCH), schematic diagram(B), SEM image(C), HER curves of defect-rich MoS₂ electrocatalyst(D)(reproduced with permission from ref.[66], Copyright 2013, Wiley-VCH) and synthetic process of MoS₂ with S-vacancies(E)(reproduced with permission, from ref.[37], Copyright 2020, American Chemical Society)

improved by doping element, modifying the surface or coupling other active materials^[31]. Our group^[69] prepared a dual functional catalyst(Co-Ni PBAs) with a nanosheet structure derived from the reduced Prussian blue. Co-Ni PBAs showed overpotentials of 140 and 300 mV for HER and OER at 10 mA/cm² due to the enhanced conductivity and distinct structure caused by the interaction of metal and boron component.

3.3 2D Non-metal Materials

Graphene is a representative 2D non-metallic material with a large potential for electrocatalytic applications^[70]. However, the perfect graphene itself is electrocatalytically inert. Moreover, graphene could be easily restacked due to the strong van der Waals force between the layers. Modifications, usually including doping heteroatoms^[71–73], and introducing defects^[74], are necessary to change its electronic structure for improving electrocatalytic activity. Dai and coworkers^[38] used chemical vapor deposition in the presence of ammonia to realize N doping into the graphene[Fig.8(A) and (B)]. The N-doped graphene showed a catalytic ORR performance with a steady-state catalytic current three times higher than that of Pt/C[Fig.8(C)]. In addition to N and P atoms, B atoms are also commonly doped into graphene to improve the electrocatalytic activity due to their electron-deficient properties. Narayanan and coworkers^[75] obtained the B-doped graphene by annealing at

1400 °C, and its ORR current density could reach 16.32 mA/cm² at –0.6 V vs. RHE. Furthermore, bi- even triple-atoms doping, such as N and P dual-doping is also developed to activate the adjacent carbon atoms for increasing HER activity^[76]. Apart from the atoms doping, the introduction of defects into graphene is also effective to enhance electrocatalytic performance. Yao and coworkers^[77] reported the selective removal of N atoms through controllable annealing to form N-defective graphene[Fig.8(D)], which showed a tri-functional catalytic activity for HER, OER and ORR[Fig.8(E)]. DFT and simulation results showed that the defects in catalysts made the reaction energy barrier lower and a suitable intermediate binding energy, thus promoted the entire catalytic reaction process.

A lot of non-metallic 2D materials other than graphene have also been extensively studied in electrocatalysis for NRR. Sun *et al.*^[78] reported a boron carbide nanosheet for NRR, and the FE of ammonia reached 15.95% and the production rate of ammonia reached 26.57 μg·h⁻¹·mg⁻¹_{cat} at –0.7 V vs. RHE. Further introduction of N-defects would improve the NRR activity of carbon nitride polymer(PCN), an ammonia yield of 8.09 μg·h⁻¹·mg⁻¹_{cat} and FE of 11.59% were achieved at a much lower potential of –0.2 V vs. RHE^[39]. The simulation results demonstrated that the N-defects in 2D PCN make N₂ adsorption easier. Moreover, B-doped graphene nanosheets(BG-1) prepared by the pyrolysis method also demonstrated promising

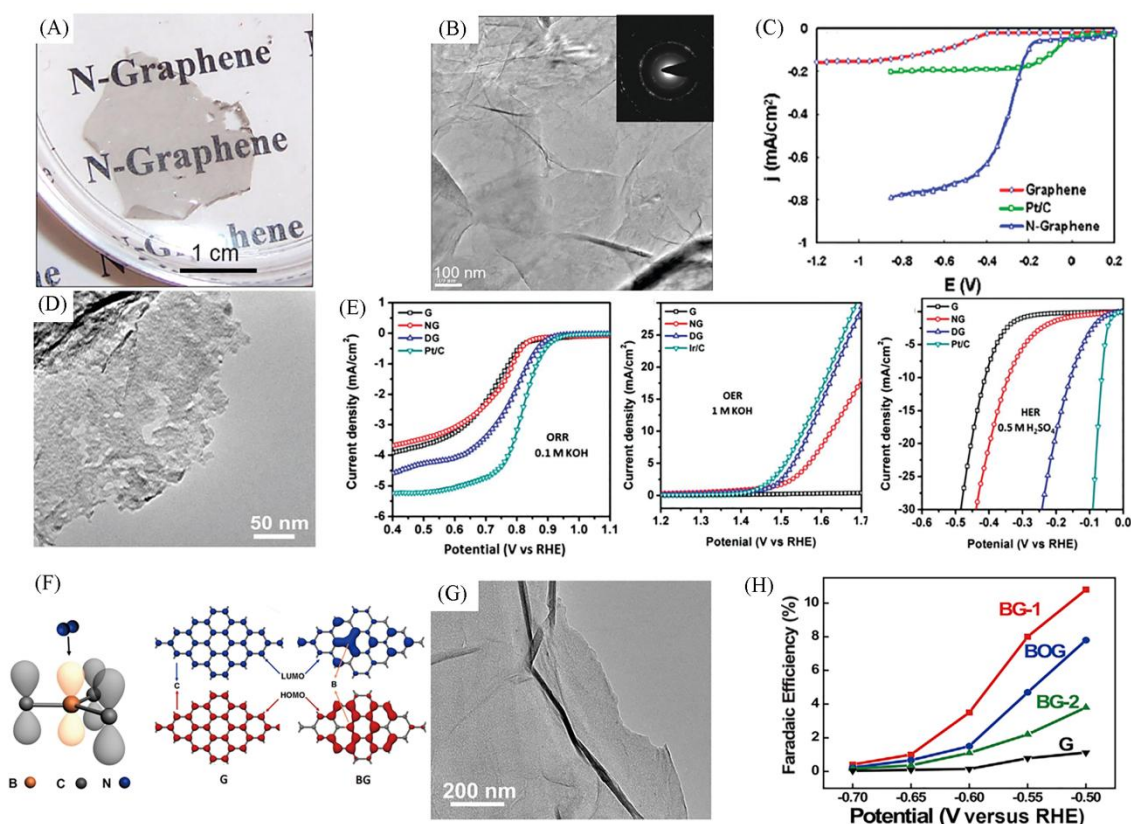


Fig.8 Photograph image(A), TEM analyses(B), and polarization curves of N-doped graphene(C)(reproduced with permission from ref.[38], Copyright 2010, American Chemical Society), TEM image(D), and polarization curves of defective graphene for ORR, OER, and HER(from left to right)(E)(reproduced with permission from ref.[77], Copyright 2016, Wiley-VCH), schematic atomic orbital of BC₃ for binding N₂(F), TEM image(G), and ammonia FE values of different BG catalysts at various potentials(H)(reproduced with permission from ref.[12], Copyright 2018, Elsevier)

activity in the NRR[Fig.8(F) and (G)]^[12]. The introduction of B atom inhibited the competitive HER by-reaction, which is favorable to improve the FE of 10.8% for the ammonia production at -0.5 V vs. RHE[Fig.8(H)].

3.4 2D Materials Incorporated Single-atom Catalysts

In recent years, single-atom catalysts(SACs) have enormous potential in the field of electrocatalysis due to their ultra-high atom utilization rate and unique electronic structure. However, due to the high surface energy of single atoms, the SACs are extremely unstable and quickly accumulate, and thus lose high activity. To this end, 2D matrix is an excellent choice to load single atoms for maintaining its single-atom state. Consequently, several 2D nanomaterials including graphene^[79,80], MoS₂^[81,82], and MXene^[83] are employed to support single-atom for electrocatalysis.

Graphene is an excellent monoatomic catalyst host due to its large plane and superior conductivity. Liu and coworkers^[41] reported the loading of Ni monoatomic onto graphene oxide for CRR catalyst. The FE of CO production at a potential of -0.63 V reached 96.5%, and the TOF value was 325.9 h⁻¹. Following the N-doping treating, single Ni atoms supported on N-doped

graphene showed an increased activity in CRR for CO generation^[84]. The TOF value of the catalyst in CO₂ reduction reached 14800 h⁻¹ and the FE of CO reached 97% at a potential of -0.61 V. Apart from that, this catalyst showed an excellent stability, it can still maintain 98% of the initial activity after 100 h at a current density of 22 mA/cm².

This economical strategy in single atomic state is also suitable for preparing precious metals catalysts. Li and coworkers^[8] reported an MXene-loaded Pt atomic catalyst (Mo₂TiC₂T_x-Pt_{SA}) with a high electrochemical activity in the HER[Fig.9(A)]. The overpotentials of this catalyst at the current densities of 10 and 100 mA/cm² were only 30 and 77 mV, and its mass activity was 40 times that of Pt/C [Fig.9(B)]. DFT calculation proved the incorporation of Pt single atoms on MXene, optimizing its surface electronic environment and improving its electron transfer rate[Fig.9(C)]. Besides, the dominance of *d*-electrons near the Fermi level was also enhanced, leading to an improved performance. Besides, MoS₂ with a 2D nano-sheet structure are also potential carriers for single atoms, such as Ni and Co atoms^[85]. The modification of Ni atoms enhanced the adsorption of H on the surface of MoS₂, thus the efficiency of HER would be improved^[82].

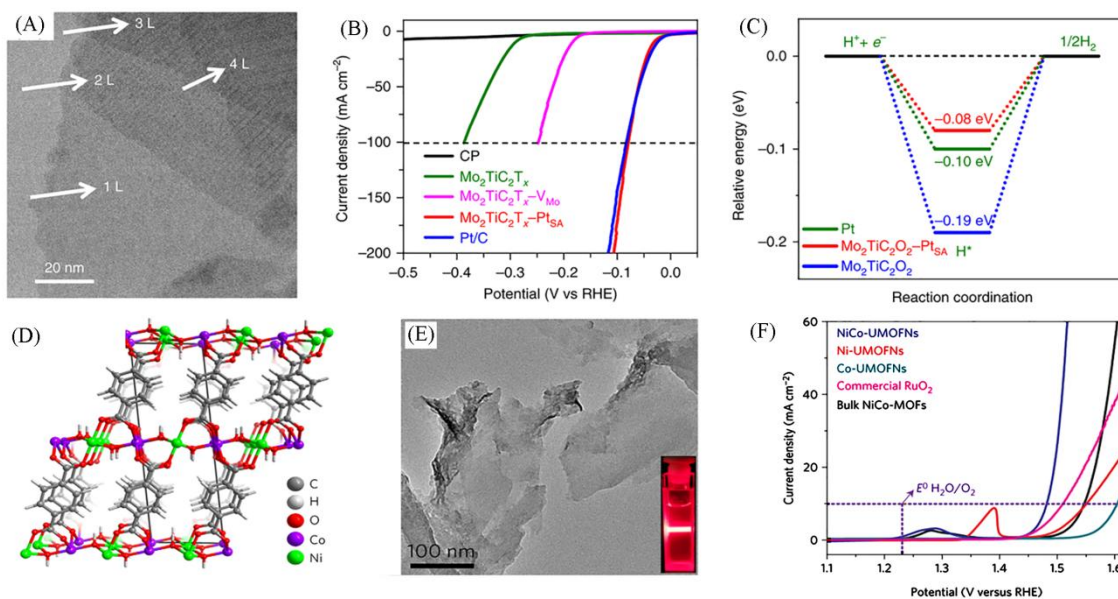


Fig.9 TEM image of Mo₂TiC₂T_x-Pt_{SA}(A), HER performance comparison of different catalysts in 0.5 mol/L H₂SO₄(B), calculated free energy of HER at the equilibrium potential for various samples(C) (reproduced with permission from ref.[8], Copyright 2018, Nature Publishing Group), crystal structure(D), TEM image and Tyndall light scattering(inset)(E), OER curves of different samples(F)(reproduced with permission from ref.[40], Copyright 2016, Nature Publishing Group)

3.5 MOFs Nanosheets

MOFs are a kind of organic-inorganic hybrid material composed of metal center and organic ligand coordination. Due to their high porosity, large specific surface area, and flexible structure, electrocatalytic applications of MOFs have been broadly studied in recent years^[86–90]. However, the disadvantages of the poor conductivity of MOFs material and the blocking of active center by organic ligands have greatly

affected its catalytic activity. Studies show that converting 3D MOF structure to 2D nanosheets is effective to realize high atomic exposure while improving the electron transportability^[40,91]. Besides, the types of metal centers, ligand, and the connection method of metal center and ligand will also have a major impact on the electrocatalytic property of MOFs^[92,93].

The natural advantages in bridging homogenous and heterogeneous catalyst of MOFs provide excellent opportunities to understand the catalytic active site and reaction mechanism.

For example, Li and coworkers^[88] reported a Zn MOF constructed by Zn²⁺ nodes and 2-methylimidazole reached a 71.9% FE of CO at 10.48 mA/cm² under the potential of -0.89 V vs. RHE. Similarly, a cobalt-based MOF catalyst was prepared using phthalocyanine, which was able to convert CO₂ into CO efficiently (close to 100%)^[94]. Theoretical calculation showed the CO-N₄ had appropriate CO* binding energy and low COOH* Gibbs free energy. Compared with single metal MOF, the synergistic effect between different metals in bimetal MOF can significantly enhance the electrocatalytic activity^[95]. Huang and coworkers^[96] found the catalytic performance of bimetallic Ni-Fe MOF was much higher than those of single-metal MOF (Ni-MOF and Fe-MOF), the OER over the bimetallic Ni-Fe MOF can be stable for more than 20 h with a current density of 10 mA/cm² at an overpotential of 221 mV. Compared to mono-metal MOF, bimetallic Ni-Fe MOF has a higher intrinsic activity and a lower charge transfer impedance. Another MIL-53(FeNi) on nickel foam also exhibited a current density of 50 mA/cm² at the overpotential of 233 mV^[97]. The calculation results showed that Fe atoms in the catalyst increased the electrochemically active area and improved the electron transfer rate. Additionally, adjusting the electronic structure of the surface metal by unsaturated coordination metal sites has been gradually investigated for the electrochemical reaction and got an excellent result^[40,98]. Tang and coworkers^[40] reported a bimetallic MOFs nanosheet (NiCo-UMOFNs) for OER with an overpotential of only 189 mV at the current density of 10 mA/cm² with an FE reaching 99.3% [Fig.9(D)—(F)]. DFT calculation results showed that the metal unsaturated coordination centers in the bimetallic MOF sheets are the active sites, and the unsaturated metal coordination increased the density of catalytic active centers, thereby its OER performance was improved. Besides, Zhu and coworkers^[99] synthesized an ultrathin 2D FeCo-MNS nanosheet with a large number of unsaturated metal coordination sites by a surfactant-free oxide template method (2dOSA). The overpotential of only 298 mV at a current density of 10 mA/cm² was achieved when FeCo-MNS was used as an anodic electrocatalyst for OER. Both the performance and the stability were superior to that of the combination of RuO₂ and Pt/C when combined with Pt/C for electrocatalytic water splitting. DFT calculations suggested that the unsaturated metal coordination sites were suitable for binding OH* intermediates over FeCo-MNS-1.0, which subsequently promoted OER. Similarly, a catalyst containing unsaturated Ni-N coordination sites was prepared for CRR^[100]. The catalyst can efficiently convert CO₂ to CO with an FE of 92% between -0.53 V and -1.03 V. DFT calculation and characterization results showed that the Ni-N unsaturated coordination sites in the catalyst promoted the conversion of CO₂.

4 Conclusions and Perspectives

As an effective strategy for interconversion of renewable energy and value-added fuels, electrocatalysis can not only effectively alleviate energy problems but also solve environmental issues raised by the combustion of fossil fuels. 2D materials have experienced extensive research in electrocatalysis

on account of their unique electronic structure and physicochemical properties. In this review, a variety of 2D materials including metals, non-metals, transition metal compounds, emerging MOFs and other new 2D materials are briefly introduced for electrocatalysis application in energy conversion related electrochemical reactions. Typically, introducing defects, doping heteroatoms, even making porous structure and hybridizing with conductive component in the 2D nanomaterials can significantly aggrandize the density of active sites or enhance their intrinsic activity.

Although significant progresses have been achieved on 2D materials for electrocatalysis, there are still many problems and enormous research gaps. (1) Based on the popular theoretical predication and machine learning, exploring and developing novel 2D materials for more than electrocatalysis would bring new interesting properties and application in the material genomes family. (2) The activity and selectivity of electrocatalysts are not high enough at present, and preparing efficient catalysts with powerful activity and durability for specific electrochemical reactions is the most important yet tremendous challenge for selectively converting fuels and energy. 2D materials naturally exhibit advantages in specific crystal facets, which is wonderful for some facet-dependent reaction and achieves selective reaction. Thus, optimizing and maxing these advantages are subsequently attractive in experimental and theoretical investigations. For example, we can use the confinement method to prepare the electrocatalysis of exposed Cu(111) crystal plane for carbon dioxide reduction. (3) The preparation of almost 2D materials is still at the laboratory level. How to prepare suitable electrocatalytic 2D materials in large-scale is a very important direction, which determine their practical application in the future energy conversion technologies. For examples, salt-template method and stripping method are reported to achieve the large-scale fabrication of 2D nanomaterials in recent years. (4) Developing new technique and equipment can help further understand their electrochemical evolution of these novel 2D nano-catalysts. For examples, some MOF or LDH materials will suffer from the oxidation and phase transformation during the electrochemical oxidation. Especially, the *in-situ* investigations can combine with theoretical calculations to understand the electrochemical reaction process in deep. Thus, these observations not only reveal their real active sites but also promote subsequent design of more efficient and active catalysts. (5) Develop new fields of electrocatalysis, such as the use of 2D materials to treat wastewater or deep electrocatalysis to obtain high value-added chemical products, which can protect the environment on the one hand and save energy on the other hand.

Finally, 2D nanomaterials have demonstrated great potential in the efficient electrocatalysis for interconversion of fuels and energy. Some crucial challenges are still in the 2D nanomaterials, but we believe 2D electrocatalysts will lead to a brighter future for renewable energy and environmental technologies with the continuous efforts of research community.

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