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Review Article

Electrocatalysis on ultra-thin 2D electrodes: New concepts and prospects for tailoring reactivity

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Abstract

The convergence of surface and bulk in 2D electrodes enables the swift exploration and control of interfacial reactivity. Owing to their versatile synthesis and modification, these interfaces have emerged as unique electrode models to study the impact of electrode composition, heterostructure formation, and the presence of defects, on their electrocatalytic response. This is because the ultra-thin nature of materials such as graphene, MoS_2, and MXenes allows to amplify the role of these structural motifs in defining their electrode responses. Their 2D geometry also facilitates the systematic tailoring of properties for enhancing reactivity using simple methodologies such as adsorption and elemental substitution. In this opinion, we showcase and discuss how these aspects make 2D materials an attractive platform for understanding electrocatalysis.

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Graphene, MXenes, Molybdenum disulfide, Electrocatalysis, Heterointerface.

Introduction

Many electrochemical processes, including classes of redox and electrocatalytic reactions, are surface-limited, *i.e.* they occur at the interface formed by two dissimilar media. The reactivity of such systems depends largely on the interfacial structure rather than on the bulk. Thus, as depicted in Scheme 1, thinning a bulk macroscopic electrode would not change the electrode response to reactions such as ferrocene oxidation or the reduction of H^+ to H_2. Scheme 1 depicts now a thinning of the electrode down to a single monoatomic layer. At this nanometer scale, quantum-mechanical effects involved in electron transfer become relevant. For example, the electron density of states and electronic coupling arguments in the theories of Marcus and Gerischer are dependent on the type and extent of materials [1,2]. Thus, bulk and 2D materials can exhibit stark differences in their reactivity. Likewise, at this atomic scale features such as edges and defects, whose activity and study are often obscured by the bulk, suddenly become evident or amplified to predominance.

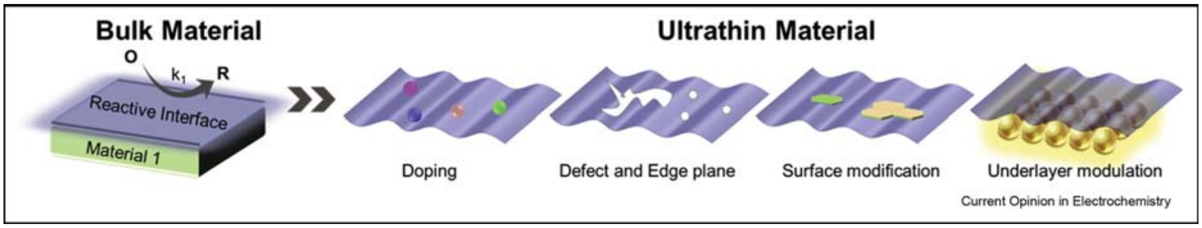
In this opinion, we address the opportunities brought by new 2D electrodes and their heterointerfaces for understanding fundamental aspects of their electrocatalysis. Electrodes made of graphene, molybdenum disulfide, and MXenes recently introduced in the literature are uniquely positioned to highlight the advantages of ultra-thin materials in exploring interfacial reactivity. These materials also represent synthetically versatile platforms on which to explore new concepts of electrode design.

The electrochemical transparency of graphene

The synthetic versatility of graphene positioned it as one of the most attractive 2D materials for exploring electrocatalyst design principles. Diverse synthesis methods enable graphene architectures from small quantum dots, nanoribbons, and reduced graphene oxide flakes, to large (doped-) graphene films and complex 3D aerogels [3,4]. Graphene is commonly used as a supporting material for electrocatalysts due to its electrochemical stability, exceptional electrical conductivity, and fascinating specific surface area [5]. The low reactivity of the graphitic basal plane towards bond breaking/forming reactions such as those involved in O_2 and H_2 electrocatalysis, makes graphene an ideal platform to understand how its interactions with other materials improve electrocatalytic function.

The atomic thickness of graphene can be exploited to modulate the reactivity of a heterointerface (Scheme 1) *via* interactive electrocatalytic coupling. Single layer graphene was explored as a semitransparent barrier for hydrogen evolution reaction (HER) on Cu [6]. In this study, a Cu/G (G stands for graphene) interface

Scheme 1



Representation of ultrathin materials for various catalytic modifications.

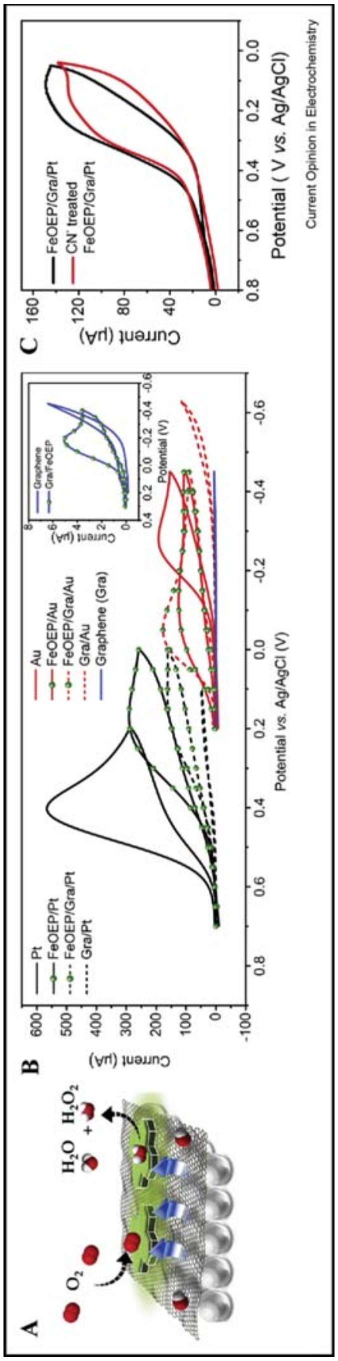
showed an intermediate HER activity when compared to Cu (more active) and graphene (less active). These observations suggested an electronic semi-transparency effect in which Cu participates partially in the reaction despite being buried below graphene. Such electronic effects have been also suggested in scanning tunneling microscopy experiments of the Cu/G interface [7], while images of graphite itself, despite its well-known honeycomb structure, reflect the impact of the electronic density of states of layers beneath the topmost carbon sheet [8]. Our group recently reported a six-fold increase in the k^0 of metal/graphene heterostructures towards outer-sphere redox reactions, which we hypothesize derive from a similar electronic transparency [9]. Furthering these observations, we performed a systematic study of various electrocatalyst heterostructures for the oxygen reduction reaction (ORR), in which the catalytic activity was tuned *via* the synergistic effect of metal substrate doping and the adsorption of a molecular catalyst (Figure 1A and B) [10]. This study resulted in two relevant observations. First, that while underlayer modification of graphene with a metal can lead to kinetic improvements due to electron donation, the surface mechanism of the reaction remains that of the overlayer, *e.g.* primarily a H_2O_2-forming route for graphene during the ORR. And second, that electronic perturbations are metal-dependent and can be propagated to molecular catalysts adsorbed onto the graphene basal plane. Specifically, the reactivity of a Pt/G/porphyrin interface was superior to its Au/G/porphyrin analogue. Furthermore, and exploiting the electrocatalyst support nature of graphene, the resulting heterointerface demonstrated excellent long-term stability and cyanide poisoning resistance due to its physical impermeability (Figure 1C) [10]. This strong coupled interaction between graphene and active component has been applied as design principle for other OER and HER electrocatalysts as well, *e.g.* Co—B and Ni—Fe Hydroxide nanosheets [15,16]. Owing to the electronically tunable and interactive nature of the basal plane of graphene, we foresee that this material will keep playing a crucial role on fundamental studies of ultrathin electrocatalysts.

Amplifying the role of defects: graphene and MoS_2

Exploring the role of structural features on 2D materials, such as edges, point defects, and the basal plane is of great interest to identify strategies to improve electrocatalytic behavior. Introducing defects to create edge-rich graphene and heteroatom doping are two common low-cost, metal-free strategies for enhancing ORR activity [11—14]. Identifying the active sites of these materials provides guidance for future design of graphene-based catalysts. Recently, Wang et al. identified the *ortho*-carbon atom nearest to pyridinic-N as the reactive site of N-doped graphene ORR electrocatalyst *via* selective acetyl group blocking [13], in agreement with first-principles calculations [14]. Furthering this concept, dual-doped graphene with two heteroatoms opens new scenarios for multifunctional electrocatalysts with enhanced activities, Figure 2A. Using the binding energies of ORR intermediates as descriptors, Li et al. calculated a volcano plot-type relationship of dual-doped graphene catalysts (Figure 2B) [14]. Simulations suggested that Z—N—P (Zigzag edge N—P) and G—B—Sb (Basal plane B—Sb) dual-doped graphene have smaller ORR overpotentials than Pt [15].By increasing the active P—N bond concentration, *Chai* et al. demonstrated a bifunctional dual-doped graphene electrocatalyst with exceptional ORR and OER (oxygen evolution reaction) activity (Figure 2C) [15]. Other combinations such as Ru—N, N—F dual-doped graphene also exhibited efficient ORR and OER properties, respectively [16,17].

We now turn to discuss the role of edges and their atomic substitutions in 2D materials. Molybdenum disulfide (MoS_2) belongs to the category of transition-metal dichalcogenides [18], and it has served as a great model system to explore the impact of surface features. Typically synthesized by chemical vapor deposition (CVD) or liquid or chemical exfoliation [19], the band gap energy and catalytic activity of MoS_2 is dependent on the crystal structure, number of layers, and the presence of defects [20]. When layers of MoS_2 are removed until a single layer remains, the bulk material transforms from an indirect-gap semiconductor to

Figure 1



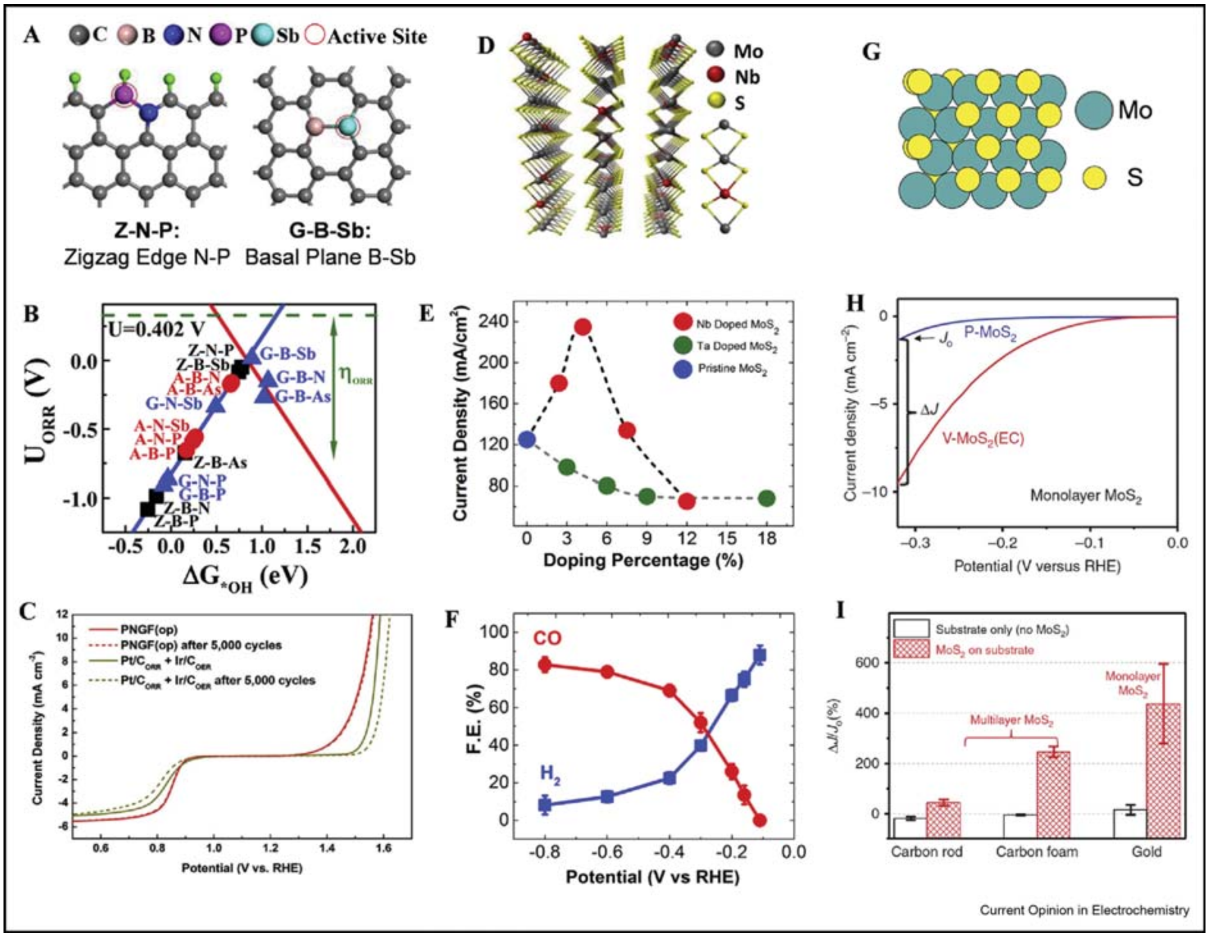
Experimental studies of basal plane modification for graphene elecrocatalysis. **A**. Schematic of ORR on molecular catalyst/graphene/Pt heterostructures. **B**, ORR behavior on various combination heterostructures. **C**. Resistance to poisoning by cyanide ion of the graphene heterointerface in A. Reprinted with permission from Ref. [10]. Copyright 2018 American Chemical Society.

a more electrochemically active direct bandgap semiconductor. This has been shown experimentally through the increase in photoluminescence with decreasing layer number [21,22]. MoS_2 is a promising candidate to fulfill the role of an electrocatalyst for two prominent reactions: the HER and carbon dioxide reduction (CO_2R) [18,23–25]. Early theoretical and experimental electrocatalytic research into single MoS_2 crystals showed an increased reactivity for H_2 production at the edge sites over the basal plane [18,26]. From these early findings there has been steady progress towards increasing the reactivity of MoS_2 for HER, either through increasing edge plane reactivity, or increasing the reactivity of the basal plane [27–30].

Similar to the HER, CO_2R is also more active at the edge site of MoS_2. To increase the performance of CO_2 reduction, Salehi-Khojin et al. chose Nb and Ta to selectively dope the edge plane of MoS_2 (Figure 2D) [30]. Using different doping levels in the CVD process the group was able to form regions of NbS_2 and TaS_2 on the edges of MoS_2 that possess a metallic behavior due to a half-filled valence band [31]. The produced ultrathin electrodes were tested in a CO_2 saturated ionic liquid. The group found that Nb acted as a more proficient dopant for CO_2R, and that Ta reduced the reactivity as compared to the pristine material (Figure 2E). They also found that $Mo_{0.95}Nb_{0.05}S_2$ produced the highest current density, faradaic efficiency, and turn over frequency (Figure 2F). Reduction of CO_2 on MoS_2 has also been shown in aqueous environments, but competition with HER results in low faradaic efficiency [25,32]. Overall, these experiments highlight the value of 2D materials in helping amplify the role of surface features in the electrochemical response of a sample, in these cases allowing correlations between structure and reactivity.

Work towards improving basal plane reactivity in MoS_2 has been achieved through various methodologies including cation intercalation, controlling underlying morphology, and generation of sulfur vacancies [27–29]. Recently a new electrochemical method was reported for creating sulfur vacancies in MoS_2 (Figure 2G) [29]. In monolayer MoS_2 supported on Au, treatment by a linear sweep voltammogram in 0.5 M sulfuric acid created a S-vacancy of ~15%, which increased the current density of HER by ~438% over pristine MoS_2 (Figure 2H). The groups furthermore showed the versatility of the electrochemical removal of sulfur by applying a potential step to multilayer MoS_2 on carbon supports. Like in the case of monolayer MoS_2, desulfurization caused an increase in current density for HER, although thicker samples were not as active as monolayer MoS_2 (Figure 2I). As shown in Figure 2I, different responses were also measured on distinct electrode supports. Considering the impact of the support electrode described by Hui et al. [9], the impact of

Figure 2



Theoretical and experimental studies of modified graphene and MoS_2 elecrocatalysis. **A**, Atomic structure of dual-doped graphene material. **B,** Volcano plot of ORR limiting potential (U_{ORR}) and *OH adsorption Gibbs free energy (ΔG_{*OH}) for various dual-heteroatom doped graphene electrocatalyst. **A** and **B** Reprinted with permission from Ref. [14]. Copyright 2017 American Chemical Society. **C**, OER and ORR activities of P-N dual-doped graphene framework (PNFG) and its comparison with Pt/C and It/C for durability. Reprinted from Ref. [15] copyright (2017), with permission from The Royal Society of Chemistry. **D**, Structure of Nb-doped MoS_2. **E**, Plot of CO_2R current density *vs.* doping of Nb and Ta on MoS_2 edge sites. **F**, Faradaic efficiency of Nb doped MoS_2. **D-F**, reprinted with permission from Ref. [30]. Copyright 2017 American Chemical Society. **G**, Structure of MoS_2 with S vacancies. **H**, Plot of current density vs voltage for pristine MoS_2 and MoS_2 with S vacancies. **I**, Normalized current density vs type of MoS_2 catalyst. **G–I**, reprinted with permission from Ref. [29].

a metallic gold *vs.* non-metallic carbon support on the band structure of MoS_2 needs to be investigated to truly parse out contributions of decreasing layer number and substrate effects. These observations also suggest a practical warning: while monolayer materials are useful as reaction models, they are also affected by underlayer structures.

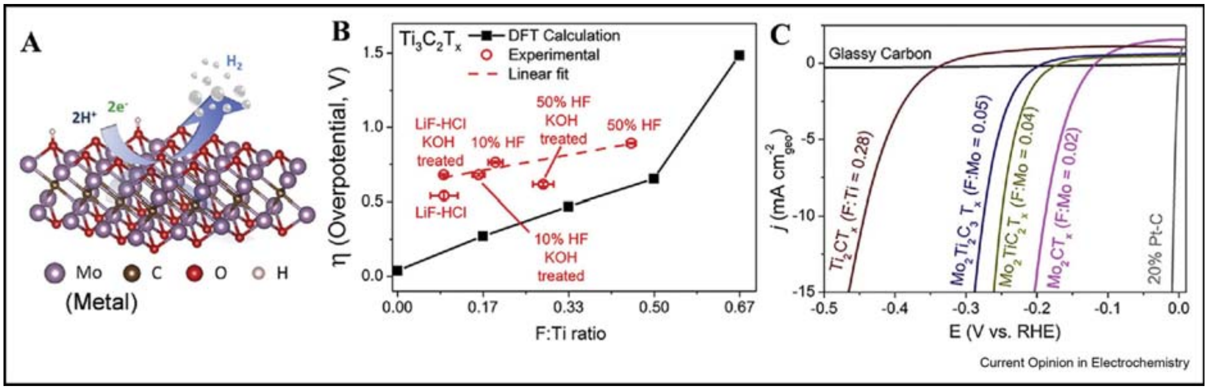
One other way in which ultra-thin electrodes can be used to amplify the impact of structural variables on their electrochemistry is by enabling unique chemo-mechanics [33]. Recently, the simultaneous impact of vacancy chemistry and strain was probed using thin MoS_2 samples in combination with scanning electrochemical microscopy [34]. In this case, effecting and measuring the strain on a thin sample is easier than in the bulk counterpart.

Exploring reactivity on the *bulk of a monolayer* via versatile MXenes

An emerging class of materials for exploring the impact of composition and surface termination on the electrocatalytic behavior of 2D structures are MXenes [35]. Derived from carbides and nitrides of the phase $M_{n+1}AX_n$, where M is an early transition metal, A is typically a group IIIA or IVA element, X is C or N, and n = 1, 2, or 3. MXenes are the product of selectively removing the A-group to form $M_{n+1}X_nT_x$, where T is a terminal functional group [36–39]. Exfoliation of MAX phase materials produces 2D nanosheets, optimal for exploring the layer number and species variability effect on reactivity.

Electrocatalysis involving MXenes has predominantly been regarding HER, where new theoretical tools such

Figure 3



DFT and experimental results on the impact of edge sites on MXenes. **A**, Structure of MXenes with a functional basal plane for HER. **B**, DFT and experimental results of overpotential of HER *vs.* F:Ti ratio for $Ti_3C_2T_x$ terminated with varying degrees of F. **C**, Plot of current density vs potential comparing the onset for HER of $Ti_3C_2T_x$ and Mo_2CT_X. Figures reprinted with permission from Ref. [42]. Copyright 2018 American Chemical Society.

as surface Pourbaix diagrams have been introduced to address the reactivity of these samples with varying transition metals and surface terminations [40–44]. An example of the synthetic versatility and amplified electrochemical response from the substitutional chemistry in an ultra-thin sample came from a collaboration of the groups of Gogotsi, Vojvodic, and Seh [42]. Using DFT the groups looked at the effect of swapping fluorine for oxygen as terminating groups on $Ti_3C_2T_x$, Ti_2CT_x, Mo_2CT_x, $Mo_2TiC_2T_x$, and $Mo_2Ti_2C_3T_x$ (Figure 3A) [43]. Testing the HER the researchers found the MXenes with the lowest ratio of fluorine terminating groups produced the highest activity, *i.e.* lower overpotential (Figure 3B). The groups also found the same trend for their Mo based MXenes, in accordance with the DFT findings (Figure 3C). The increase in electrochemically active surface area and the decrease in mass of material by decreasing layer of MXenes exemplifies the beneficial qualities of 2D electrodes over their bulk counterparts. This is further highlighted by the simple preparation methods used in these studies, where F substitution was achieved by exposure to fluoride containing solutions.

The number of layers that compose MXenes suggests also thickness-dependent activity. When the researchers used sonication to break up the basal plane of Mo_2CT_x, the overpotential for HER almost doubled. Seh et al. concluded this means that the basal plane of MXenes is inherently active towards HER, unlike graphene and MoS_2 discussed above. It is an exciting time for discovering new MXenes, where these materials present exciting prospects in the search for superior non-precious metal electrocatalysts. These 2D interfaces create new opportunities for systematically exploring how chemical and structural substitutions on the *bulk of a monolayer* impact reactivity [45].

Outlook

Chemical versatility is essential for swiftly tuning the properties of materials to explore their electrochemical behavior. As highlighted here, by working with ultrathin electrodes it is possible to amplify the structural and chemical motifs that lead to improved electrochemical reactivity. Graphene, MoS_2, and MXenes serve as exemplary platforms for diverse chemical alterations that can be systematically modified to generate new electrocatalytic performances. The synthetic versatility of these materials facilitates the identification of new chemistries and new reactive trends. Here, we showed how simple procedures such as molecular adsorption, ion substitution, and defect creation can be conveniently explored in 2D materials to impact dramatically their activity. The electroanalysis of interfacial properties will always be essential for designing next generation electrocatalysts, and ultra-thin electrodes are ideal platforms for concentrating experimental efforts where it counts: at the interface.

Conflicts of interest statement

Nothing declared.

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