What Makes On-Chip Microdevices Stand Out in Electrocatalysis?

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Clean and sustainable energy conversion and storage through electrochemistry shows great promise as an alternative to traditional fuel or fossil-consumption energy systems. With regards to practical and high-efficient electrochemistry application, the rational design of active sites and the accurate description of mechanism remain a challenge. Toward this end, in this Perspective, a unique on-chip micro/nano device coupling nanofabrication and low-dimensional electrochemical materials is presented, in which material structure analysis, field-effect regulation, in situ monitoring, and simulation modeling are highlighted. The critical mechanisms that influence electrochemical response are discussed, and how on-chip micro/nano device distinguishes itself is emphasized. The key challenges and opportunities of on-chip electrochemical platforms are also provided through the Perspective.

1. Introduction

Today, the ever-increasing energy depletion and environmental pollution crisis highly require the development of efficient energy technologies and systems.[1] Electrochemistry has been focused as one of the most sustainable and renewable pathways to facilitate energy conversion and supply clean energy sources.[2] Among them, water splitting, carbon dioxide reduction, nitrogen reduction, etc. through the electrochemical conversion catalyzed by materials, i.e., electrocatalysts, are remarkably attractive and have raised broad research interests. Up to now, with regards to different catalytic reactions, researchers have established myriad approaches to design highly-efficient catalysts and developed state-of-the-art techniques to enable systematic study of specific electrocatalysis scenarios.[3] In particular, the accurate identification and monitoring of an electrocatalytic reaction is crucial to increase fundamental understanding of electrocatalyst and catalytic process. However, the classic methodologies to record information from materials are based on mean-field description of average signals of the whole reaction and system. For example, the ink loaded on glass carbon disk electrode contains at least catalysts and binders, which unfortunately complicate direct observation of catalyst itself and the correlation between nanoscale/molecular level local properties with catalytic evolution. In micro/nano devices, the electrode is directly connected with the nanomaterials, and the selective window opening only allows the exposed area to participate in the reaction, which makes the individual reaction well extracted.

The exploration of cutting-edging characterization techniques would promote deep understanding and future catalyst development. Recent decades have seen massive advances in nanoscience and nanotechnology and their interdisciplinary research on nano-electrochemistry, nano-reactor, and micro/nano devices. In the realm of electrochemistry, a micro/nano platform designed by nanoelectronic method is used to generate a local change as a measurable property. Such change can be a decrease in contact resistance caused by a local phase change,[4] an over-potential change caused by a generation of defects on the base surface,[5] or an increase in catalytic activity caused by the simple movement of the reaction site (basal surface to edge).[6] Such micro/nano platform meets the newly proposed concept of Single-Entity Electrochemistry.[7] Rather than rebuilding a new test platform, it needs to incorporate special methods or use new tools to help extend the possibilities of on-chip test systems across length and time scales. The focus of electrochemical research is to reveal the mechanism of electrochemical reactions and capture the intermediate state of the reaction process. And for the catalytic reaction, the evolution law of the catalyst material should be considered the most. In light of this, several approaches are developed to monitor the properties of materials during electrochemical processes in real time, such as in situ Fourier transform infrared spectroscopy (in situ FTIR), in situ Raman spectroscopy, in situ transmission electron microscope (in situ TEM), etc. Besides, artificially manufacturing defects, inserting an appropriate amount of special atoms in the material, or providing external conditions

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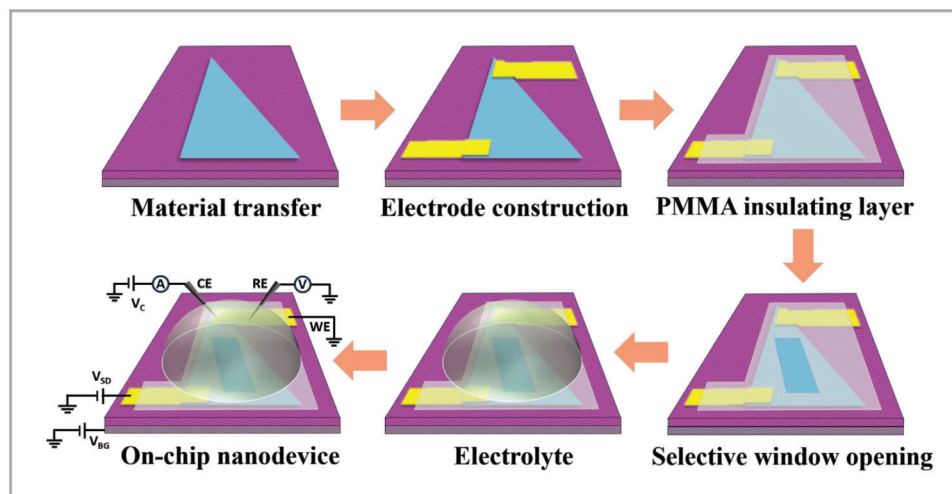University of Oxford
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Figure 1. Construction and test methods of on-chip micro/nano devices.

such as an additional electric field during the catalytic process have been developed.

Low-dimensional materials with unique atomic and electronic structures have exhibited great potential toward high-efficiency electrocatalysis. First, 2D materials have excellent mechanical flexibility. Due to their thin and flexible structures, they can be tightly integrated with other materials, adapting to the compact and integrated requirements of modern microelectronics.[8,9] Second, in-plane high carrier mobility and low electron scattering of 2D materials make it exhibit excellent electron transport performance at high frequency and high speed.[10] At the same time, 2D materials exhibit a series of unique optical and electrical properties. These properties allow 2D materials to be used in photoelectric conversion devices, such as sensors, solar cells, etc.[11,12] Because 2D materials have precise control and assembly capabilities at the nanoscale, their characteristics can be adjusted by adjusting size, shape, alloying, and other methods.[13] This controllability provides a wide range of application possibilities for different types of on-chip devices.

From this perspective, we focus on the extraction of individual response, the selective definition of active sites, the combination of modern methodologies, and the cross-application of multiple disciplines. In particular, we provide an overview of material structure analysis, field-effect regulation, in situ monitoring, and simulation modeling, discuss critical challenges, and then outline future directions for on-chip micro/nano characterization platforms.
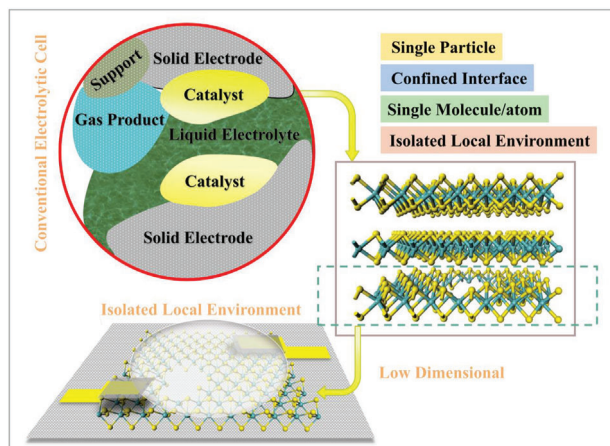
2. To Extract Individual Response from the Bulk

The manufacturing process of the on-chip electrocatalytic microdevice is shown in **Figure 1**. In general, nanowires or nanosheets are placed on a clean substrate (SiO_2/Si) by means of spin coating, dry/wet transfer, etc. This step aims to position the electrocatalytic active material in a specific location and ensure its good adhesion and structure. Next, the metal electrode is deposited at the desired location. The lithography technique is used to define the pattern of the electrode, and then the metal materials are deposited on the electrode area by physical vapor deposition. Usu-

ally, Au/Cr or Au/Ti electrodes are used, where Cr or Ti provide good adhesion between Au and SiO_2. In order to prevent short circuits between the electrodes and interference from impurities, an insulating layer needs to be formed between and around the electrodes, usually using a polymethyl methacrylate (PMMA) layer. Finally, the required window is formed in the insulation layer through the photolithography process and etching steps. This removes a specific area in the insulation, exposing the material, forming the area needed to bring the substance under test into contact with the electrode and perform an electrocatalytic reaction.

The micro / nano devices are tested with a three-electrode system, which consists of a counter electrode (CE), a reference electrode (RE), and a working electrode (WE). A small amount of electrolyte forms droplets on the chip through surface tension, which requires that the CE and RE used must be small enough to ensure that they are fully immersed in the electrolyte. Finally, the device is connected to a specific test equipment through the probe table. The reaction window controls the reaction region and is beneficial to in situ characterization, and the unique layered structure also allows back gate (V_{BG}) modulation to regulate the reaction.

The most prominent virtue of on-chip micro/nano platform is to enable direct observation of individual response from the bulk. An example of electrocatalytic hydrogen evolution reaction (HER) or oxygen evolution reaction (OER) system involves three state-types substances, i.e., solid electrode or support, liquid electrolyte, gas products, and their mutually formed interfaces. The collected information or response of the whole system represents a unit of entity which is not always straightforward or fully representative. If we understand how an individual "thing" turns over at catalyst reaction, an accurate understanding of the underlying mechanism can be better determined. An individual "thing" here (**Figure 2**) can be referred to an isolated local environment, a confined interface, a single particle, or even a single molecule/atom. On-chip micro/nano platform offers an incredible capability to define and study an individual as an alternative to present measure techniques.

To extend electrochemical research from conventional scale to micro/nano scale, researchers have made bold attempts. In 2010,

Figure 2. An illustration of the process of extracting the individuals from the bulks.

Figure 3. An illustration of on-chip micro/nano devices to selectively define different catalytic factor that matters.

Mai et al. reported a micro/nano solid-state battery whereby the structural evolution, transport property, and charge/discharge states of a single nanowire electrode are correlated.[14] This pioneering work has provided a unique on-chip micro/nano platform to enable in situ nanoscale electrochemical diagnosis, which stood out as a "proof-of-principle tool" to offer crucial insights on various electrochemical reactions including electrocatalysis.[6,15] In 2015, Duan et al. first realized the in situ monitoring electrical transport based on a four-electrode micro/nano device configuration.[16] The use of nanoelectronic signal pathways enables the dynamic observation of electrochemical interfaces characteristics with a focus on how the adsorbed molecules interact with ultrathin platinum nanowires (PtNWs) electrocatalysts. A comprehensive review from Zhai and co-workers summarizes the device configurations and introduces how to precisely design and build on-chip electrocatalytic microdevices via nanofabrication methods.[17] These pioneering works have laid a solid foundation for subsequent research.

One of the main reasons for separating the individual signal from the overall response is to study the contribution of a single individual to the bulk. With an understanding of how a single material works, the structure and composition of the material can be purposefully tuned to optimize the reaction. To directly observe the catalytic state of β-Co(OH)$_2$, J. Tyler et al. combined the probe station and X-ray microscopy technology to fabricate a set of micron-scale electrochemical devices.[18] They found that unlike the bulk Co oxidation reaction, the OER current of individual Co does not depend on the scan rate under submonolayer mass loading, suggesting that no catalysis occurs inside the particle. This indicates that the nanosheet-structured Co catalysts are pretty different from bulk Co. On-chip micro/nano devices are a very efficient and valuable platform for studying the properties of tiny nanomaterials(nanosheets/nanowires). At the same time, it enables the characterization of materials to achieve the transition from macro to micro, and realizes the essential measurement of the catalytic performance of a single material (nanowire, single molecule).[19,20]
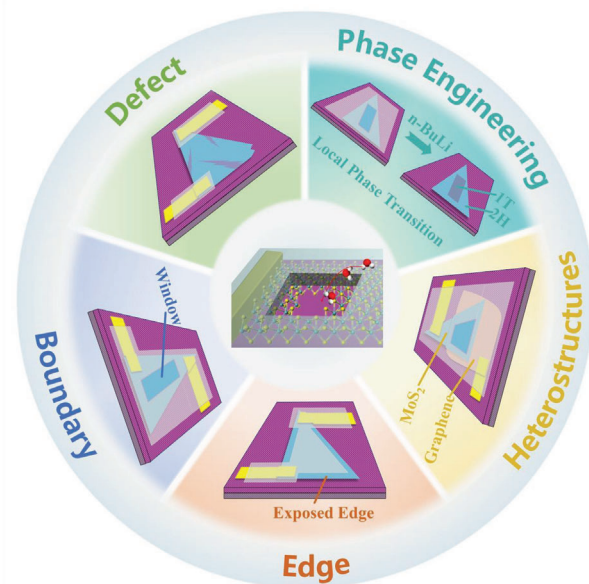
3. To Define Catalytic Factor that Matters

On-chip micro/nano devices serve as platforms to selectively study single active factor of materials, including material edge, boundary, and defect, as well as phase transition and different heterostructure (**Figure 3**). In this section, the enormous benefits brought by highly self-selective and quantitative control based on customized window opening technology will be presented.

3.1. Edge/ Boundary/ Defect

2D transition metal dichalcogenides (TMDs) have aroused widespread attention due to their extraordinary physicochemical properties as well as great potential application in HER. 2D-TMDs typically feature exposed edge and basal planes with different catalytic reactivity. A typical representative is molybdenum disulfide (MoS$_2$), whose metallic edges are basically active relative to the inactive 2H basal planes.[21] To accurately extract information from the local area of the heterogeneous catalysts requires a combination of spatial resolution standards and surface sensitive studies. Numerous follow-up studies have been strived based on a micro/nano electrocatalytic device (can also be referred as a micro reaction cell). A representative work is Lou et al. used selected-area e-beam lithography to open reaction windows at sites of interest on blocking layer-covered monolayer MoS$_2$.[6] Local HER measurements on the selective regions, namely edge or basal planes of 1T', 2H MoS$_2$ were successfully carried out. Additionally, the quantitative analysis of the terms of turnover frequencies for MoS$_2$ active sites on the selected areas demonstrates differences in the intrinsic mechanism between TMDs and metal catalysts. This work opens a door to the quantitative and localized analysis of catalyst efficiency in electrochemical reactions.

Significant advances in understanding the high catalytic activities of 2D-TMDs originating from its edges have also aroused

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much concern on domain boundary area. The challenge of extracting information from domain boundary is more daunting for conventional methods that look into entire catalysts. While local probe characterization based on a micro/nano electrocatalytic platform exists as a good example to accurately study. The idea of observing selected areas enabled by the lithography method helps to reveal that 2H-2H and 2H-1T domain boundaries in basal plane of monolayer MoS_2 function as new highly active and tunable sites.[22] Furthermore, the monolayer MoS_2 electrocatalysts with high-density domain and phase boundaries can be feasibly scaled up on a wafer which significantly increases application promise for HER.[23]

Synthesizing catalysts with more exposed edge sites is an effective strategy to improve catalytic performance. In addition, artificially creating more defects by means of plasma and electron beam etching is also a common method to enhance the electrochemical activity of materials. For example, Zhai's group used O_2 plasma technology to control the oxidation degree of oxidized $MoTe_2$ by adjusting the treatment time.[24] The incorporation of oxygen atoms into pristine $MoTe_2$ leads to lattice shrinkage and surface charge enrichment, with a marked increase in HER activity. The on-chip microreactor provides an ideal platform for studying reaction kinetic parameters, long-term device stability, repeatability, energy dissipation, and structure-activity relationship for this work. Wang et al. reported a method of selective vapor etching, which can establish highly active edge sites on the inert MoS_2 substrate and improve its reactivity.[25] In the vapor etching process, various boundary shapes, such as 1D nano-grooves, 2D in-plane triangular depressions, and 3D out-of-plane cavities, can be obtained by controlling different etching temperatures. On-chip microdevices provide a medium for the characterization and quantitative testing of materials. Relying on the traditional three-electrode system, it is difficult to accurately measure the electrocatalytic activity that characterizes the boundary and defect sites of the material. The on-chip micro/nano platform solves this problem well.

3.2. Local Phase Engineering

The physical chemistry of a material is greatly influenced by its crystal structure. Taking the typical MoS_2 as an example, according to the arrangement of atoms in its 2D atomic crystal structure, it can be divided into the 2H phase of the semiconductor state and the 1T phase of the metal state.[26] However, the metal phase with higher electrocatalytic activity for HER is less stable than the semiconductor phase. It is basically impossible to test the catalytic activity of different phases of MoS_2 on the same nanosheet in a conventional electrochemical test system. Benefiting from the advantages of selective area testing of the on-chip micro/nano platform, the activity characterization of different phases of the same nanosheet can be realized. The contact resistance of MoS_2 was first proposed in a report by Voiry et al. in 2016.[4] In the micro/nano electrocatalytic device they designed, the phases of different parts of MoS_2 are changed through local phase transitions, thereby producing different contact impedances (2H-phase MoS_2 itself is a semiconductor, and contact with the Au current collector will make a Schottky barrier; MoS_2 in 1T phase has metallic properties and forms ohmic con-

tact with Au). The results show that the performance of HER is significantly improved with the decrease of contact impedance. This makes the research on the correlation between material phase and catalytic activity more in-depth and introduces the concept of contact resistance for subsequent analysis.

High contact resistance will reduce the electron transport rate and exhibit low electrocatalytic HER performance. On this basis, Zhang et al. further tested the HER performance of metallic phase and semiconductor phase MoS_2 under low contact resistance. [27] They used the method of local phase transition and selective area opening to transform the phase of the part connected to the gold electrode into a metal phase to form an ohmic contact. This on-chip microdevice excludes the effect of contact resistance, which makes the phase of material only matters. And it was confirmed that under the condition of low contact resistance, the HER performance of 2H-MoS_2 with applied back gate voltage is better than that of 1T-MoS_2. In conclusion, on the basis of micro/nano devices, it is possible to systematically and quantitatively study the phase regulation process of electrocatalytic materials, and provide a method for establishing microscopic phase diagrams.

3.3. Heterostructures

Constructing a micro/nano device based on heterostructures, especially 2D stack heterostructure, has been extensively investigated and has become more prevalent recently in the field of photocatalysis, optoelectronic devices as well as fundamental electrocatalysis.[28–30] Heterostructure catalysts, with two or multiple components of active sites, exhibit extraordinary advantages via a synergetic effect. Usually, the electronic coupling at the interfaces of the heterostructures offers possibility to tune the catalytic performance.[31] In the study of heterostructure electrocatalysts, assembling heterostructures is a crucial step before addressing their electrical characteristics through micro/nano platforms. For example, Zhang et al. developed a two-step, low-pressure chemical vapor deposition (CVD) strategy to fabricate MoS_2/hexagonal boron nitride (h-BN) heterostructure stack on Au foils, which was then transferred onto a micro/nano device as a whole.[32] The electrical characterization reveals the high crystalline quality and electronic properties of the fabricated MoS_2/h-BN van der Waals heterostructures, which promotes further electrocatalysis studies in bulk level. In another case of hybrid structures for on-chip electrocatalysis diagnose, Zhou et al. fabricated the MoS_2-WTe_2 heterostructure as a model system to study heterostructure contacts enhancement mechanism.[33] The combination of electrochemical microreactors and theoretical simulation reveals that efficient charge injection through heterojunctions and effective screening of mirror charges induced from the semimetallic nature of WTe_2 favour HER enhancement. The micro/nano electrocatalytic platform presents a pivotal approach to probe interfacial effects in various catalysis schemes.

In conclusion, the electrochemical testing platform based on on-chip micro/nano devices provides a new strategy for catalytic active sites. Selective exposure of different parts of the catalyst enables accurate study of the active sites. The platform has strong operability on nanoscale and makes it easier to control a single variable and find out the factors (Edge, boundary, defect, phase

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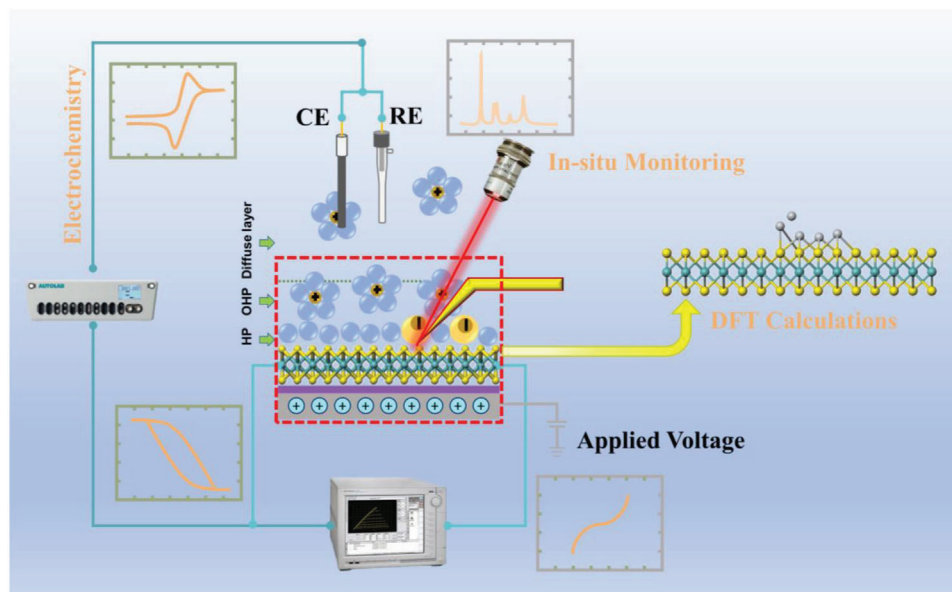
Figure 4. The introduction of modern methodologies (such as in situ characterization, modern calculation, and simulation method) into materials on microscale.

and contact impedance, etc.) that play a catalytic role. Undoubtedly, it makes the quantitative analysis of materials easier with more precise positioning ability and provides a convenient and versatile channel.

4. To Couple Modern Methodologies Down-to Nanoscale

The application of modern advanced materials characterization methods to microscopic materials can bring significant benefits (**Figure 4**). Furthermore, the incorporation of field effect is adaptable due to the higher specific surface area and stronger quantum effects of low-dimensional nanowires/sheets. At the same time, such micromaterials are high-quality objects for theoretical calculations, especially for the research of the doping properties of a small number of atoms.

4.1. Field-Effect Modulation

Field-effect modulation of solid state matter usually refers to the study of electrical transport of a semiconductor or materials with intriguing band gaps (such as graphene, heterostructures) under an applied external physical (electric/magnetic/light etc.) field.[34] This regulation aims to alter carrier concentration or electronic density of state through optimization of the band gap, which is similar to the working principle of field-effect transistor (FET).[35] While most semiconductor-type electrocatalysts display poor conductivity without external electric field, which would remarkably increase internal resistance and overpotential.[36,37] Fortunately, a field-effect regulation on micro/nano electrocatalytic platform, when merged with other fields, can be exploited. The success of these field effect studies requires careful current modulation and overcomes signal-to-noise limitations. Hence when coupling

field-effect regulation down to nanoscale electrocatalysis, the micro/nano electrocatalytic platform is highly considered relative to classic three-electrode bulk electrochemical system.

In 2016, Mai et al. first studied that HER performance of MoS_2 can be enhanced through electric-field-facilitated electron transport.[38] When a back gate is applied on metallic VSe_2 whose conductance would not be affected to exclude the influence of resistance of electrode materials, then the surface ion adsorption dynamics are tuned to result in an enhancement of HER.[14] Importance of this work was also underscored in a photo-electrochemical HER device based on individual MoS_2 nanosheets whereby the electron injection from electrode to active site (considered as contact resistance) is highlighted.[39] Later work further studied that electrons are injected into the conduction band with an applied vertical back-gate voltage, and thus a decreased Fermi level of 2H-MoS_2 as well as a shorter Debye screen length are retained.[27] More recently, field effects have also been demonstrated to amplify the effect of energy storage. For a single α-MnO_2 nanowire, a 3 V back gate voltage can increase its stored charge by 2.5 times and extend its reaction beyond the surface.[40]

The self-gating effect in semiconductor electrocatalysis was discovered by He et al., that is, the conductivity of semiconductor catalysts will be turned on or off during the reaction.[35] This is a reasonable explanation for the high activity of semiconductor catalysts. In the micro-reaction cell, while the electrocatalytic performance is tested, the conductivity of the material is also monitored and saved in real time. It was found in the work that when scanning to a specific potential, the conductivity of MoS_2 is significantly improved, and then the HER begins. This is similar to the field effect regulation of FET, indicating that the material undergoes a process identical to the bottom gate regulation of FET conductance in the electrocatalytic process. Later, after a series of confirmations, the theory was extended to the entire semiconductor system. This discovery is widely applicable to most of the semiconductor catalysts reported so far, and it can screen out

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suitable catalysts for the reaction in advance. At present, many reports have pointed out that in conventional electrochemical test cells, only applying a certain strength of magnetic field can directly enhance the catalytic activity of oxygen reduction reaction (ORR) or OER.[41–44] These studies take the field effect into consideration and provide new ideas for the optimization of catalytic rate and selectivity. Based on precise testing and convenient characterization of micro/nano devices, quantitative testing of the magnetic field enhancement relationship may be realized. Such methods and more are included in recent works and reviews, which provide great perspective of field effect modulation in low-dimensional electrochemistry[45,46] and 2D physics.[47–49]

4.2. In Situ Monitoring

Electrochemical reaction is a complex process involving multiple states of matter. For example, the general HER involves solid catalysts, liquid electrolytes, and gaseous products. During this process, there are changes in both bulk and surface structure of the materials, including modifications in their chemical composition, chemical bonds, and morphology.[50] These changes are accompanied by variations in the electronic structure and conductivity. These are the key factors affecting the performance of electrochemical reactions. The in situ study of electrochemical surfaces is the focus of research on the theory and mechanism of electrocatalytic reactions. However, it has been extremely difficult to introduce spectroscopic techniques into conventional electrochemical cells, and the vacuum environment required by these techniques is often repulsive to the environment in which electrolytes are present. Moreover, additives such as binder and conductive carbon need to be added in the preparation process of conventional electrocatalysts, which will also affect the accuracy of the results. Due to its high integration, patterning, and direct contact with materials, in situ monitoring based on on-chip micro/nano devices has become a cutting-edge method in electrochemical surface research.

The electrical transport spectroscopy (ETS) technique based on the dual-channel (electrochemistry and electrical transport) measurement of micro/nano devices provides a new way for in situ electrochemical surface research. The electrical conductivity of metal nanowires is a vital signal pathway in the study of electrocatalytic kinetics. In 2015, the on-chip micro/nano devices designed by Ding et al. performed on-chip cyclic voltammetry (CV) and in situ conductance tests on PtNWs.[16] It was found that oxygen and its derivatives did not thoroughly permeate PtNWs in the process of OER, which overturned the previous hypothesis. In addition, because the ETS signal has strict surface selectivity, compared with the traditional CV test, ETS can be used for quantitative analysis of the electrode surface. This is also the advantage of on-chip micro/nano device characterization compared with traditional characterization. Similarly, Duan and his colleagues also quantitatively studied the kinetics of adsorption and oxygen reduction of different anions on Pt-based catalysts.[51] In their work, they found that the adsorption of competing anions can inhibit the adsorption of reaction products and the formation of intermediate products, resulting in catalyst poisoning and affecting the ORR process. The current understanding of OER dynamics is limited, especially at the electrode/electrolyte interface. Mai's

team found that dissolved oxygen in the electrolyzer had an inhibitory effect during the OER process.[52] In situ IV test results show that the higher the oxygen content, the higher the initial resistance. At the same time, on-chip micro/nano devices also provide a convenient and practical platform for studying the charge transport behavior of electrode materials in electrolyte systems. The self-controlled gate phenomenon of semiconductor catalysts discovered by He et al. is also realized with the support of in situ electronic/electrochemical measurement techniques.[35] Therefore, the combination of on-chip micro/nano devices and ETS can become an efficient in-situ analysis method, and can obtain important information of electrochemical signals in various complex electrochemical reactions.

Most current studies use traditional spectroscopic methods to analyze factors such as rate-limiting steps and reactivity in the reaction process.[53,54] In a new strategy to exfoliate few-layer flakes from bulk MoS_2 by electrochemical treatment, Pan et al. used in situ Raman spectroscopy to monitor the process.[55] The exfoliation method is driven by the oxidation reaction in the lateral direction of the edge, and the exfoliated MoS_2 rapidly accumulates to form a few-layer structure. The process was monitored by in situ Raman spectroscopy and cross-sectional scanning transmission electron microscopy (STEM). In addition, in situ X-ray diffraction (XRD)[56] techniques and in situ STEM coupled with electron energy loss spectroscopy (EELS) , [57] and electrochemical in situ FTIR[58] based on their fingerprints and surface selection rules etc. are powerful methods to obtain real-time information about the chemical properties of adsorbates and the kinds of solutions involved in electrochemical reactions.

The in situ electron microscopy characterization of materials under extreme conditions such as high vacuum has made significant technological progress in the past decade. For example, Zeng's group demonstrated a reliable process for fabricating in situ liquid-phase TEM electrochemical chips.[59] The top and bottom chips are respectively fabricated by photolithography and electro-etching, and then assembled into the final electrochemical device. The fabricated electrochemical devices can observe the transformation of morphology in electrochemical reactions at the nanoscale in real time, such as the growth of lithium metal dendrites, the formation of solid electrolyte interphase film, electrochemical alloying and dealloying reactions, lithiation reaction. In situ electrochemical surface characterization technology provides a new method for complex electrochemical surface state monitoring and reaction mechanism research, and it has great advantages that cannot be replaced by conventional characterization techniques. These articles can be referred to for more details.[60,61]

4.3. Theory Calculation and Simulation

In the study of electrochemical reactions, pursuing the improvement of efficiency, selectivity, and stability is the core goal of scholars studying catalysts. Based on first-principles calculations of density functional theory (DFT), the electronic structure of the entire catalytic system can be calculated, providing predictive results of catalytic performance without the need for completed synthesis of materials in advance. This computational approach has great research potential for studying the structure-activity

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relationship, providing analysis at the atomic level. With the rapid development of computer technology, it can promote the revelation of electrochemical reaction mechanisms and the prediction of the formation of promising catalysts.[62]

For best-practice modeling studies of electrocatalysis, a fundamental requirement is clearly defining the set of active sites at molecular level.[63] At the macroscopic level, an active site is a fully well-characterized one. This is not the case for first-principles calculations, which require a clear structure file that clearly describes all species and atomic positions around the atom under the synergistic action of the reaction intermediate species. In fact, during the material reaction and electron transfer process, there are usually several intermediate states, which are difficult to detect due to their extremely short life cycle and complex local environment. Molecules on the catalyst surface are highly activated, and molecular motions are difficult to predict on the picosecond scale. This invariably leaves the active site indeterminate and the corresponding catalytic mechanism ambiguous. Therefore, the second critical step is to clearly define all the possibilities that will arise in the selected activity site. This also requires us that in the simulation process, the local value required for electrocatalysis cannot be simply treated like a macro, but the complex dynamic relationship between the active site and the local value must be properly handled. Local values, also known as local environments, provide true local values rather than self-consistently gleaned from reactors or batteries. Microdevices can define active sites and nearby local environment on micro/nano scale, which is consistent with the scale of modeling, especially the theoretical calculation based on first-principal theory (atomic-level to nano-scale). Therefore, the establishment of a microdevice is more conducive to the combination of experiments and theoretical calculations.

The electron transport in the reaction cell or device determines the local environment (pressure, temperature, concentration, pH value, etc.) at different locations, and the local environment in turn determines the coverage of the catalyst surface. Depending on these coverings, catalysts can be well adapted to different (surface) structures and compositions. Obviously, this relationship is difficult to utterly dynamic capture on a single scale. In the process from electrons to micro-nano devices to electrochemical cells, multi-scale frameworks mainly use the differences in time scale and length scale to establish hierarchical coupling, and use rough simulation techniques to capture physical phenomena on larger scales.[64–66] Unfortunately, current multi-scale simulation methods can only statically transfer basic first-principles electronic-level detail information to a coarser level, making computational models susceptible to initial reaction networks and material structures. Meanwhile, all the necessary information needs to be continuously calculated, the high cost considerably limiting the complexity of mechanisms and structures that can be addressed. The localized microenvironment of on-chip platforms provides an opportunity for this. Also, in simulations of active sites, typically only one site type is setting for each reaction intermediate involved, and it does not vary with coverage, reaction conditions, or materials (in the chosen material space). Extending the complexity of these simulations by considering the complex underlying processes on abundant unequal active sites is one of the main challenges.[67–69] We firmly believe that the effective combination of theory and experiment will change the

traditional trial-and-error approach to catalysts and pave the way for the rational design of novel efficient catalysts.

The low-dimensional material information and refined local environment provided by on-chip micro/nanodevices are beneficial. Some cases validate the advantage of micro/nanodevice toward to multiscale simulation. Mai's team experimentally found that sputtering a small amount of Ti clusters (1-3 atoms) on the surface of monolayer MoS_2 can significantly improve the sensitivity of Raman spectroscopy.[70] More importantly, their theoretical calculations also involved a model consisting of the exact number of Ti atoms (1, 3, 7, and 10 Ti). This case strongly confirms that the establishment of a microdevice is more conducive to the combination of experiments and theoretical calculations. Zhai et al proposed a spontaneous molecular intercalation method to confine N_2H_4 in the hybrid superlattice of TaS_2.[71] The selective exposure of nanodevices eliminates the interference of other factors and allows the direct study of intercalation-dependent electrocatalysis. The DFT calculation results of Gibbs free energy of S sites at the edge and base of $2H\text{-}TaS_2$ explain the reason for the enhanced electrocatalytic activity of $TaS_2\text{-}N_2H_4$ hybrid superlattices from thermodynamics. Consequently, the microenvironment refined by on-chip platform is expected to provide a more accurate description of a simulation model (atomic to nanoscale) to the most extent.

5. To Enable New Principal beyond Electrocatalysis

With the increasing development of portable and integrated electronic devices, the demand for microscale electrochemical energy storage devices is urgent. Recently, on-chip micro-batteries, as an energy storage device, have attracted considerable attention due to their excellent fast charging and discharging performance, high power density, and long-life cycle with minimal maintenance. In 2010, Mai et al. established a new general-purpose model suitable for in situ characterization of the electrochemical process of a single nanowire.[14] The device realizes the precise integration between the micro/nano circuit and the energy storage device, and has high detection accuracy and strong acquisition signal. On this basis, researchers can directly observe the complex reaction mechanism in the process of energy storage and conversion, so as to deduce the working principle of energy conversion.

In the field of microelectronics, integrated circuits made of micro/nano devices have the advantages of small size, low power consumption, high reliability, and robust scalability. Optoelectronic device is developed on the basis of microelectronics technology to realize the mutual conversion between light and electricity. This type of device has begun to play an increasingly important role in social production practice and it is widely used in solar photovoltaic cells,[72] light-emitting diodes (LEDs),[73] photoelectric detection[74–76] and other fields. Recently, an on-chip light-incorporated in situ transmission electron microscopy technique has been reported, which can in situ characterize the optical response behavior of metal halide perovskites (MHPs) at nanoscale.[77] The window on the in situ chip can fit multiple sample loading nets and this helps to have a deeper understanding of the degradation behavior of MHPs in vacuum under light. The micro-nano characterization system has great potential in material selection and lifetime prediction of solar cells. In the

application domain of micro-LED, a magnetic-force-assisted dielectrophoretic self-assembly technology (MDSAT) has been proposed, which can accurately capture and assemble micro-LED by combining magnetic and dielectrophoresis forces.[78] MDSAT has strong scalability and high transmission efficiency, which makes the screen equipped with the micro-technology has uniform photoluminescence, good transfer characteristics, and has a strong competitiveness in the mainstream commercial products. In recent years, the pursuit of high efficiency and accuracy of photon control has been increasingly desired. In this regard, the on-chip platforms with optical switches or optical modulators are critical and highly demanded to address the above issues.

A thermoelectric device refers to a device that uses the thermoelectric effect to achieve energy conversion when there is a temperature difference between two different conductor materials. Micro/nano thermoelectric devices have a wide range of applications, including energy conversion and storage,[79] temperature measurement and control, biosensing, temperature sensors,[80] thermoelectric generator,[81] etc. Nano thermoelectric refrigerators[82] have high cooling efficiency, low cooling temperature, fast response, small size, light weight, and low power consumption, and can be used in micro-refrigeration, electronic component heat dissipation, and optical device cooling. The development of micro/nano thermoelectric devices is of great significance to the development of micro/nano technology and energy technology. It will provide new solutions for future miniaturization, intelligence, greening, and sustainable development.

The application range of micro/nano devices is not limited to photoelectric and pyroelectric signals, but has been extended to humidity detection, pressure sensing, and superconductivity. AgNLs-based humidity sensor[83] is highly sensitive to small humidity changes in the environment, and can even monitor breathing, which has excellent application prospects in biomedicine. Moreover, researchers explored a special metal-hydrogel-metal (M-H-M) nanocavity structure by exploiting the property of hydrogels that are very sensitive to humidity changes.[84] The thickness of the nanocavity can be adjusted by encoding, which can be applied to triple nanoprinting imaging technology with independent information encryption and color multiplexing schemes. The performance of the flexible wearable pressure sensor is even better than that of human skin in terms of sensitivity and response time.[85] With its ultra-low power consumption and high stretchability, it can be applied to long-term wearable application scenarios. The superconducting nano-droplets can realize stretchable and printable superconducting microcircuits, breaking through the drawbacks of rigidity and poor connectivity of traditional high-temperature superconducting materials, and can be integrated into flexible micro/nano devices.[86] The role of micro-nano devices in microelectronics, materials science, physics, chemistry,[87] biology, and medicine[88] cannot be ignored, and it promotes the interdisciplinary comprehensive application.

6. Perspective

This perspective primarily summarizes the progress in micro/nano devices for in situ characterization of electrochemical reactions, particularly in electrocatalysis. The coupling with other techniques such as nanochemistry, spectroelectrochemistry, and scanning electrochemical microscopy is highly desired. In order to fully understand and unveil the potential of on-chip electrocatalysis microdevices, there is much work left to be done, as this field presents a plethora of opportunities and challenges.

First, due to the limitations of technology, only low-dimensional nanomaterials can be used. At present, most of the raw materials for on-chip micro-nano devices are nanowires/sheets, which limits the scope of application of the platform. At the same time, the measurement of materials is still limited to simple IV testing, bottom gate control, Raman spectroscopy testing, etc., which does not give full play to the mature measurement advantages of modern semiconductor research. Due to the corrosion of the electrode material by the reaction itself, the device does not support long-term continuous measurement. Regarding electrochemical reactions, on-chip platforms are primarily used in simple reactions such as HER and OER. For complex reactions involving reactants with more phases (such as the gas phase), further development and verification are required.

Second, the decoupling of resolution of materials and protocols. Since materials are at the micro/nanometer level, the electrochemical current is also small, at the nanoampere (nA) level. This means that the results are particularly susceptible to disturbances, and even minimal disturbances will cause large deviations. In addition, it is equally essential to decouple the information obtained from the test, and the spatial and temporal resolution of conventional characterization techniques on micro/nano devices also needs to be improved.

Finally, a real reaction environment. At present, the operating environment generally defaults to conventional conditions (room temperature, room pressure, etc.), and most of the processing is still focused on the material itself. For the whole device, adjustment methods such as additional electric, magnetic, or light fields are also worthy of attention. For the material itself, more adjustment strategies need to be developed to make it more like a real environment. Factors such as sudden changes in temperature, time corruption on itself, and light in real environments should all be taken into consideration.

To mitigate the above issues, what to expect and where do we go from here?

Materials Scheme: This calls for high-quality materials which can be scaled up. For example, a routine approach to construct vertical heterostructure stack involves polymer-assisted transfer of exfoliated layers which inevitably induces interfacial contamination and results in device performance degradation. For the preparation of 2D materials by CVD, the influence of defects can and should be excluded. Today, the magnetron sputtering technology is quite mature. It has the advantages of high speed, low temperature, low damage, and uniform coating. Most materials (metals, semiconductors, etc.) can be sputtered as long as they can be made into targets. It has great potential to replace the chemical synthesis of 2D materials and ensures the uniformity and purity. Exploring more efficient and gentle synthesis and transfer methods is still an important part. Moreover, efficient back gate regulation is still plagued by additional energy consumption and difficult operation for practical applications and is limited by ultra-thin materials. For this, other field modulations (magnetic field, light field, force field, etc.) deserve attention.

Instrumental Advances: In recent years, scanning electrochemical microscopy can directly and selectively characterize the local activity of nano-electrocatalysts. At the same time, differential electrochemical mass spectrometry, electrochemical quartz crystal balance, and other technologies are used to realize simultaneous identification of various intermediate reactants and products, and to conduct in-depth analysis of their catalytic performance.[2] In situ attenuated total reflection surface-enhanced infrared absorption spectroscopy (in situ ATR-SEIRAS), is an infrared spectral analysis technique for surface adsorbates.[89,90] Its high selectivity, better time resolution, and no sample pretreatment are required. Combined with the on-chip platform, it will play a greater advantage in the field of microscopic analysis. Unfortunately, handling unforeseen irregularities in nanoscale materials can be a challenge when working with equipment for bulk and may even require specialized molds to ensure accurate and consistent results. Sometimes, major changes to existing equipment are not pursued, while optimizations in sample preparation, device construction, and connection mode are more encouraged to fit the equipment, which is usually operated toward bulk materials.

Integrated Techniques: On-chip micro/nano devices are mainly based on the measurement of physical properties and cannot directly generate chemical information like spectroscopy. It is crucial to explore more direct and efficient in situ characterization techniques. In addition, compared with traditional electrochemical cells, the reactants and products of micro/nano devices are not tolerant, and the gas-liquid phase detection technology needs to be further improved. Using simulation technology based on computer science is one of the important research methods. The use of device simulations coupled with multiple physical fields can not only reduce the difficulty of theoretical analysis, but also provide more comprehensive data support for experimental observations and theoretical models. Introducing emerging machine learning techniques in multiscale device framework models can greatly advance the development of electrochemical technologies.

Extending Application Scenario: In addition to simple electrocatalysis like HER and OER, the on-chip micro/nano platform has the potential to be applied to other electrochemical reactions,[91] which has been extensively studied recently. In addition to electrochemical research, on-chip integrated micro-nano devices have essential application values in energy conversion, information storage, biosensing, and nanomedicine.

7. Conclusion

This perspective answers what makes on-chip microdevices stand out in electrocatalysis. We outline the significant advantages of on-chip micro/nano devices in electrochemical reactions of nanomaterials, which can extract individual response from the bulk. In addition, we highlight its selective properties for functional active sites. Specifically, through the selective exposure and adjustment of the exposed area of specific regions, such as the edge, interface, and defects of the catalyst material, it can provide a precise control strategy while avoiding the interference of other factors. At the same time, the introduction of modern methods such as electric field regulation, in situ characterization, and theory calculation has made reaction measurement more accurate and convenient, providing new ways for performance optimiza-

tion. More importantly, there is a vast research potential in other fields. The evolution of materials and the upgrading of equipment will endow us with more opportunities to disclose more interesting phenomena and uncovered science issues. However, on-chip micro/nano devices are still in their infancy, and their potential has not been fully realized. There are many hurdles to overcome to fully understand and fully exploit its potential. We hope this Perspective can make researchers cutting-edge and provide a prospectus of where we might go.

Conflict of Interest

The authors declare no conflict of interest.

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