

Regulating the steric effect at the zero-dimensional interface

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The regulation mechanism of a zero-dimensional interface towards a catalytic reaction in the setting of a single-atom catalyst has been elusive to researchers. In a recent article published in *Journal of the American Chemical Society*, Zeng and Zhou et al. differentiated the electronic and steric effects on the oxygen evolution reaction at two distinct zero-dimensional interfaces. The steric interaction resulted in the desired adsorption behavior of intermediates at the interface, which lowered the energy barrier to the rate-determining step (RDS) and thus facilitated the oxygen evolution reaction. For the first time, this work validated the impacts of electronic and steric effects on the atomic interface of catalysts by delicately designing the anchoring site of single atoms on the support. The elegant design concept presented in this work pushes the research field of interface engineering to the atomic level and blazes a trail for the rational development of high-performing catalysts.

The completion of a heterogeneous catalysis process relies on the elementary steps occurring at the surface or interface of a catalyst, including the adsorption of intermediates, the chemical reactions between the intermediates to yield the desired products, and the desorption of the products^[1]. Thus, the interface, a place where two completely different components meet, plays a vital role in the catalytic reaction. Though the construction of an interface appears to be the addition of one component onto another, the effect is not the simple addition of the original functionalities associated with the two components. As the species changes abruptly at the interface, distinct electron transfer channels are created, and thus, the electronic structure of each component at the interface tends to diverge from the inherent one^[2–4]. Such a feature can be utilized to modulate the adsorption strength of intermediates. Moreover, the disparity between the two materials at the interface introduces various sites to regulate the adsorption configuration of the intermediates, contributing to the optimization of reaction pathways. As a result, the activity and selectivity can be finely tuned through interface engineering^[5].

Single-atom catalysts have received considerable attention, as the atomically isolated species not only reaches an unprecedentedly high utilization efficiency but also serves as a perfect model for mechanistic study^[6]. However, despite the prevalence of single-atom catalysts in recent years, the underlying regulation mechanism of their unique zero-dimensional interfaces towards catalytic reactions remains unclear as opposed to that of the one-dimensional interfaces in conventional heterogeneous catalysts.

To fill this knowledge gap, Zeng and Zhou et al. designed two iridium (Ir) single-atom catalysts with different Ir interfa-

cial sites^[7]. Specifically, Ir single atoms coordinated to IrO₆ were doped into the lattice of CoOOH and anchored onto the surface of CoOOH, and the as-obtained catalysts were denoted as Ir₁/CoOOH_{lat} and Ir₁/CoOOH_{sur}, respectively. The authors first assumed that the edge-sharing octahedra configuration between IrO₆ and CoO₆ in Ir₁/CoOOH_{lat} induced a noticeable electron exchange between the Ir and Co species, while the corner-sharing octahedra configuration had a negligible effect on the electronic structure of the Co species. Density functional theory (DFT) calculations confirmed this assumption, illustrating a considerable amount of overlap between the projected density of states (PDOSs) of the Ir and Co species and the significant lifting of the Co *d*-band center in Ir₁/CoOOH_{lat} with respect to the CoOOH substrate. In contrast, Ir₁/CoOOH_{sur} displayed disentangled Ir and Co PDOSs near the Fermi level, and its Co *d*-band center remained almost unchanged compared with that of CoOOH. These results demonstrated that the electronic interaction between Ir and Co species in Ir₁/CoOOH_{lat} was strong, whereas the electronic interaction between Ir and Co species was weak in Ir₁/CoOOH_{sur}.

In addition to electronic structure, calculations of the Gibbs free energies of intermediates towards the oxygen evolution reaction (OER) following the adsorbate evolution mechanism were also used to predict the catalytic activities of different catalysts. Under the adsorbate evolution mechanism, the evolution of the adsorbed *O to *OOH was determined to be the rate-determining step for all three catalysts. The free-energy diagram of Ir₁/CoOOH_{lat} indicated that the lifted *d*-band center of Co in the catalyst caused a universal increase in adsorption strength for all intermediates with respect to the CoOOH

substrate. In contrast, the intermediates exhibited differentiated adsorption behavior on Ir₁/CoOOH_{sur}. The adsorption strength of *O was weakened on Ir₁/CoOOH_{sur} compared with that on the CoOOH substrate, whereas the adsorption strength of the subsequent *OOH species was strengthened with respect to that on CoOOH. Such a trend was attributed to the steric interaction at the Ir–OH–Co interface, which effectively repelled *O and induced hydrogen bonding of 2.1 Å to strengthen the adsorption of *OOH, thus lowering the energy barrier to the rate-determining step from *O to *OOH.

Guided by DFT prediction, the authors constructed lattice-doped and surface-adsorbed Ir single-atom catalysts through the substitutional wet-chemistry method and the electrochemical deposition method, respectively. The successful incorporation of the single-atom Ir species into both Ir₁/CoOOH_{lat} and Ir₁/CoOOH_{sur} was evidenced by aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) images. The extended X-ray absorption fine structure (EXAFS) confirmed the IrO₆ coordination of the Ir species in both samples. X-ray absorption spectroscopy results showed that the valance state of Co in Ir₁/CoOOH_{sur} remained unchanged compared to that in CoOOH, while the valance state slightly decreased in Ir₁/CoOOH_{lat}, indicating significant electron transfer from Ir to Co species in Ir₁/CoOOH_{lat}. The disparity in the Co valance state of the single-atom catalysts corroborated the results of DFT calculations, indicating that the Ir species doped in the lattice could induce considerable electronic transfer between Ir and Co species, whereas the Ir on the surface has a negligible effect on the electronic structure of the Co species.

The OER activities of both samples were evaluated in 1.0 mol·L⁻¹ KOH. Ir₁/CoOOH_{sur} showed an overpotential of 210 mV at a current density of 10 mA·cm⁻², which outperformed Ir₁/CoOOH_{lat} by 110 mV. At an overpotential of 300 mV, Ir₁/CoOOH_{sur} exhibited a 29.17 times higher specific activity and 36.82 times higher mass activity than Ir/CoOOH_{lat}. The

comparison demonstrated that the steric effect outweighed the electronic effect on OER activity enhancement in the Ir/CoOOH single atomic system. Among the three catalysts, Ir₁/CoOOH_{sur} delivered the lowest Tafel slope. In addition, the charge transfer resistance of Ir₁/CoOOH_{sur} was the smallest, as evidenced by the smallest semicircle diameter of Ir₁/CoOOH_{sur} among the three samples in their electrochemical impedance spectra. The above results suggested that Ir₁/CoOOH_{sur} delivered the fastest kinetics towards OER among the three samples.

The authors also used in situ infrared spectroscopy to capture the emergence of *OOH intermediates during the OER on CoOOH, Ir₁/CoOOH_{lat}, and Ir₁/CoOOH_{sur}. The redshift of the *OOH peak indicated that the O–O bond vibration was weakened on Ir₁/CoOOH_{lat} and Ir₁/CoOOH_{sur} compared to CoOOH, implying that the adsorption of *OOH on Ir₁/CoOOH_{lat} and Ir₁/CoOOH_{sur} increased with respect to CoOOH and thus corroborated the results of the free-energy diagram. The increase in adsorption strength of *OOH on Ir₁/CoOOH_{lat} could be attributed to the electron transfer between Co and Ir on Ir₁/CoOOH_{lat}, while the reduced O–O vibration accompanying strengthened adsorption of *OOH on Ir₁/CoOOH_{sur} resulted from the hydrogen bonding at the Ir–OH–Co interface that induced steric interaction between the active sites and the intermediates.

This work followed an uncommon research philosophy that inspires researchers to think from a different aspect. First, this work discovered that steric interaction matters in electrocatalytic reactions. In the past few decades, scientists have been relentlessly working on discovering universal descriptors to efficiently predict trends in various catalytic reactions and thus have developed a complete methodology for elucidating the origin of catalytic performance improvements. Specifically, such improvements are ultimately attributed to the variation in the electronic structure of the catalyst in most cases, which leads to a change in the adsorption strength of the

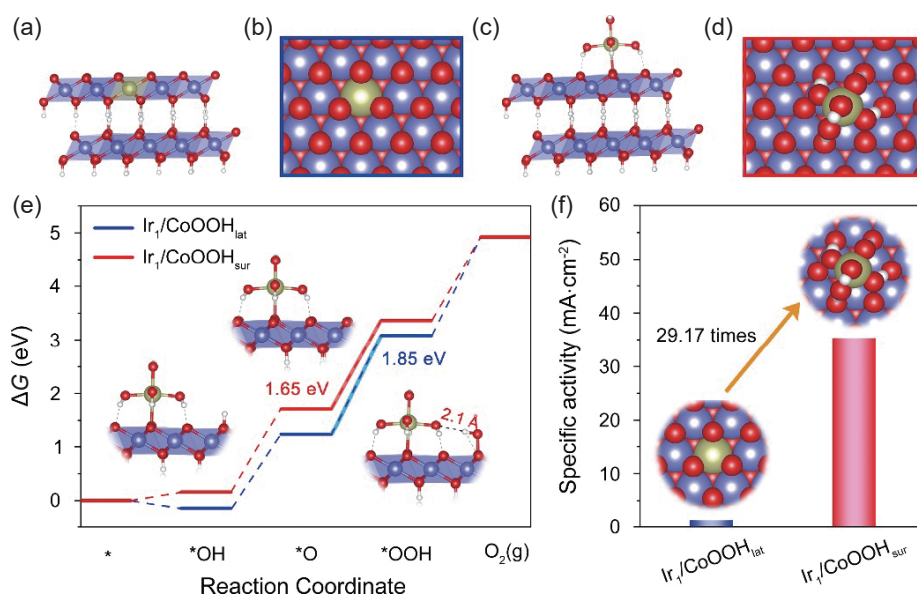


Fig. 1. Regulating the steric effect at the zero-dimensional interface. (a) The side view and (b) top view of Ir₁/CoOOH_{lat}; (c) the side view and (d) top view of Ir₁/CoOOH_{sur}. (e) The free energy diagrams of Ir₁/CoOOH_{lat} and Ir₁/CoOOH_{sur} towards OER. (f) The specific activities of Ir₁/CoOOH_{lat} and Ir₁/CoOOH_{sur} at an overpotential of 300 mV. Adapted with permission from Ref. [7]. Copyright 2022, American Chemical Society.

intermediates in direct contact with the catalyst, thereby lowering the energy barrier of the RDS. With the electronic effect being the dominant factor in explaining catalytic performance enhancement, the steric effect is often ignored. However, the role of such an effect should never be underestimated, as it induces additional interaction, in this case, hydrogen bonding, on the intermediates just like the electronic effect does. The interaction is the key to regulating the adsorption strength of the intermediates, which eventually contributes to the decrease in the rate-determining step barrier and the improvement of catalytic performance. In this work, the authors effectively demonstrate how to achieve performance improvement through the steric effect while leaving the inherent electronic structure of the catalyst unchanged. Moreover, because the interaction induced by the steric effect does not influence all intermediates equally, the discovery of such an effect opens up the possibility of breaking the scaling relation in the OER without introducing additional active sites into the catalyst^[8].

Second, this work reveals an obscure yet feasible route to interface engineering. Interface engineering has been an actively explored topic in heterogeneous catalysis, as interfaces play a decisive role in the activity and selectivity of a catalyst. For multicomponent catalysts, tuning the composition of catalysts has become the most widely used strategy for interface engineering since modulation of the composition could effectively regulate the electronic structure of the catalyst. However, the regulation of the electronic structure is not the ultimate goal of interface engineering but rather a means of optimizing the adsorption strength of intermediates to reach the final goal of reducing the energy barrier to the RDS^[9]. Now that the steric effect has been noticed, interface engineering can be approached from a different perspective. Herein, an unprecedented yet facile way of interface engineering was proposed, that is, altering the position of single atoms without changing the overall composition of the catalysts or the single-atom coordination in the catalysts. The outcome is impressive. Such a facile way of interface engineering sets a well-defined boundary between the electronic and steric effects in the respective catalysts. The act not only provides a platform for the mechanistic study of the two effects individually but also significantly improves the OER activity for practical purposes.

Third, this work shows how theoretical calculations could be conducted prior to experiments to reach the preconceived design and guide the physical implementation of the catalysts^[10]. In addition, it shows how theoretical prediction and in situ measurements can be integrated concertedly to elucidate the origin of performance improvement. The rational design of the catalysts and the following in silico verification of feasibility in this work gives a good demonstration of how to circumvent the trial and error procedure in the wet lab, which saves a considerable amount of time and effort. In this work, the theoretical calculation results were not the last piece of evidence that was added to the main idea but rather a powerful tool that successfully predicted the activity difference of the catalysts of interest. Moreover, the results from theoretical calculations were later proven by in situ experimental data, demonstrating the self-consistency of the main idea in this work from both theoretical and experimental

perspectives.

In summary, by rationally designing single-atom catalysts with the same components but different atom-support connection modes, the authors modulated the electronic and steric effects in heterogeneous catalysis induced at distinct interfaces. In Ir₁/CoOOH_{lat}, the electron transfer between Co and Ir caused the lifting of the Co *d*-band center, which eventually led to an increase in the adsorption strength for all intermediates. In contrast, for Ir₁/CoOOH_{sur}, the steric interaction at the Ir–OH–Co interface resulted in an optimized adsorption behavior, thus contributing to the significant enhancement in the OER.

Biography

Younan Xia is the Brock Family Chair and Georgia Research Alliance (GRA) Eminent Scholar at the Georgia Institute of Technology. He received a B.S. degree in Chemical Physics from the University of Science and Technology of China (USTC) in 1987, a M.S. degree in Inorganic Chemistry from University of Pennsylvania (with Professor Alan G. MacDiarmid) in 1993, and a Ph.D. degree in Physical Chemistry from Harvard University (with Professor George M. Whitesides) in 1996. His group has invented a myriad of nanomaterials with controlled properties for widespread use in applications related to plasmonics, electronics, photonics, photovoltaics, display, catalysis, energy conversion, nanomedicine, and regenerative medicine. Xia has co-authored more than 840 publications in peer-reviewed journals, together with a total citation of more than 180,000 and an h-index of 211. He has been named a Top 10 Chemist and Materials Scientist based on the number of citations per publication. He has received a number of prestigious awards, including American Chemical Society (ACS) National Award for Creative Invention (2023), Materials Research Society (MRS) Metal (2017), ACS National Award in the Chemistry of Materials (2013), NIH Director's Pioneer Award (2006), David and Lucile Packard Fellow in Science and Engineering (2000), and NSF CAREER Award (2000). More information can be found at <http://www.nanocages.com>.

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