Supporting Information

The Influence of Nanoconfinement on Electrocatalysis

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The Influence of Nanoconfinement on Electrocatalysis
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Abstract: The use of nanoparticles and nanostructured electrodes are abundant in electrocatalysis. These nanometric systems contain elements of nanoconfinement in different degrees depending on the geometry, which can have a much greater effect on activity and selectivity than often considered. In this review, we firstly identify the systems containing different degrees of nanoconfinement and how they can affect the activity and selectivity of electrocatalytic reactions. Then we follow with a fundamental understanding of how electrochemistry and electrocatalysis are affected by nanoconfinement, which thanks to the development of new, atomically precise manufacturing and fabrication techniques, and advances in theoretical modelling, is beginning to be uncovered. The aim of this review is to help us look beyond using nanostructuring as just a way to increase surface area, but also to break the scaling relations imposed on electrocatalysis by thermodynamics.

1. Introduction

Nanoconfinement is beginning to attract interest as a strategy for influencing electrocatalytic performance and hence it is crucial to understand the impact of nanoconfinement on electrocatalytic processes. In fact, an important review by Montoya et al. proposed nanoconfinement as one of six strategies to break the scaling law limitation. By definition, nanoconfinement is confinement in a nanosized region, with the prefix nano- commonly described as being of dimensions less than 100 nm. From a functional perspective for electrocatalysis, nanoconfinement can be better described as confined regions where the solution environment is different to that observed at a macroscale surface. Such differences could present themselves as changes in reactant adsorption energies, or as changes in electrolyte composition and reactant concentration, due to changes in mass transport of reactants and products to and from the electrode surface. Nanoconfinement is of such interest as it can provide benefits above the common paradigm in thinking in electrocatalysis that is dominated by the Sabatier principle. The Sabatier principle focuses on the optimal catalyst having a balance between adsorption energies, so reactants bind, but not too strongly to allow bonds to dissociate and the products leave the surface. Implicit in this principle is that the optimal binding energy pertains to the rate determining step. The optimization of a catalyst based on adsorption energies however have a theoretical limit. This limit in catalysis development arises when the same bonds are involved in the adsorption of reactants and desorption of products and are referred to as the linear scaling law limitation. To further enhance the activity of a catalyst beyond optimizing binding energies, a common approach is to increase the number of exposed active sites by increasing the surface area using nanostructures. This nano-structuring often results in confined spaces between the solid material. A key question this review aims to shed light on is how significant is the existence of these nonconfined spaces on electrocatalytic performance? Because of the emphasis in electrocatalysis on the Sabatier principle, the enhancement we often see when using nanostructured electrocatalysts are sometimes attributed to electronic effects. While the effects of electrons should not be dismissed, other effects, including increased collisions due to short diffusion lengths, steric hindrance, reactant accumulation, and electrical double layer overlapping that can arise in nanoconfined spaces, should also not be overlooked. Synthesizing or fabricating experimental systems with well-defined nanoconfinement however can be challenging so our understanding of nanoconfinement in electrocatalysis is in its infancy.

Recently, it has become evident that nanoconfinement in highly porous electrocatalysts may also be contributing to improvements in specific activity of electrocatalysts. In fact, there are studies that show nanoconfinement is the predominant factor in influencing the selectivity and kinetics of electrochemical reactions. In this review, we first give an overview of nanostructures, grouped by their relative degree of nanoconfinement freedom, with examples highlighting how electrocatalytic performance is affected by the presence of nanoconfined spaces. In subsequent sections, we discuss fundamental aspects of electrochemistry under nanoconfinement and how the different extents of confinement that these nanostructures bring affects electrocatalysis.

2. Overview of nanoconfined systems

Electrocatalytic systems with elements of nanoconfinement that contribute to electrocatalytic performance are becoming more widespread in the literature. The extent of nanoconfinement is determined not only by the spacing distances between opposite sides of a channel or pore, but also by the degree of freedom by which a species can enter and leave the nanoconfined space. As such, we categorize nanoconfined systems based on their degree of freedom. The lower the degree of freedom, the greater the confinement of the electrocatalytic system. We will discuss four scenarios, as depicted in Figure 1a.

2.1. Nanoconfinement between particles, pillars, and branches

Architectures that potentially exhibit some nanoconfinement, but possess the highest degree of freedom, include nanowires, close spaced nanoparticles on an electrode, or nanoparticles with branches or spikes (Figure 1a). Mass transport between the confined regions and the bulk solution is largely unimpeded, with the effects of nanoconfinement only experienced when the solution species are located between closely spaced protrusions. The effects from nanoconfinement were demonstrated theoretically by Chang and co-workers showing that the faradaic efficiency for
the CO₂ reduction reaction (CO₂RR) to CO over the competing hydrogen evolution reaction (HER) was improved.

This was attributed to the stabilisation (increased adsorption energy) of the key reaction intermediate (*COOH) due to its van der Waals interactions with the confining surface (*COOH) due to its van der Waals interactions with the confining surface (Figure 1b) in nanoconfined spaces between Au and Ag nanoparticles and. Using modelling Nesselberger et al. [2b] has also observed an increased specific activity for the oxygen reduction reaction (ORR) occurring between proximal Pt nanoparticles due to a decrease in adsorption energy of oxygen caused by double layer overlap in the nanoconfined region. They suggest that overlapping electrical double layers decrease the potential drop in the space between nanoclusters that have sufficiently small edge-to-edge distances. This decreases the adsorption strength, and hence coverage, of oxygenated species on the electrode surface, resulting in a sharp increase in specific activity for ORR as the edge-to-edge distance between particles decreases.

Ma and co-workers,[10] have shown selectivity for C₂, products for the CO₂ reduction reaction with Cu nanowire arrays of varying length and density. This was attributed to the higher local pH in the nanoconfined spaces compared to the bulk pH caused by hindered diffusion of HCO₃⁻ into and produced OH⁻ out of the Cu dense nanowire array. Higher local pH can both hinder HER and facilitate the reduction of the intermediate CO to C₂H₄, C₂H₆, ethanol and propanol.[10] Hence the nanoconfinement within high density nanowire arrays can locally counteract the buffering ability of the electrolyte solution, thus increasing the local pH and promoting the formation of such products. In a contrasting example, Myekhlai et al.[11] highlighted using Pd-core Ru-branching nanoparticles for the oxygen evolution reaction (OER) that the produced oxygen bubbles become entrapped in the nanoconfined spaces effectively limiting the electrolyte/catalyst interface. This

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became more prominent when the branch number per nanoparticle increased such that the spacing between branches decreased.

2.2. Nanoconfinement between two parallel planes

This geometry restricts the movement of species to the space between the planes, decreasing the degree of freedom compared to nanowires (Figure 1a). An example of how the level of nanoconfinement arising from this geometry affects electrocatalytic reactions was given by Zhou and co-workers looking at combinations of graphene-covered metallic surfaces for HER using DFT calculations (Figure 1c). Different HER rates compared to their bare metal counterparts were observed and was attributed to weakened adsorption of hydrogen when it is confined between the graphene and metal surfaces. This was observed for all metals investigated and was attributed to both the energy penalty caused by lifting the graphene overlayer to provide enough space for the adsorbed H, and graphene pushing H to be closer to the metal.

Yao et al. also observed weakened CO adsorption by the presence of a graphene overlayer on a Pt surface using simulations and DFT calculations, which facilitates CO oxidation with lower apparent activation energy compared to a bare Pt surface. The sub-nanometre distance between the graphene overlayer and the metal substrate allows charge transfer between graphene and the CO and O adsorbates to weaken the C-O bond promoting the formation of the O-CO bond during CO oxidation. Experimental results by Zhang and co-workers supports the studies above. With a Pt surface under a 2D hexagonal boron nitride (h-BN)
overlayer, CO adsorption on Pt was significantly weakened due to the effect of confinement in between the layers, alleviating the CO poisoning effects, and hence facilitating CO oxidation at the interface. Within their own study, the authors compare the adsorption energy decrease seen when using a h-BN overlayer compared to a graphene overlayer, and they suggest that it is the electronic interaction between the overlayer and the metal surface that determines the influence of the effect of confinement. A more significant decrease is seen for the polar h-BN sheet, which may interact more strongly with the metal substrate than the nonpolar graphene.

2.3. Nanoconfinement in mesoporous nanoparticles and films

Mesoporous films and nanoparticles are the most common structure investigated experimentally. These materials have interconnected pores and thus an even lower degree of freedom, compared to the previous two geometries (Figure 1a). This is because a solution species entering the mesoporous environment can only move along the pore spaces, resulting in noticeable changes in solution environment compared to the bulk solution. A 3D-system comprises of interconnected mesopores, however, can still be thought of as a single mass transport system (Figure 2b) as distinct from the parallel plates or completely isolated nanopores (see below) where each nanoconfined space is a separate mass transport system (Figure 2c-d). There are important consequences of this difference, including more facile diffusion due to higher accessibility for species to enter and leave unimpeached.\[13\] This type of confined system with interconnected, open pores can provide a different solution environment to the bulk solution, which can impact both the activity and selectivity. Using porous Ni-Pt surfaces, Benn et al.\[14\] demonstrated selectivity for the ORR even in the potential ranges normally dominated by hydrogen evolution (HER) and was ascribed to the depletion of H\(^+\) inside the nano-pores hindering HER whilst oxygen reduction proceeds via a water dissociation mechanism not requiring H\(^+\). Porous geometries can also act as a sieve to exclude larger species as shown by Ding et al.\[15\] with nickel nanostructures within a silica nanochannel membrane for glucose oxidation. The 2-3 nm diameter silica channels enabled molecular selectivity by blocking large biofouling molecules and allowing small glucose molecules to permeate through the channels, resulting in increased sensitivity and a low limit of detection.

Snyder and co-workers\[13\] observed that both ORR mass transport and specific activity increase as the depth of Pt-Ni surface porosity decreases (Figure 1d (left)). They hypothesized that the active surface area of porous electrodes may not always equal the surface area determined by H\(_{UPD}\), and that the active area may be a function of potential. At high overpotentials (Figure 1d (top)), the active area is effectively equal to the electrode geometric area as nearly all reactant-substrate interactions result in electron transfer. However, in porous materials at low overpotentials (Figure 1d (bottom)), the 2 nm diameter pores increased the frequency of collisions and hence enhanced probability of electron transfer. Less reactant depletion also means that oxygen can reach further into the porous geometry resulting in a higher electroactive surface area.

2.4. Nanoconfinement in isolated channels

This is the most confined geometry, with the fewest degrees of freedom (Figure 1a). Like the planar geometry, where each parallel plate is isolated from the others, once a species diffuses into an isolated channel, it is not only restricted from entering another channel, but the species in one channel is not influenced by species in adjacent channels. Similar to the mesoporous systems mentioned above, collision frequency in isolated channels is significantly augmented compared with a planar surface (Figure 2a). Isolated channels experience less facile diffusion compared to pores as there is only one opening for reactants and products to enter and exit, (Figure 2d) so each isolated channel is a separate discrete diffusion system with each channel forming a steady state flux.

Improved selectivity for the CO\(_2\)RR with isolated channels was shown by Yang et al.\[16\] who developed an array of isolated Cu channels with tunable depths and widths. Different channel dimensions resulted in different retention time of species in the channels, with longer and narrower pores showing increased faradic efficiency for C\(_2\) over C\(_1\) products. Similarly, Zhuang et al.\[17\] showed the formation of C\(_2\) products from CO reduction inside hollow Cu nanoparticles, which can be seen as a single channel in a nanoparticle, by concentrating C\(_2\) species via steric confinement, promoting the coupling of C\(_2\) and C\(_1\) intermediates. Recently, our group synthesized Pt-Ni particles with isolated channels resembling the substrate channels in enzymes.\[14, 15\] The outside surface remained passivated with a hydrophobic surfactant, allowing ORR to occur only inside the isolated channels (Figure 1e). The specific activity inside the channels was 3 times higher than the activity on the nanoparticle external surface and two times higher than nanoparticles with interconnected mesopores of similar confined space diameters.

This was attributed to a higher concentration of reactant species at low overpotentials. The work is the first demonstration of how different levels of confinement affects activity by comparing no confinement, interconnected pores, and isolated channels (blue, red, and black in Figure 1e, respectively). What emerges from this overview is that many nanomaterials and nanostructured surfaces are being synthesized as electrocatalysts, with phenomenological experimental studies attributing observations to nanoconfinement and theoretical papers describing nanoconfinement effects. The study of nanoconfinement in electrocatalysis has not yet reached the maturity of designing experiments based on theoretical studies. This is partly a consequence of the challenges in fabricating nanoconfined systems that are sufficiently well-defined to test the theoretical predictions and the complexity of the modelling to include mass transport, changes in the solution environment,
adsorption behavior, electrostatics, and reaction kinetics. Recent developments in materials design have enabled many nanoconfined systems to be synthesized. Covalent and molecular organic frameworks with highly ordered, sub-nanometer confinement and versatile properties,[16] liquid crystal templates with a high degree of control to produce isolated channels of varying height and width,[17] and carbon nanotubes[18] and other carbon allotropes have potential for very controlled studies into nanoconfinement. The variability in nanoscale systems we can fabricate at this stage does create some limitations on the types of questions that can be addressed in electrocatalysis at this time, unlike in nanoconfined sensing systems that use biologically generated nanoconfined systems such as protein nanopores where subtle effects related to chemical bonding and chemical interactions can be studied.[19] Despite the limitations in questions that can be asked by our current capabilities to fabricate well-defined nanoconfined systems, some important knowledge regarding nanoconfinement in electrochemistry are emerging and will be discussed in the next sections.

3. Under what electrochemical conditions are the effects of nanoconfinement most prominent?

Any influence of nanoconfinement on an electrochemical reaction will be most prominent when the reaction is limited by electron transfer kinetics rather than mass transport. This is because in the mass transport regime reactants will be depleted in the nanoconfined spaces, resulting in reactions only occurring on the exterior of a nanoporous material.[20] Hence, depending on the electron transfer kinetics relative to the rate of mass transport not all the nanoconfined regions will be involved in the reaction. That is, under mass transport control, the current from a porous electrode can converge to that observed at a planar electrode, as the internal pore space remains un-utilized in the reaction (Figure 3a (top)).[22a, 23a] Implicit in the assertion that nanoconfinement effects will be greatest in the kinetic regime, is that the impact of nanoconfinement will be greater for reactions with sluggish reaction kinetics such that there is minimal reactant depletion inside the nanoconfined environment. In such cases, nanoporous electrodes will present larger specific activity, than electrodes with less nanoconfinement, due to the higher number of collisions between the reactant and the catalyst that the confined spaces facilitate.

Figure 3. Conditions where nanoconfinement are most prominent. (a) Scheme illustrating the volume of the porous electrode surface that participates in the reaction when the reaction is fast (mass transport limited, top) and slow (kinetically limited, bottom). (b) Linear sweep voltammograms of a flat and porous Pt electrode in oxygen saturated 0.1 M phosphate buffer containing chloride. Currents are normalised to electrochemical surface area. The effect of degree of adsorption on collision frequency due to nanoconfinement for (c) adsorption reactions (e.g., 1-butanol oxidation) and (d) non-adsorption reactions (e.g., 2-butanol oxidation). Kinetic current densities calculated from Koutecky-Levich plots from 0.8–1.0 V (RHE) for nanzymes with (e) small (black), medium (blue), large (red) channels, and mesoporous particles (white); (f) small channel particles without surfactant (black), medium channel particles without surfactant (blue), large channel particles without surfactant (red), and mesoporous particles without surfactant (white). Error bars represent standard deviation from triplicate experiments. Adapted with permission from: a, ref. 12b, Copyright 2010 Elsevier; b, ref. 20a, Copyright 2010 American Chemical Society; c-d, ref. 22a.
Bae and co-workers\cite{20a} demonstrated this with the electrooxidation of 1-butanol and 2-butanol on nanoporous Pt. As the probability of a collision resulting in electron transfer is higher for the strongly absorbing 1-butanol, the effect of nanoconfinement arising from the enhanced collision frequency in the nanoporous electrocatalysts, versus non-confined electrode materials, contributes less to the activity of the catalyst than for 2-butanol. At higher overpotentials, this results in lower specific activity for the porous electrode, relative to the planar electrode, as the reactant is mostly adsorbed, and hence consumed, near the outside surface of the porous catalytic material (Figure 5c). In contrast, with the weakly binding 2-butanol, higher specific activity is obtained for the porous Pt than the planar electrode as the increase in collision frequency within the nanoconfinement compensates for the lower probability of a collision resulting in adsorption, and hence reaction. The result is an enhancement in the reaction kinetics (Figure 5d).

We recently showed that the effect of nanoconfinement is more dominant under kinetic control.\cite{24} The effect of channel diameter on ORR kinetics have shown that smaller channels were more active at lower overpotentials due to more confined spaces and higher reactant concentrations. However, larger channels, which are less confined, eventually become more active with increasing overpotential as they have a higher number of active sites at the entrance of the channel, which is where ORR is mostly happening when the reaction becomes diffusion controlled. Note that in this study, all nanoparticles with nanoconfinement (Figure 3e) are always more active than those without (Figure 3f) within the potential range studied, showing that nanoconfinement has an effect even under mixed kinetic-mass transport control.

4. How is mass transport affected by nanoconfinement?

Although the effects of nanoconfinement are more prominent when the reaction is under kinetic control, the effect on mass transport cannot be disregarded. The rate of mass transport, in particular diffusion and migration, has a strong dependency on the local solution environment. This is especially the case for sluggish reactions that will still be under a mixed kinetic-mass transport control at relatively high overpotentials. Particularly important in altering the local concentration in nanoconfined volumes is the impact on the electrical double layer (EDL). If the radius of the nanoconfined space is less than twice the thickness of the EDL, then the double layers from each side of the nanoconfined space walls overlap. This can be achieved by either decreasing the nanoconfined size or using an electrolyte with a lower ionic strength, as shown in Figure 4a where the concentration of counter and co-ions in a 2 nm wide channel never become equal to the bulk concentration in 0.5 mol L$^{-1}$ electrolyte, resulting in an excess of counterions within the confined space.\cite{21} In contrast, at high ionic strength, counter-ion and co-ion concentration becomes equal in the center of the channel as EDLs do not overlap (Figure 4b). This charge imbalance inside the channel can affect mass transport into the channel and will depend on whether the ions making the EDL participate or not in the electrochemical reaction. Diffusion is usually the dominant mode of mass transport in electrochemical reactions. However, when there is EDL overlap in confined spaces, and the species that make up the EDL are consumed in the reaction, it creates an imbalance of charge that can cause counter ions to be drawn into the nanoconfined space by migration. The mass transport of a charged reactant can either be enhanced or retarded by migration, depending on the charge of the reactant. In the case of ORR, with increasing reduction potentials, H$^+$ are drawn from the bulk electrolyte into the channels by migration, enhancing the reaction rate due to the higher flux of reactants, and hence increased concentration near the electroactive surface (Figure 5a).\cite{22}

Migration will then be the most significant mode of mass transport for charged species as they cannot diffuse against the concentration gradient formed inside the nanoconfined space, while uncharged species do not have the benefit of migration as they can only be transported by diffusion. If the nanoconfined space is sufficiently wide, or the concentration of electrolyte is sufficiently high, there is no EDL overlap, and the main mode of mass transport into the nanoconfined volumes will be diffusion. The species being consumed at the EDL can then be readily replaced by the ones in the bulk-like electrolyte located in the center of the channel (scheme in Figure 5b) just as it does on a planar electrode.

Changing the size of the nanoconfined space can also affect reaction kinetics due to strain caused by changes in curvature and coordination number\cite{23} affecting the binding energy of species. While the contribution of strain to catalytic activity may still be important, experimental evidence shows that EDL overlapping can play a major role in nanoconfined isolated channels. This was shown by us with the same system described in Figure 1e. When H$^+$ in overlapped EDLs are consumed during the ORR, higher specific activity at low overpotentials is seen due to increased migration of H$^+$ into the channel (Figure 5c-d). Changes in the degree of overlap of the diffuse double layers of the EDL by either changing channel size or electrolyte concentration can be directly correlated with the specific activity. Interestingly, the activities were very similar in samples with different channel diameters (and hence differences in the degree of curvature and strain) when there was no EDL overlapping (Figure 5b), suggesting that the mass transport effect is dominant.\cite{24}

In the example above, the effects of EDL overlapping on migration-facilitated mass transport was demonstrated with an isolated channel system. Although EDL overlapping can also occur in interconnected pores, the impact on specific activity is not as significant because the greater degree of freedom in the interconnected pores results in reactants not being accumulated to the same extent as in isolated channels.\cite{24} This suggests that the
effects of migration are more noticeable with isolated channels where diffusion is restricted. We were able to demonstrate a greater effect of migration with isolated channels versus connected pores by comparing nanoparticles of identical size with both isolated channels and interconnected pores of similar sizes. Compared to a system with no confinement, the specific activity was 3.3 times greater in the nanoconfined system comprised of isolated channels, whereas a specific activity increase of only 1.7 times is seen for the interconnected pores (Figure 1e).[15]

3.3 times greater in the nanoconfined system comprised of isolated pores by comparing nanoparticles of identical size with both where diffusion is restricted. We were able to demonstrate a nanozymes with small (< 2 nm; red) and large (> 2 nm; black) channels at applied potential. Kinetic current densities for ORR from 0.95 – 1.0 V (RHE) for + in narrower channels. H+ during diffusion limited reduction of oxygen, showing higher H+ mobility along the axis of nanochannels via a single layer of “frozen” water molecules traversing the nanopore, forming a highly orientated hydrogen bonded chain.[11a, 26] When comparing carbon nanotubes of 0.8 nm and 1.5 nm diameter, Tunuguntla et al.[18d] saw increased H+ transport rates for the heavily confined 0.8 nm tube which, due to its size, formed a wire of single water molecules in a chain. This was not the case for the 1.5 nm channels, where the behavior was more similar to that of bulk electrolyte. Differently from nanosilts and nanochannels, Sofronov and co-workers[27] discovered that in nanodroplets, where the movement of H+ is confined in all three dimensions, the mobility of H+ is up to 10 times slower than in bulk water. This was ascribed to the fact that if a water molecule forms fewer than two hydrogen bonds then it cannot efficiently accept the H+ due to decreased basicity, increasing the average residence time at each water molecule.

Ion transport can also be affected by nanoconfinement. Ions entering nanoconfined spaces of a few nanometers often need to partially shed their hydration layers. Ionic selectivity can arise from variations in hydrated radius and hydration energy for dehydration) between different ions.[28] While high ionic mobility in nanoconfined spaces at low ionic strength has been reported,[29] Ma et al.[30] found that at high electrolyte concentrations (>1 M), ion mobility is lower compared to the bulk due to an enhancement in the number of pairing and collisions between partially dehydrated ions of opposite charge inside the nanopore. Despite the presence of numerous experimental and theoretical contributions focusing on ionic and molecular mobility in confined systems, the literature is less developed for how this influences electrochemical reactions.

Even in systems that do not exhibit EDL overlapping, similar effects were observed by Chen et al.[25] using a thin-layer electrochemical cell that was a few hundred nanometer wide. At supporting electrolyte concentrations low enough for the EDL to extend a significant distance into the solution, increased activity for the hexaaminoruthenium(III) chloride redox couple (Ru(NH3)6Cl32+) was observed. This was attributed to ion enrichment in the EDLs at the surface of the cathode caused by enhanced ion migration of the redox species. The use of recessed microelectrodes in this study allowed the beneficial effects of confinement to be seen even at mass-transport limiting potentials. In addition to inducing mass transport via migration, when the confined space and EDL dimensions are comparable, the physical properties of ions and water structure become significant and can affect ion transport inside the confined environment. H+ mobility is heavily influenced by water structure as the mechanism by which protons move involves a transfer of a single positive charge hopping from one hydrogen bonded water molecule to the next (Grotthuss mechanism). Highly ordered systems of water molecules, like those found in angstrom-scale nanochannels, enhance H+ mobility along the axis of nanochannels via a single layer of “frozen” water molecules traversing the nanopore, forming a highly orientated hydrogen bonded chain.[11a, 26] When comparing carbon nanotubes of 0.8 nm and 1.5 nm diameter, Tunuguntla et al.[18d] saw increased H+ transport rates for the heavily confined 0.8 nm tube which, due to its size, formed a wire of single water molecules in a chain. This was not the case for the 1.5 nm channels, where the behavior was more similar to that of bulk electrolyte. Differently from nanosilts and nanochannels, Sofronov and co-workers[27] discovered that in nanodroplets, where the movement of H+ is confined in all three dimensions, the mobility of H+ is up to 10 times slower than in bulk water. This was ascribed to the fact that if a water molecule forms fewer than two hydrogen bonds then it cannot efficiently accept the H+ due to decreased basicity, increasing the average residence time at each water molecule.

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5. How can nanoconfinement break scaling relationships?

As discussed in the introduction, reaction overpotential can be minimized by optimizing the binding energy of a key intermediate to ensure the binding is strong enough for successful electron transfer, but weak enough for the product to be immediately released from the catalytic active site. Binding energies can be tuned by surface faceting, elemental alloying, surface defects, and coordination numbers.[23, 31] As mentioned previously, nanoconfinement itself can also be used to selectively weaken adsorption energies between the reactant and catalytic surface.[22a]

However, manipulating binding energy of one intermediate will simultaneously affect the binding energy of other intermediates, possibly creating a new limiting step involving the other intermediate.[22] Thus, the manipulation of binding energies will not result in activities higher than that dictated by the scaling relations. Nanoconfinement can break scaling relationships in two distinct ways. One way is by preferentially stabilizing one adsorbed reaction intermediate while not affecting the adsorption of the other intermediates. Doyle et al.[32] demonstrated this theoretically with adjacent RuO2 and IrO2 parallel plates for the OER (reaction mechanism shown below) and found that the effect of nanoconfinement depends on the rate limiting step.

\[
\text{H}_2\text{O} + \text{M} \rightarrow \text{M-OH} + \text{H}^+ + \text{e}^-
\] (1)
The HOO* intermediate was stabilized due to hydrogen-bond formation with the opposite channel wall while no changes in adsorption energy were seen for the smaller HO* intermediate. Reactions that fall on the right side of the volcano plot (Figure 6a (right)), i.e., at IrO$_2$ surfaces, are rate limited by the deprotonation of HO* to O* (Eq. 2, red line in Figure 6a (bottom)) when the spacing between plates is greater than 1 nm (d > 1 nm), which is not affected by confinement. However, when d < 1 nm the rate limiting step becomes the removal of HOO* from the IrO$_2$ surface (Eq. 4, blue line in Figure 6a (bottom)). The stabilization that arises from confinement hinders the removal of HOO* from the surface. Hence, for IrO$_2$, the overpotential for OER increases as channel size decreases. Conversely, on the left side of the volcano plot, i.e., RuO$_2$, reactions are potential limited by the addition of a second water molecule to O* to form HOO* (Eq. 3, green line in Figure 6a (top)), so increased stability of HOO* due to confinement results in increased activity. The overpotential for RuO$_2$ decreases to about 200 mV at d = 0.7 nm, forming a new volcano plot whose summit reaches closer to the presently unattainable 0 V overpotential. This approach can be used for other reactions involving multiple intermediates that have different spatial orbital extent. Nearly identical results were obtained more recently by Sours et al.\textsuperscript{[33]} using density functional theory calculations of bimetallic porphyrin-based MOFs, demonstrating hydrogen-bonding stabilization of the HOO* intermediate. The optimal separation between the two confining layers was found to be ca. 0.7 nm, and a decrease in overpotential was seen for reactions whose rate is limited by the formation of HOO*.

Another way nanoconfinement can break scaling relationships is by increasing residence time of species near active sites in nanoconfined spaces, leading to enhanced kinetics as well as selective formation of more complex products in multi-product reactions. For multi-step, multi-product reactions like the CO$_2$RR, scaling relationships can be broken by using interfacial sites that each catalyse one step of the cascade reaction. Huang and co-workers\textsuperscript{[34]} used nanodimer particles containing Ag and Cu to lower the overpotentials required for CO$_2$RR, increasing the selectivity for C$_2$ products. To obtain even higher order products, like propa-nol, higher concentration, and long retention times of C$_2$ and CO intermediates are necessary. Recently, our group used interfacial sites in combination with nanoconfinement to break scaling laws and demonstrated the formation of C$_3$ products, such as propanol, from CO$_2$RR at -0.6 V (RHE), which is the lowest overpotential for C$_3$ products reported to date, by developing cascade nanozymes.\textsuperscript{[40]} The nanozymes consist of nanoparticles with a Ag-core and porous Cu-shell. CO$_2$ diffuses to the Ag core and is reduced to CO at low overpotentials with high faradaic efficiency. High local concentrations of CO build up within the porous Cu shell leading to enhanced C-C coupling between C$_2$ products and CO. Products can be selectively tuned by changing the intermediates retention time and local concentration of CO.\textsuperscript{[35]} This is analogous to cascade reactions in enzymes which is achieved via substrate channeling, which is the direct transfer of an intermediate from one active site to another without leaving to the bulk solution. The nanoconfinement induced cascade reaction is observed in a “potential window” where the overpotential is sufficient to convert the CO formed on the Ag sites to higher order products at the Cu sites inside the porous shell, but not too high that the CO$_2$RR is mostly happening directly at the Cu sites at the nanozyme outer surface (Figure 6b). In the “nanozyme window” (-0.60 to -0.65 V), higher order products, like n-propanol (Figure 6c), is produced at very low overpotentials.

6. Conclusion and Outlook

With the development of techniques to fabricate nanoporous materials with fine control of morphologies, nanoconfinement is becoming progressively more important in electrochemistry. However, at present we only have a nascent understanding of the importance of nanoconfinement in electrochemistry and the impact it can have on improving electrocatalysis. A few studies have investigated how the nature of the electrolyte in nanoconfined spaces changes during an electrochemical reaction. Similarly, there have been only a few investigations that looked at how nanoconfinement influences the kinetics and selectivity of these reactions. From these initial studies there are already some hints that nanoconfinement can have a profound influence on electrochemical reactions. We have learnt that in nanoconfined spaces the structure of water can change which has impacts on mass transport processes in these nanoconfined spaces.\textsuperscript{[18, 26-27, 28c]} Similarly, the size of the spaces can cause some species to be excluded simply based on their size,\textsuperscript{[36]} whilst overlapping diffuse electrical double layers in highly confined spaces can result in
species being brought into or expelled from the channels by migration.[4a, 15, 25] This can then result in very different concentrations of species in the nanoconfined spaces compared with the reaction kinetics observed in some nanoconfined systems. For example, nanoconfined spaces often have high curvature which could suggest the enhanced reaction kinetics observed in some nanoconfined systems. For example, nanoconfined spaces often have high curvature which could suggest the enhanced reaction kinetics observed in some nanoconfined systems.

Questions remain, however, regarding the attribution of the reasons for the improved reaction kinetics observed in some nanoconfined systems to further improve our understanding of nanoconfined spaces. For example, nanoconfined spaces often have high curvature which could suggest the enhanced reaction kinetics observed in some nanoconfined systems. For example, nanoconfined spaces often have high curvature which could suggest the enhanced reaction kinetics observed in some nanoconfined systems. For example, nanoconfined spaces often have high curvature which could suggest the enhanced reaction kinetics observed in some nanoconfined systems.

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**Keywords:** electrocatalysis • electrochemistry • ion migration • nanotechnology • scaling relationships

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Advances in nanoscale fabrication techniques have promoted the development of electrocatalysts where electrochemical reactions occur within a nanoconfined space. This review explores how different degrees of freedom of nanoconfinement affects electrocatalytic activity for a range of reactions and how implementing nanoconfinement can help break linear scaling relationships.