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Multiscale Principles To Boost Reactivity in Gas-Involving Energy Electrocatalysis

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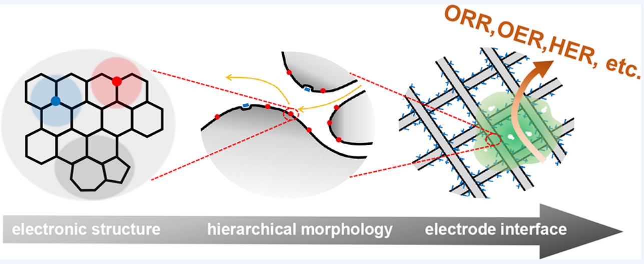

CONSPECTUS: Various gas-involving energy electrocatalysis, including oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER), has witnessed increasing concerns recently for the sake of clean, renewable, and efficient energy technologies. However, these heterogeneous reactions exhibit sluggish kinetics due to multistep electron transfer and only occur at triple-phase boundary regions. Up to now, tremendous attention has been attracted to develop cost-effective and high-performance electrocatalysts to boost the electrocatalytic activities as promising alternatives to noble metal counterparts. In addition to the prolific achievements in materials science, the advances in interface chemistry are also very critical in consideration of the complex phenomena proceeded at triple-phase boundary regions, such as mass diffusion, electron transfer, and surface reaction. Therefore, insightful principles and effective strategies for a comprehensive optimization, ranging from active sites to electrochemical interface, are necessary to fully enhance the electrocatalytic performance aiming at practical device applications.

In this Account, we give an overview of our recent attempts toward efficient gas-involving electrocatalysis with multiscale principles from the respect of electronic structure, hierarchical morphology, and electrode interface step by step. It is widely accepted that the intrinsic activity of individual active sites is directly influenced by their electronic structure. Heteroatom doping and topological defects are demonstrated to be the most effective strategies for metal-free nanocarbon materials, while the cationic (e.g., Ni, Fe, Co, Sn) and anionic (e.g., O, S, OH) regulation is revealed to be a promising method for transition metal compounds, to alter the electronic structure and generate high activity. Additionally, the apparent activity of the whole electrocatalyst is significantly impacted by its hierarchical morphology. The active sites of nanocarbon materials are expected to be enriched on the surface for a full exposure and utilization; the hybridization of other active components with nanocarbon materials should achieve a uniform dispersion in nanoscale and a strongly coupled interface, thereby ensuring the electron transfer and boosting the activity. Furthermore, steady and favorable electrochemical interfaces are strongly anticipated in working electrodes for optimal reaction conditions. The powdery electrocatalysts are suggested to be constructed into self-supported electrodes for more efficient and stable catalysis integrally, while the local microenvironment can be versatilely modified by ionic liquids with more beneficial gas solubility and hydrophobicity.

Collectively, with the all-round regulation of the electronic structure, hierarchical morphology, and electrode interface, the electrocatalytic performances are demonstrated to be comprehensively facilitated. Such multiscale principles stemmed from the in-depth insights on the structure−activity relationship and heterogeneous reaction characteristics will no doubt pave the way for the future development of gas-involving energy electrocatalysis, and also afford constructive inspirations in a broad range of research including CO_2 reduction reaction, hydrogen peroxide production, nitrogen reduction reaction, and other important electrocatalytic activation of small molecules.

1. INTRODUCTION

Developing sustainable energy conversion and storage technologies is one of the most important issues confronted in the modern society, concerning the global energy security, environment degradation, and daily consumption. After decades of research, electrochemistry has provided a versatile and ideal solution. We can utilize the electrical energy generated from renewable resources (e.g., water, solar, wind, tide, and geothermy) to produce carbon-free fuels via electrocatalytic water splitting,[1] and then locally convert chemical into electrical energy using fuel cells[2] and metal-air batteries[3] upon demand. However, the energy efficiency and practical application of these technologies are remarkably limited by some imperative gas-involving energy electrocatalysis, including oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER), due to the sluggish kinetics and large overpotential, which trigger tremendous efforts to boost their reactivity.

Generally speaking, gas-involving electrocatalysis occurs only at the interface of solid electrocatalyst, liquid electrolyte, and gaseous reactants/products, where electron and ion/molecule

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can contact at catalytic active sites, so-called triple-phase boundary regions. In this framework, several critical steps are sequentially coupled with each other and significantly affect the overall reactivity as schematized in Figure 1: (1) mass diffusion in the electrolyte toward and from the electrochemical surface; (2) electron transfer from the conducting support to active sites and then redox intermediates; and (3) surface reaction involving the adsorption of reactants, interfacial charge transfer, and the desorption of intermediates/products at active centers. Judiciously engineering the existing electrocatalysts or developing novel candidates has attracted enormous attention to improve the electrocatalytic performance.[4−6] The intrinsic catalytic activity of an electrocatalyst is always determined by the adsorption or desorption of some crucial intermediates, with a volcano-shaped plot correlating the activity and surface adsorbing property.[7] It has been widely recognized that the physicochemical properties, especially the electronic structure of a solid catalyst, can directly influence its surface adsorption behavior for favorable active sites. Nevertheless, it is notable that, with the evolution of electrocatalysts from noble metals to transition metal compounds, metal-free nanocarbon, and their hybrids, the typical electrochemical interface is also altered.[8] Because some metal compounds are poorly conductive, it is crucial to optimize their nanostructure and interface with conducting supports for a smooth electron transfer pathway and full accessibility of active sites.[9] Furthermore, the mass transport and diffusion issue should also be taken into account,[10] yet relatively neglected, to achieve optimal reaction conditions in the triple-phase boundary regions. The interface concentrations of reactants and intermediates, in addition to the bulk concentrations, are supposed to determine the reaction rates. Accordingly, the overall reactivity in gas-involving electrocatalysis will benefit from the multiscale optimization of these factors governing the mass diffusion, electron transfer, and surface reaction.

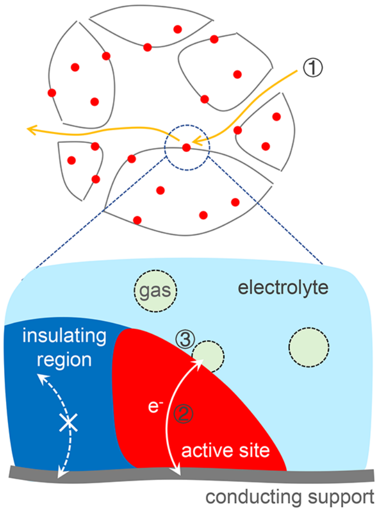

Figure 1. Schematic representation of the gas-involving electrocatalysis. Three critical steps are coupled with each other, including (1) mass diffusion, (2) electron transfer, and (3) surface reaction.

Based on the in-depth understanding of heterogeneous electrochemistry characteristics and universal structure−activity relationships, we have established multiscale principles to boost reactivity in a series of gas-involving energy electrocatalysis during the past few years. In this Account, we will give an overview of our promising practices under these multiscale principles, which are correspondingly divided into three branches: (1) regulation of the intrinsic electronic structure for accelerated surface reaction; (2) tailor of the extrinsic hierarchical morphology to ensure high utilization efficiency and smooth electron transfer; and (3) engineering of the working electrode interface with favorable mass diffusion and interface conditions.

2. REGULATION OF THE INTRINSIC ELECTRONIC STRUCTURE

2.1. Nitrogen Doping in Metal-Free Nanocarbon

The catalytic activity of metal-free nanocarbon materials is revealed to be derived from the electroneutrality break and charge/spin redistribution in sp^2 conjugated carbon matrix after the incorporation of heteroatoms (e.g., N, S, B, P, and multiheteroatoms).[11] In particular, nitrogen doping is the most promising strategy to regulate the intrinsic electronic structure of nanocarbon materials, thereby leading to remarkable reactivity for ORR or OER.[12] With a smart design of the nanostructure, a novel N-doped graphene/single-walled carbon nanotube hybrid (NGSH) was reported to exhibit excellent bifunctional activity for both ORR and OER pioneeringly.[13] The NGSH not only provided an intrinsic dispersion of graphene and carbon nanotubes (CNTs) without aggregation or stacking (Figure 2a,b), but also ensured the full dispersion of nitrogen dopants within a highly conductive scaffold (Figure 2c). Thus, the electrocatalytic activity was significantly superior to two constituent components and the undoped counterpart (GSH) in spite of a relatively low nitrogen content (0.53 atom %) (Figure 2d,e). In addition to the enhancement of activity, the appropriate nitrogen doping can also improve the selectivity. The thermally reduced graphene oxide with a large oxygen content (10.3 atom %) preferentially reduced oxygen to hydrogen peroxide through a two-electron pathway in acid,

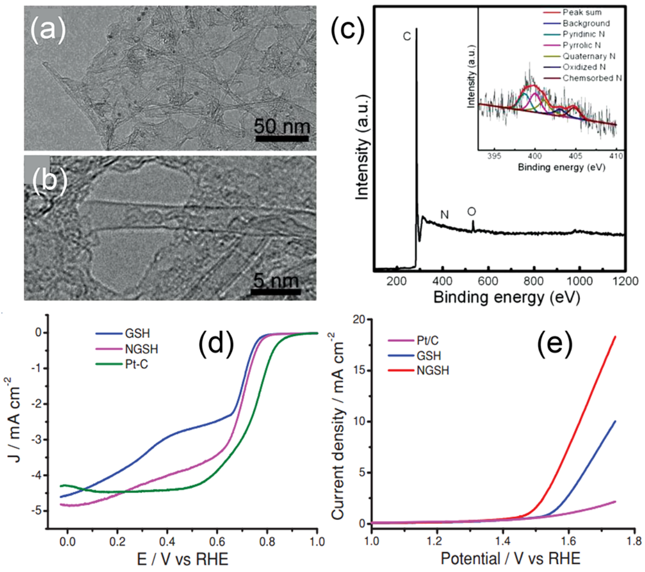

Figure 2. Nitrogen-doping in metal-free nanocarbon for ORR/OER. (a) TEM and (b) high-resolution TEM images of NGSH. (c) XPS spectrum of NGSH with high-resolution N 1s spectrum (inset). (d) ORR and (e) OER polarization curves obtained in 0.10 M KOH. Reproduced with permission from ref 13. Copyright 2014 John Wiley and Sons.

whereas the N-doped graphene was revealed as an efficient four-electron ORR electrocatalyst due to the synergistic effect between the oxygen (3.64 atom %) and nitrogen (7.48 atom %) functionalities.[14] Notably, the heteroatom doping introduced via in situ synthesis or post-treatment is inevitably concomitant with other structural modifications, such as the enlarged graphite interlayer distance (0.345 nm), more exposed graphene edges and defects in N-doped herringbone carbon nanofibers.[15] These features are likely to influence the intrinsic electronic structure and electrocatalytic activity as well, which extends the probe of activity origin beyond doping.

2.2. Topological Defects in Nanocarbon

Most recently, the rational combination of theoretical calculation, customized synthesis, and high-end characterization renders the possibility to clearly recognize all active sites and thoroughly understand the altered electronic structures. We have systematically studied all the possible active sites derived from nitrogen-doping, topological defects, and edge effects in graphene, as illustrated in Figure 3a, by density functional theory calculations.[16] The doping at edge was revealed to be more beneficial than those in bulk, while the topological defects at edge were demonstrated to be even more active than doping and edge sites. It is surprising that an activity−adsorption volcano plot was well satisfied for both heteroatom doping and topological defects (Figure 3b). A dopant-free topological defect composed of adjacent pentagon and heptagon (C5 + 7) was identified as the optimal configuration at the volcano peak for both ORR and OER. Specifically, the adjacent pentagon and heptagon with different electron densities can induce a permanent dipole moment and regulate the local electronic structure, thus achieving a moderate surface adsorption and higher activity. To validate such predictions, a series of graphene electrocatalysts with different abundance of topological defects and nitrogen doping were fabricated by MgO-templated carbonization of carbon/nitrogen precursors.[16] The as-obtained (N-doped) graphene mesh (GM or NGM) was dominantly few-layers thick with abundant nanosized holes (Figure 3c). Remarkably, the GM with trace N (0.41 atom %) delivered a substantially higher current density than the N-doped graphene oxide (NG) with a much higher nitrogen content (7.48 atom %) but few in-plane holes, clearly implying the critical importance of topological defects (Figure 3d). This concept has been further corroborated by the investigation with dopant-free defective graphene[17,18] and visualization using aberration-corrected high-resolution transmission electron microscopy.[19]

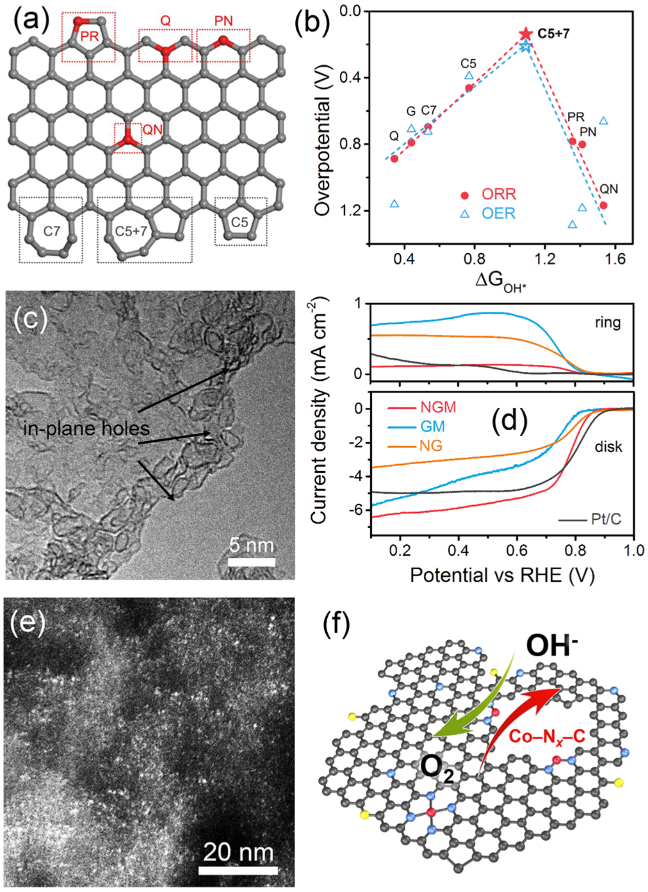

Figure 3. Intrinsic activity and utilization of topological defects in nanocarbon. (a) Schematic graphene nanoribbon with different kinds of N-doping or topological defects. (b) ORR and OER volcano plots of overpotential versus adsorption free energy of OH*. (c) High-resolution TEM image of NGM. (d) ORR current recorded on a rotating ring-disk electrode in O_2-saturated 0.10 M KOH. Panels (a)−(d) are reproduced with permission from ref 16. Copyright 2016 John Wiley and Sons. (e) Dark-field high-resolution TEM image of NGM-Co. (f) Schematic of NGM-Co with atomic Co−N_x−C species for ORR/OER. Panels (e) and (f) are reproduced with permission from ref 20. Copyright 2017 John Wiley and Sons.

With a synergistic combination of heteroatom doping and topological defects, the intrinsic electronic structure of nanocarbon electrocatalysts can be effectively regulated and thus superb bifunctional reactivity for ORR and OER can be achieved.[16,21] Further, we proposed a defect engineering strategy to directly utilize the intrinsic topological defects of nanocarbon to construct atomically dispersed metal−N_x−C species,[20] which were acknowledged as the most promising active sites for ORR but suffering from effective synthetic methodology.[22] Similar to the synthesis procedure of NGM, cobalt salt was additionally introduced into the precursors and acid leaching was conducted after carbonization to remove nanoparticles. Ultimately, a high dispersion of Co atoms coordinated with pyridinic N in the porous graphene was achieved in NGM-Co (Figure 3e). As illustrated in Figure 3f, the interaction between p-electrons in the carbon basal plane and d-electrons of metal atoms was indicated to modify the local electronic structure for optimized adsorption strengths and thus facilitated ORR and OER in Zn-air batteries.

Taken together, both the chemistry and engineering of topological defects provide new opportunities to effectively regulate the electronic structure and boost the reactivity for nanocarbon catalysts.[24] In fact, all these diverse active sites, including heteroatom doping, edges, topological defects, and metal−N_x−C, are revealed to work analogously at the level of electronic structure, to modify the charge/spin distribution on sp^2-conjugated carbon matrix with optimized surface adsorption properties and match the valence orbitals for smooth charge transfer (Figure 4).[23] Such syncretic understanding is expected to promote the elaborate design of highly effective active sites in nanocarbon electrocatalysts, among which the specific doping (heteroatoms or metal atoms) at defective edges should be a promising direction.[20,25]

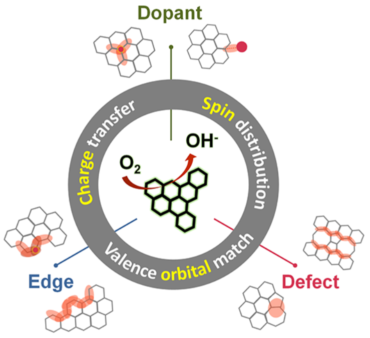

Figure 4. Schematic illustration of various active sites and underlying mechanism of nanocarbon catalysts for ORR. Reproduced with permission from ref 23. Copyright 2017 John Wiley and Sons.

2.3. Cationic and Anionic Regulation in Metal Compounds

Although nanocarbon-based electrocatalysts have achieved impressive advances in ORR, other active components are strongly required to effectively boost the reactivity in OER and HER, such as various transition metal compounds (oxides, hydroxides, hydroxysulfides, sulfides, nitrides, phosphides, etc.). Typically, the OER is supposed to occur on a surface metal site (on top or bridge), with metal−oxygen bonding for a series of oxygen-containing intermediates.[26] The regulation of the electronic structure of metal cations can effectively alter the metal−oxygen bonding strengths toward the peak of activity−adsorption volcano plots, resulting in favorable reactant adsorption or product desorption and improved reactivity.

It has been widely investigated that the substitution of metal cations is a mature method to modulate the electronic structure of active sites in metal compounds, also referred as cationic regulation. For example, with the Fe content increasing, a phase evolution from Fe doped $Ni(OH)_2$/NiO(OH) to Ni doped FeO(OH) was revealed in the case of NiFe (oxy)hydroxides (Figure 5a).[27] Although the NiO(OH) and FeO(OH) frameworks exhibited distinct properties and activities, a moderate guest metal substitution into the host oxyhydroxide framework can substantially enhance the OER reactivity (Figure 5b). The wise cationic regulation with an optimal Fe/Ni ratio is able to alter the local electronic structure with more favorable intermediate adsorption.[27] The incorporation of ternary metal Co into NiFe hydroxides was demonstrated to further regulate the electronic structure with improved conductivity and enhanced reactivity for OER/HER.[28] In addition to the bulk substitution, surface etching is more efficient to generate exposed active sites on surface with high-energy hanging bonds and dispersed empty electron orbitals. Accordingly, a novel p-block metal regulation strategy was proposed to increase the OER activity for perovskite electrocatalysts.[29] During electrochemical activation, the Sn^{4+} cations facilely dissociated from the solid SnNiFe perovskite nanodots, leading to abundant surface defects and higher oxidation states of adjacent Ni ions favorable for OER.

On account of the intimate electron interaction between anions and cations, anionic regulation is recently considered as another effective route to regulate the electronic structure and electrocatalytic activity for metal compounds.[30,31] Specifically, the polarization of the anions is believed to govern the covalency and ionicity of the interaction between cations and anions. A suitable polarization degree attained by coordinating nonpolarized and polarized anions can reasonably optimize the electronic structure of cations for facilitated adsorption and desorption properties simultaneously (Figure 5c).[30] As a proof of concept, the couple of oxygen and sulfur was selected as tunable anions in NiFe compounds for OER.[30] The OER reactivity and sulfurization degree were revealed to be well correlated via a typical volcano plot, at whose peak a fine balance of covalency and ionicity was achieved with optimized electronic structure and boosted reactivity. Nonetheless, the sulfurization process always involves high temperature treatment or toxic organic chemicals, which can cause more variation in addition to electronic structures, such as phase transformation and particle agglomeration. Correspondingly, we further developed a versatile room-temperature sulfurization strategy to fabricate hydroxysulfide electrocatalysts with efficient sulfurization and good morphology-preservation for the first time.[32] The sulfurization was achieved by simply immersing metal hydroxide precursors into a solution with high concentrated S^{2-}, where the S^{2-} continuously replaced the OH^- in the solid phase according to the solubility equilibrium. The resultant sulfurization degree can be facilely adjusted by the S^{2-} concentration and the immersing duration, and the morphology was excellently replicated from hexagonal sheets (~1 μm) or confined nanoparticles (~20 nm). In fact, the cationic and anionic regulation can be achieved simultaneously two-in-one (multimetallic compounds with multianions) to fully optimize the electronic structure of cationic centers and remarkably improve the reactivity.[32,33]

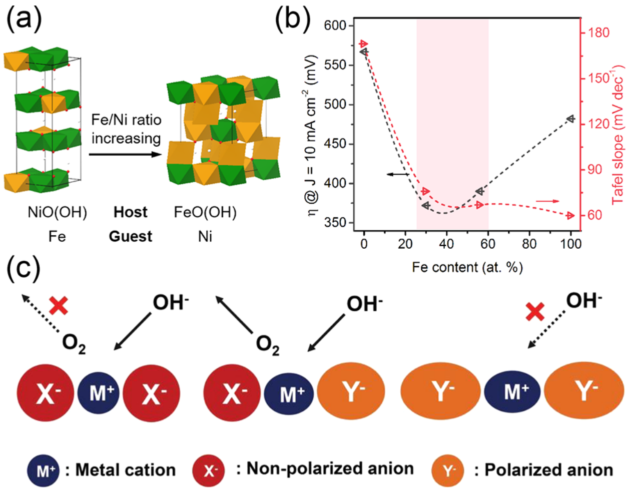

Figure 5. Cationic and anionic regulation in metal compounds. (a) Schematic of the phase evolution in graphene/NiFe (oxy)hydroxide composites induced by Fe doping. (b) Relationship between Fe content and OER performance for graphene/NiFe (oxy)hydroxide electrocatalysts. Panels (a) and (b) are reproduced with permission from ref 27. Copyright 2016 Royal Society of Chemistry. (c) Schematic of anionic regulation by optimizing the electronic structure of active sites for OER. Reproduced with permission from ref 30. Copyright 2017 John Wiley and Sons.

3. TAILOR OF THE EXTRINSIC HIERARCHICAL MORPHOLOGY

3.1. Surface-Enriched Utilization of Active Sites

In general, the heteroatoms incorporated into metal-free nanocarbon materials by routine synthesis uniformly distribute in the whole carbon matrix. The bulk dopant atoms, however, not only contribute to the catalytic activity scarcely due to the poor accessibility, but also create defects in the sp^2 conjugated graphene lattice with hindered electron transport. Therefore,

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the active sites are expected to be enriched at interface where they can be fully accessible to reactants for sufficient utilization.[34] For instance, a CNT@NCNT coaxial nanocable was proposed to enrich the nitrogen atoms in the outer shell of CNTs (NCNTs) and preserve the inner continuous CNTs toward full exposure of active sites on surface and rapid electron transfer inside (Figure 6a).[35] The turbostratic NCNT shell was epitaxially grown on the pristine CNT wall by simple chemical vapor deposition (CVD) of pyridine as carbon and nitrogen source. The surface N/C ratio (0.0809) was revealed to be twice of that in bulk, and the electrical conductivity (3.3 S cm^{-1}) was over 3 times higher than that of routine bamboo-like NCNT. As a result, the current normalized based on the N content for CNT@NCNT (0.57 mA μgN^{-1} for ORR and 2.01 mA μgN^{-1} for OER) was much higher than that for bulk doped NCNT electrode, suggesting the higher utilization efficiency of active sites in such unique surface-enriched hierarchical structure. In addition to the coaxial structures for 1D CNTs, this concept can also been applied as sandwich-like structures for 2D graphene,[36] and even 3D porous framework (Figure 6b).[37] Notably, such hierarchical nanostructure with surface-enriched active sites is also beneficial in other multielectron electrochemical reactions in rechargeable batteries.[37]

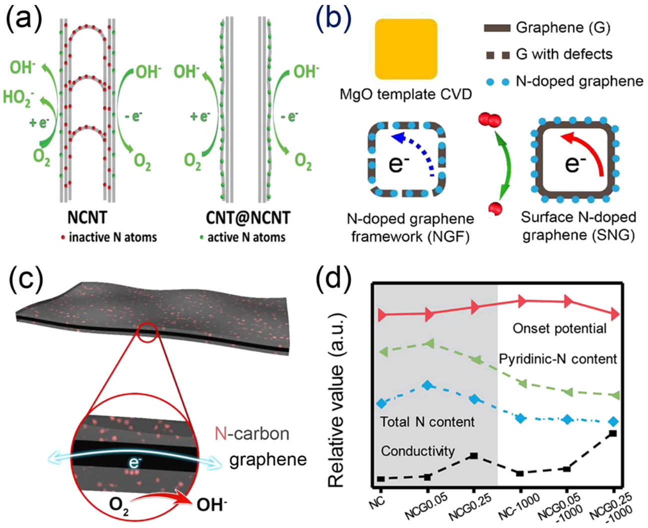

Figure 6. Surface-enriched utilization of active sites. (a) Scheme of CNT@NCNT coaxial nanocables for ORR/OER. Reproduced with permission from ref 35. Copyright 2014 John Wiley and Sons. (b) Scheme of surface N-doped graphene. Reproduced with permission from ref 37. Copyright 2018 Elsevier. (c) Sandwich-like hybrid of N-carbon/graphene/N-carbon with adjustable active sites and conductivity, and (d) the resultant relationship between electrocatalytic activity and material properties. Reproduced with permission from ref 36. Copyright 2016 Royal Society of Chemistry.

In fact, the surface-enriched principle not only offers a promising strategy to develop highly efficient electrocatalysts, but also decouples the active sites and conductivity, thereby conducing to the facile investigation of their roles on resultant performance. Ultrathin lamellar graphene oxide is a versatile substrate to anchor and direct the carbonization of nitrogen-containing precursors (such as chitosan) for surface-enriched active sites, and also provide a favorable matrix with tunable conductivity (Figure 6c).[36] Therefore, a series of sandwich-like hybrids with adjustable active sites and conductivity can be obtained simply by changing the mass ratio of graphene oxide/chitosan and high-temperature annealing. The correlation between electrocatalytic performance and material properties revealed that a low electrical conductivity resulted in conductivity-dependent ORR activity due to the limited exertion of active sites, while the amount and type of active sites became critical factors when conductivity was no longer a limitation (Figure 6d). Analogously, the active surface/conductive matrix hierarchical nanostructure is expected to inspire the material engineering and mechanism understanding in other categories of electrocatalysts, such as core−shell transition metal compounds.

3.2. Spatially Confined Hybridization of Active Phases

Although the intrinsic activity of transition metal compounds can be effectively enhanced by cationic and anionic regulation, their poor conductivity highly requires a favorable substrate, such as CNTs and graphene.[38−40] It has been widely demonstrated that there is strong interplay between these two components, which renders a smooth electron transfer across interface and also triggers electronic modification on the metallic active phases, synergistically boosting the apparent reactivity. To take full advantage of the active phases and nanocarbon substrates, several features are strongly expected in the obtained hybrids: (1) nanosized metallic active phases with more exposed active edges and smaller insulating regions; (2) strongly coupled interface to accelerate the interfacial electron transfer and electronic structure regulation; (3) robust hybridization in nanoscale for a high utilization and durability.

To achieve all these goals, we scrupulously proposed a nanoscale spatial-confine strategy to versatilely manipulate the hybridization metal compounds onto nanocarbon substrates with optimal hierarchical morphologies and fully improved catalytic performance.[41] A nitrogen-doped mesoporous graphene framework (NGF) was employed as both the conductive substrate and multifunctional nanoreactor (Figure 7a). The NGF was fabricated via MgO templated CVD, followed by the incorporation of NiFe layered double hydroxides (LDHs) via urea-assisted precipitation. Both abundant nitrogen dopants and topology-induced defects in NGF tended to adsorb and anchor metal precursors for defect-anchored nucleation, and then the templated mesopores spatially confined the growth of metal hydroxides inside (Figure 7b). Consequently, the as-obtained NiFe LDHs exhibited an average nanosize of 5 nm, and were uniformly decorated into the NGF scaffold with graphene layers encircled. The high-resolution Ni 2p spectra revealed a ca. 0.7 eV shift to higher binding energy for NiFe LDHs after the hybridization with NGF, clearly indicating a strongly coupled interface and modified local electronic structure for Ni cations. As a result, the NiFe LDH/NGF hybrid delivered a remarkably enhanced activity, kinetics, and durability for OER, even outperforming the commercial Ir/C catalysts. Furthermore, this unique structure provides a favorable material platform to probe the catalytic mechanism of insulating active phases,[27] and can be generalized to other systems, such as mildly oxidized graphene/CNT hybrids,[42] perovskites,[29] and transition metal hydroxysulfides/oxysulfides.[32] Of note, a hierarchical porous nanocarbon scaffold with moderate defects is the prerequisite factor for such effective hybridization. In addition to the governed nucleation and growth of active phases, the spatial-confine effect of porous nanocarbon scaffolds can also benefit the targeted regulation of active phases, such as mild sulfurization[32] and defect engineering[29] with preserved nanostructure and interface.

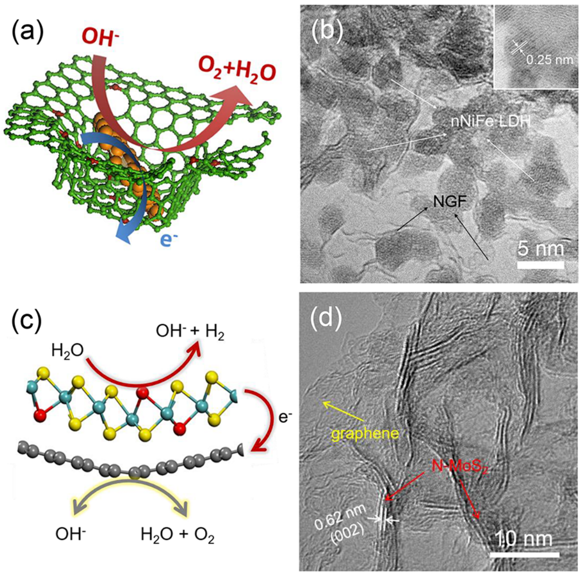

Figure 7. Spatially confined hybridization of active phases. (a) Scheme of nanosized NiFe LDH spatially confined in NGF, and (b) its typical high-resolution TEM image. Panels (a) and (b) are reproduced with permission from ref 41. Copyright 2015 John Wiley and Sons. (c) Scheme of G@N-MoS_2 heterostructures with electron transfer effects toward improved electrocatalytic activities. (d) High-resolution TEM image of G@N-MoS_2. Panels (c) and (d) are reproduced with permission from ref 43. Copyright 2017 John Wiley and Sons.

Apart from the liquid precipitation to incorporate various metal hydroxides as active phases, CVD is another effective method in synthesizing nanomaterials, especially 2D materials with epitaxial growth on graphene to form fascinating van der Waals (vdW) heterostructures. With these in mind, we devised a 3D mesoporous graphene/nitrogen-doped MoS_2 vdW heterostructure (G@N-MoS_2, Figure 7c) and proposed a two-step sequential CVD method to facilely synthesize such vdW solid materials.[43] A mesoporous graphene framework was first grown on MgO templates using CH_4 as carbon source at 950 °C, and then ultrathin N-MoS_2 was in situ deposited on graphene using $MoCl_5$, sulfur, and NH_3 as precursor materials at 800 °C. In contrast to conventional 2D films, as-obtained N-MoS_2 nanosheets were locally curved and intimately merged with the previously deposited graphene on mesoporous MgO templates, simultaneously forming a vertical vdW heterostructure and 3D mesoporous framework (Figure 7d). Such hybrid nanostructure was demonstrated to afford an all-round modification of both components, including the morphology, edge, defect, interface, and electronic structure, hence leading to significantly enhanced electrocatalytic performances. It was revealed that the HER reactivity was substantially accelerated on the N-MoS_2 side while the ORR and OER activities are remarkably improved on the graphene side (Figure 7c), suggesting promising reactivities for trifunctional energy electrocatalysis.

4. ENGINEERING OF THE WORKING ELECTRODE INTERFACE

4.1. Binder-Free Self-Supported Electrode

Although tremendous progresses have been accomplished in exploring and optimizing catalysts, there is a long way to go for the ultimate goal of developing practical energy devices. The conventional electrode fabrication procedure by drop-casting is efficient for the high-throughput activity evaluation of electrocatalysts; however, it inevitably results in undesirable electrode interfaces, such as uneven distribution induced by coffee-ring effects, a plenty of dead volumes and higher resistance due to the use of binders, and peeling of catalysts during gas evolution. In contrast, the fabrication of freestanding electrodes with binder-free and self-supported configuration, especially by direct deposition of active materials on substrate, is of particular superiority to demonstrate the reactivity in practical devices.[44]

Taking NiFe LDHs and Ni foam for example, if the poorly conductive LDH sheets thickly packed on the Ni surface, the electron transfer to outer active sites and the mass diffusion toward inner ones would be significantly limited with insufficient utilization. Aiming at this problem, an ultrathin graphene layer was introduced to modulate the growth behaviors and interface structure of NiFe LDHs on Ni foam substrate (LDH/G/Ni, Figure 8a).[45] NiFe LDHs were hydrothermally coprecipitated on graphene covered Ni foam (G/Ni) instead of the naked Ni substrate. The CVD-grown graphene was hydrophobic and low-defective, which can separate the precursor solution from Ni substrate, and increase the nucleation resistance. Therefore, only small LDH clusters were gradually grown on G/Ni (Figure 8b), while swarms of LDHs were rapidly generated and continuously covered on the surface of naked Ni foam (LDH/Ni). Furthermore, the electronic structure of Ni cations was effectively modulated toward a higher oxidation state (0.4 eV shift in Ni 2p spectrum) by the graphene interface. As a result, the specific OER current density based on the amount of LDHs was greatly increased for LDH/G/Ni compared to LDH/Ni (Figure 8c), implying the improved utilization efficiency of active phases. However, the high utilization efficiency was actually obtained in the sacrifice of active component amounts, which is less-then-ideal to boost the whole reactivity. It was demonstrated that electrodeposition method can be very attractive for a controllable incorporation of electrocatalysts on substrate for highly efficient water-splitting (OER and HER), achieving well-arranged thin film with abundant highly accessible active sites in seconds and also facilely regulated electronic structures (such as ternary doping).[28]

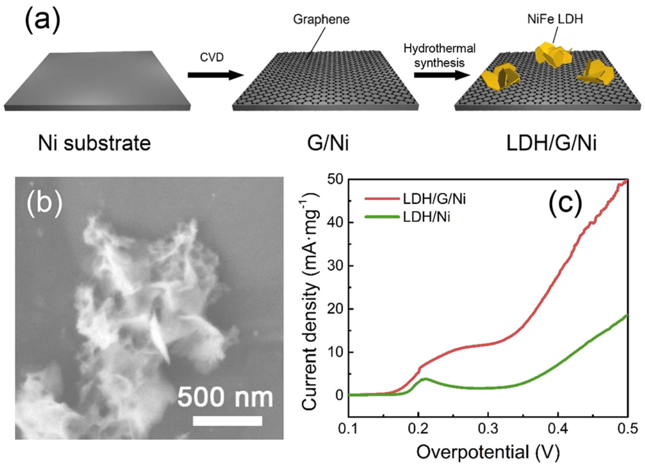

Figure 8. Binder-free self-supported electrode. (a) A graphene barrier modulates the growth of LDHs on Ni foam. (b) Morphology of as-obtained LDH/G/Ni. (c) OER polarization curves obtained in 0.10 M KOH. Reproduced with permission from ref 45. Copyright 2015 Royal Society of Chemistry.

In some cases, there exists an intrinsic contradiction in the direct hybridization of active components with monolithic substrates. Most of the used conductive frameworks (e.g., carbon and metal foam) are reductive and will be destroyed under oxidative atmosphere, which is however necessary for the fabrication of some electrocatalysts (such as perovskite oxides). To address this issue, we inaugurated a peroxidation coupled electrodeposition strategy for in situ incorporation of oxidized $LaCo_{0.8}Fe_{0.2}O_3$ perovskite oxides onto reductive Ni foam.[46] The Co^{2+} precursor can be oxidized to Co^{3+} via two-electron ORR-coupled cobalt Fenton process in O_2-saturated electrolyte. Therefore, the moderate annealing in Ar, instead of O_2, is able to transform the hydroxide intermediates into crystallized perovskite oxides by inheriting the Co^{3+} from the aqueous peroxidation step. With a wise combination of interface engineering and synthesis innovation, various favorable electrodes with highly active electrocatalysts and self-supported frameworks can be constructed, aiming at promising performance in devices.

4.2. The Microenvironment in Triple-Phase Boundary Region

As bridge from nanostructured electrocatalysts to working electrodes, the triple-phase boundary region is the crucial place where electrocatalytic reactions actually proceed, along with a series of complex phenomena. The microenvironment, including local ion concentrations, adhesion behavior of gas, inner diffusion in catalyst films, and interfacial electron transfer pathway, is supposed to directly influence the activity and kinetics for gas-involving energy electrocatalysis. On the basis of this consideration, we proposed a novel but general concept of microenvironment manipulation for metal-free nanocarbon catalysts aiming at enhanced ORR performances with higher activity, kinetics, and stability.[47] Concretely, oxygenophilic and hydrophobic ionic liquids were employed to modify the surface of nanocarbon by forming a water-equilibrated secondary medium between solid catalyst and liquid electrolyte, thus generating more favorable triple-phase contact points around the active sites (Figure 9a). The surface modification was achieved simply by addition of ionic liquids into the electrocatalyst slurry with thorough mixing. An ultrathin ionic liquid layer was formed on the surface of nanocarbon with unchanged morphology, but obviously increased hydrophobicity (Figure 9b). Two ionic liquids with different properties, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (IL1) and 1-ethylimidazolium bis(trifluoromethylsulfonyl) imide (IL2), were used for in-depth investigation. Their O_2 solubility are both much higher than that in aqueous electrolytes, but the extra "N−H" acidic site in IL2 almost triples the mole fraction solubility of water in ionic liquid due to hydrogen bonding. Besides, IL1 is a typical aprotic ionic liquid, while IL2 is protic. ORR polarization curves clearly showed that the IL-modified catalysts exhibited better activity, and the IL2 was more beneficial than IL1, in both alkaline and acid conditions (Figure 9c). It suggested the necessity and superiority of high O_2 solubility and hydrophobic nature for gas diffusion, and more importantly, the high water solubility for sufficient $H^+/H_3O^+/OH^-$ conductivity. Analogously, microenvironments with locally increased gas solubility, high hydrophobicity, interconnected water pathway, and sufficient $H^+/H_3O^+/OH^-$ conductivity are strongly expected for gas-involving electrocatalysis, either by chemical modification or material nanoengineering.

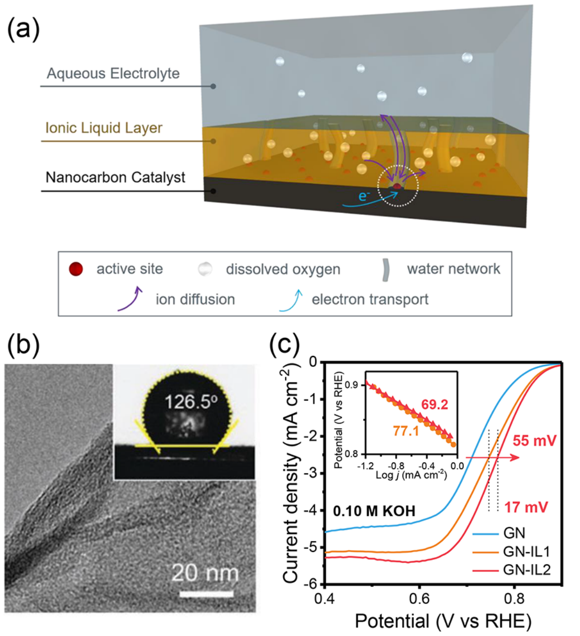

Figure 9. The microenvironment in triple-phase boundary region. (a) Illustration of ionic liquid-modified nanocarbon catalysts for ORR. (b) TEM image of GN-IL1 and corresponding static water contact angle measurement. (c) ORR polarization curves obtained in O_2-saturated 0.10 M KOH solution, and corresponding Tafel plots (inset). Reproduced with permission from ref 47. Copyright 2017 Royal Society of Chemistry.

5. CONCLUSIONS AND PERSPECTIVES

Gas-involving energy electrocatalysis has been strongly considered because of its significant importance for both fundamental concepts and technological applications. In this Account, we reviewed our recent progress from both materials design and synthetic methods, and established the multiscale principles ranging from the intrinsic electronic structure, extrinsic hierarchical morphology, to working electrode interface. Looking forward, some challenging but promising directions are still needed to be concerned, as listed below.

(1) Electronic structure: In-depth understanding of the actual active sites for various electrocatalysts are extremely important, which can be possibly attained by the combination of experimental and computational strategies. Then the subtle regulation of corresponding electronic structures is expected to be conducted by some novel and effective approaches, such as atomic and molecular design and reticular chemistry. (2) Hierarchical morphology: It is difficult but urgently required to accurately identify the interface and nanostructure in hierarchical morphologies, by means of advanced spectroscopy, microscopy, and tomography. Hunting for innovative methods of materials design and synthesis is always important beyond nanoscale to enlarge the particle size and increase the active loading. (3) Electrode Interface: More smart and efficient free-standing electrodes can be fabricated by electrospinning and 3D printing with diverse scaffolds (such as bioinspired or fractal structures) and active components. The microenvironment deserves more attention to probe its specific influence mechanism on reactivities and develop new strategies to achieve favorable hydroxyl/proton or electron availability.

It is reasonable to expect that the electrocatalytic performance (activity, durability, and selectivity) can be effectively improved under the multiscale princples with timely updated strategies. Owing to the general characteristics and wide prospects, the discussions presented here not only pave the way to optimize the reactivity of ORR/OER/HER for water splitting and metal-air batteries, but also strive to inspire the development of other important gas-involving electrocatalysis, including CO_2 reduction reaction, chlorine production, hydrogen peroxide production, and nitrogen reduction reaction.[48]

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