

## Peer Review File

**Manuscript Title:** Site-specific reactivity of stepped Pt surfaces driven by stress release

### Reviewer Comments & Author Rebuttals

#### Reviewer Reports on the Initial Version:

----- Referees' comments -----

Referee #1 (Remarks to the Author):

This work provides an overdue missing link in the fundamental understanding of electrocatalysis. The established view of active sites on monometallic electrodes distinguishes only between crystal facets and lower dimensional structural features such as steps, kinks, edges, point defects. Spatial inhomogeneities in the adsorption (and thus catalytic) properties of nominally smooth and homogeneous terraces have been postulated in some cases, but have not been properly analysed or described.

Here, the authors apply density functional theory to a library of stepped Pt surfaces to demonstrate that the positions of Pt atoms within the unit cells vary slightly depending on their position relative to the ascending and descending step edges and the nature of these step edges. These variations are convincingly attributed to stress release resulting from the absence of binding partners at the step edges. The resulting local surface strain reaches 5.5% compression, which is well above the strain that can be achieved, for example, by a pseudomorphic monolayer of larger atoms on a more densely packed substrate. Accordingly, the local changes in adsorption properties are also huge, creating a situation where a small fraction of surface atoms are responsible for high electrocatalytic activity (as shown for the example of oxygen reduction).

The authors also show how Au atoms (chemically and catalytically inert) can further enhance the effect by decorating the step edges and (due to their larger atomic radius) by pushing the Pt terrace atoms even further inwards, thus further increasing the strain.

The computationally predicted effects on adsorption properties and electrocatalytic activity are exemplarily verified on a well-selected collection of stepped Pt surfaces, with and without Au decoration at the step edges. The experimental results are in good agreement with the computational predictions.

The authors not only demonstrate the importance of considering the spatial variation of strain on stepped surfaces (with and without foreign metal atoms), but also provide a framework for mapping this behaviour. In particular, they provide a rational approach to understanding trends in the catalytic activities of stepped single crystal surfaces. As they rightly point out in the abstract, the resulting effects are as important for a comprehensive understanding of active sites as the more obvious variations associated with defects or facets. Their work will be the starting point to fill some gaps in previous work: e.g. the postulated variation of adsorption energies in wider bands near island and step edges on Pt-modified Ru(0001) as visible in thermal desorption spectra (PCCP, 2012, 14, 10919) or the longer range effect of Au patches alloyed into Pt(111) surfaces on electrochemical hydrogen adsorption at Pt atoms (ChemPhysChem, 2010, 1505).

Beyond the specific community with an interest in single crystal surface chemistry, the paper is of interest to a wider audience. It is written in a clear and logical style, providing a quick overview with sufficient background in the main paper combined with a lot of interesting experimental and computational data in the supplementary information.

In summary, the paper is suitable for publication in Nature.

Harry Hoster

Referee #2 (Remarks to the Author):

In this paper, a joint experimental and theoretical work is reported which addresses the oxygen reduction reaction (ORR) on stepped Pt surfaces. They find that stepped Pt surfaces exhibit a modified activity with respect to the ORR which they relate to surface stress release. The authors propose that their findings demonstrate "that manipulation of surface stress and strain fields is a flexible and powerful strategy for control of catalytic activity" and "creates a new paradigm for heterogenous catalyst design". In fact, their proposition is not really new. Already more than 10 years ago, Robert Schlogl and coworkers suggested in a series of papers that lattice strain could affect the activity of catalysts (see, e.g. *Angew. Chem. Int. Ed.* 46, 7324 (2007)). However, eventually this assumption could not be substantiated, for good reasons, as I will address below. So although both the presented experimental and theoretical results are scientifically sound, they do not represent an advance in understanding likely to influence thinking in the field, and hence this paper does in my opinion not merit publication in *Nature*.

1) On the second page of the manuscript, the authors correctly state that the "cleavage of bulk metal ... leads to attractive interactions between surface atoms". However, I would have expected that the authors explain at least in one sentence why the cleavage leads to attractive interactions.

2) The authors estimate that the "surface pressure" on Pt(111) corresponds to a "huge" pressure of  $2 \times 10^5$  atm. I do not consider it appropriate to compare gas pressure to interatomic interactions. On the atomistic level, chemistry is based on electrostatic interactions which is 40 orders of magnitude stronger than the gravitational interaction, so it is no surprise that forces based on interatomic interactions are much stronger than forces corresponding to atmospheric pressure.

3) On page 7, the authors state that their "results additionally suggest that the catalytic activity of stepped surfaces is significantly more complex than what is implied by the widespread assumption that reactivity is identical for all terrace atoms. Specifically, as perfect Pt(111) single crystal surfaces are well known to bind too strongly to reaction intermediates for common electrocatalytic reactions, such as ORR, large."

I do not think that there is indeed a "widespread assumption that reactivity is identical for all terrace atoms", as there have already been DFT studies of adsorption energies across step edges and adjacent terraces. Furthermore, the second sentence cited above saying that Pt(111) binds too strongly appears strange considering that Pt is still considered to be the best ORR catalyst. Following this line of thought, it should rather be said that all other catalysts bind too strongly as their ORR activity is less than that of Pt.

4) At the same page, the authors state for the first time in the article that close to the steps there is "an enhancement factor of  $\sim 50$  times compared to that of perfect Pt(111)". However, the reader does not have any chance to comprehend why there is an alleged enhancement of 50 times as no information is given how this enhancement is derived. Only when reading the methods section on page 18 of the manuscript, it becomes clear how this factor is derived. I understand that the full derivation given in the methods section should not be part of the main text. However, the authors should at least briefly explain how this factor is derived.

5) An enhancement factor of 50 sounds to be large. However, on the other hand the authors state on page 5/6 that "the maximum reduction in binding strength ... is in the range of 0.06-0.11 eV", which appears to be rather small. The factor 50 simply results from the fact that the change of at most 0.1 eV simply enters exponentially in the activity. In my opinion it is only fair to admit this fact. Changes in the adsorption energy by about 0.1 eV through some manipulation are usually not considered to be really large. It appears that by emphasizing the factor 50 the authors somehow exaggerate the strength of the change they observe close to the step sites.

5) As mentioned above, only when carefully reading the theoretical methods section, it becomes clear where the enhancement factor comes from. It is based on the sentence: "For Pt(111) surface, the potential-determining step is OH\* protonation to produce H<sub>2</sub>O, in which

$U_4$  ( $\Delta G_4(U_4) = 0$ ) is the maximum potential". This means that the catalytic activity of the ORR on Pt depends on one single adsorption energy. However, the authors do not give any reference for this central statement. It is based on the well-known scaling relations. As Christensen et al., JPC C 120, 24910 (2016) put it:

"Based on the scaling relation, it is possible to use adsorption free energies as predictors for catalyst activity. For ORR, the adsorption free energy of OH\* can be used as predictor with the optimum at  $(4.92 \text{ eV} - 3.2 \pm 0.2 \text{ eV})/2 = 0.9 \pm 0.1 \text{ eV}$ . Catalysts which adsorb OH\* slightly ( $\sim 0.1 \text{ eV}$ ) weaker than Pt have been found to display improved activity over Pt."

However, this is an exception rather than the rule. Typical catalytic activities depend on more than one adsorption energy. For example, activation barriers correspond to the difference between the energy of the system in the transition state and in the initial state. Now a lattice expansion of a late transition metal typically leads to stronger binding according to the d-band model. However, the stronger binding in the initial, the transition and the final state can all be different so that it cannot be predicted whether any activation or any reaction energies increases or decreases as a function of the lattice strain. Therefore in principle no general trends in the catalytic activity as a function of the lattice strain can be really predicted which is why the studies of Schlogl et al. mentioned above did not reveal any general trend.

The authors of the present study consider a particular systems in which one single adsorption energy can be used as a descriptor for the catalytic activity. However, again, this is an exception rather than a rule. Therefore the results of this particular study do not create "a new paradigm for heterogeneous catalyst design" and the manipulation of surface stress does not correspond to a "powerful strategy for control of catalytic activity" in general activity. In my opinion, this is the most critical point about the present study. Hence this paper is only suitable for a more focussed journal, but only once the special nature of the ORR on Pt(111) with respect to its dependence on one single adsorption energy is properly acknowledged in the manuscript.

Referee #3 (Remarks to the Author):

In the present submission, Liu et al. aims at revealing an underestimated, more precisely not accounted for, influence of monoatomic step on the resulting strain experienced by the atoms at the vicinity of the steps, and the resulting influence of it on the catalytic activity of the whole surface. The oxygen reduction reaction has been chosen as model reaction, but the finding of the authors should be generalizable to any catalytic reactions.

Formally, the effect of tensile/compressive strain on adsorption and (electro-)catalytic transformations with planar periodically ordered surfaces is already well documented in the literature, both computationally and experimentally (see e.g. works published by A. Gross and R.J. Behm). The authors, focusing on such effect induced by the presence of monoatomic step on the surface, bring the topic to a step further towards the direction of more realistic catalytic surfaces such as those employed into practical application, which are highly defective. Albeit the claim of the authors that it offers a new paradigm and design strategies for practical materials is in my view overstated, revealing and detailing effects that would allow for a better definition of the approximations applied in computational modelling is of critical importance to enable more accurate predictive capabilities. Furthermore, the search for the effect driving the rate of the catalytic reactions down to the atomic scale level is as old as the research in the catalysis field. In that sense, the approach undertaken by the authors is highly valuable.

At first glance, the manuscript proposed by the authors is quite appealing. It is well structured and well written. Methodology/approximation employed for the computational modelling, description of the catalytic reaction and experimental methods correspond to the state of the art and are well described. Nevertheless, a comparison of the findings/claims with literature records reveals some issues impeding the publication of this manuscript.

According to the results previously published by the Feliu's group (Electrochim. Acta 334 (2020)

135452) very (very) little influence of the step density is observed experimentally for the ORR kinetics on Pt[(111)x(110)] stepped surfaces in perchloric acid solutions with respect to Pt(111) (the surfaces modelled in the present submission). On the other hand a much more pronounced influence can be observed for Pt[(111)x(100)] (op. cit.) stepped surfaces, being furthermore non-monotonic. This raises two questions/comments regarding the claim of the authors:

- If the effect of stress release at the step vicinity in determining the final performances of the catalytic surface is of outstanding importance as claimed by the authors for these modelled surfaces, why an enhancement of the reaction rate is hardly detected experimentally?
- Within the frame defined by the authors, how the symmetry of the step (either (110) or (100)) influences the stress release at the vicinity of the steps in the model of the authors to cope with the experimental observations where the enhancement of the ORR with the step density present different magnitude depending on the symmetry of the atomic step?

To support the generality of their finding, the authors partially covered a Pt stepped surface in a systematic fashion with Au adatoms, and probed the resulting enhancement on the ORR. Very little influence of the Au coverage is observed up to ca. 0.5 ML on the ORR activity, followed by a significant increase for higher Au coverage. Interestingly, earlier report from Behm's group (J. Electroanal. Chem. 716 (2014) 71-79) on Pt<sub>x</sub>Au<sub>1-x</sub>/Pt(111) surface alloys showed an almost completely suppressed hydroxyl adsorption for Au content higher than 50%, and suggesting that the size of atomic ensembles is larger than Pt<sub>3</sub> for the hydroxyl adsorption. Thus, the experimental results of the authors could be as well explained by an atomic ensemble effect, being too small at high Au coverage and leading to the destabilisation of the hydroxyls on the Pt surfaces. This would result as well into an enhancement of the ORR activity of the non-covered Pt surface. Thus, the strain/strain might not be the root cause of the enhancement of the ORR activity at high Au coverage.

Since the authors claim that accounting for the modified surface stress at the vicinity of the atomic step 'resolve' long-standing issues related to the identification of the catalytic site for the ORR, I believe that a simple graphical representation would be helpful for the reader to track progresses and impact in detailing catalysis down to the atomic scale level. For example, showing the mismatch between predictions and measurements of the kinetic current density, accounting or not for such effect, would be valuable from a quantitative perspective. Comparing Fig. 3c and Fig. 4b, the computational model proposed by the authors seems to overestimate by one order of magnitude the enhancement of the ORR rate.

In summary, the modification of the strain experienced by atoms at the vicinity of atomic steps/defects is likely to occur. These atoms will indeed present different properties for the adsorption of species, and consequently different catalytic activity. Yet, it is in my view not demonstrated that i) the magnitude of this effect rationalizes the changes of the catalytic activity for the whole surface and ii) accounting quantitatively for this effect lowers significantly the mismatch theory/experiment.

----- End of comments -----

## Author Rebuttals to Initial Comments:

### Point-by-by response to the referees' comments

General remark: We would like to thank all referees for taking the time to carefully review our manuscript and provide constructive comments, which contribute significantly to improving the clarity, completeness, accuracy, and thus the overall quality of the manuscript. We have thoroughly addressed all the comments and revised the manuscript accordingly. **The revisions are highlighted in the manuscript.** The point-by-point responses are listed below, with the referees' original comments shown in **bold** and our responses shown in *italics*.

Response to referee 1: *We would like to thank the referee for taking the time to carefully review our manuscript and providing profuse comments regarding the significance, originality, and novelty of our current work. We also would like to thank the referee for directing us to those two publications that we have inadvertently neglected. Now, we have cited and acknowledged them in our revised version. Along with other revisions in response to another two referees' comments, we hope our manuscript is clearer, more complete, and more accurate now.*

**Referee #2 (Remarks to the Author):**

**Q: In this paper, a joint experimental and theoretical work is reported which addresses the oxygen reduction reaction (ORR) on stepped Pt surfaces. They find that stepped Pt surfaces exhibit a modified activity with respect to the ORR which they relate to surface stress release. The authors propose that their findings demonstrate "that manipulation of surface stress and strain fields is a flexible and powerful strategy for control of catalytic activity" and "creates a new paradigm for heterogeneous catalyst design". In fact, their proposition is not really new. Already more than 10 years ago, Robert Schlogl and coworkers suggested in a series of papers that lattice strain could affect the activity of catalysts (see, e.g. *Angew. Chem. Int. Ed.* 46, 7324 (2007). However, eventually this assumption could not be substantiated, for good reasons, as I will address below. So although both the presented experimental and theoretical results are scientifically sound, they do not represent an advance in understanding likely to influence thinking in the field, and hence this paper does in my opinion not merit publication in *Nature*.**

*Response: We would like to first thank the referee for acknowledging that our work is scientifically sound for both the experimental and theoretical parts. We understand that the referee had concerns regarding the foundation of the current work, i.e. the strain effects, because the effect of surface strain on catalytic activity proposed by Robert Schlogl and coworkers was not substantiated by their data. In principle, we agree with the referee on the assessment of Robert Schlogl and coworkers' data. Actually, Robert Schlogl and coworkers themselves also admitted that they cannot distinguish between the effects of the strain and other effects because their samples are very complex: there are Cu nanoparticles, ZnO nanoparticles, Al<sub>2</sub>O<sub>3</sub> nanoparticles and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> interfaces in their samples. Also, for Cu nanoparticles, there are faults and twins, in addition to a wide size distribution. **While such complexity makes it possible to take advantage of all possible catalytic effects, known or unknown, for real-world applications, the ill-defined nature of the catalysts hinders the disentangling of any single specific effect, such as the strain effects.***

*To isolate and demonstrate the strain effects (and many other effects), it is desired to employ more well-defined systems. Great efforts have indeed been made along this line both computationally and experimentally since 1990s, such as the work done by Mavrikakis, Norskov, Behm, Wadayama, Cui, Jia, Jin and others (as detailed in the response of the referee's 2<sup>nd</sup> to last comment below). These efforts demonstrate that generating and tuning surface strain is indeed an effective strategy for improving catalytic activity of chemical reactions that are sensitive to surface strain. Thus, we also agree with the referee that the effect of surface strain on catalytic activity is not new. Then, the question is what is new in the current work. That is "revealing an underestimated, more precisely not accounted for, influence of monoatomic step on the resulting strain experienced by the atoms at the vicinity of the steps, and the resulting influence of it on the catalytic activity of the whole surface.", as summarized by the third referee*

*In addition, the third referee stated that "Albeit the claim of the authors that it offers a new paradigm and design strategies for practical materials is in my view overstated, revealing and detailing effects that would allow for a better definition of the approximations applied in computational modeling is of critical importance to enable more accurate predictive capabilities." While this referee also raised concern about the semantics of the current work, they explained why our work can influence thinking in the field, i.e., enabling a more accurate prediction and design of heterogeneous catalysts, by revealing atomic site-specific strain at the vicinity of the step edge induced by surface stress release and its impact on ORR activity enhancement. We have revised our statement correspondingly, i.e. from "creates a new paradigm*

*for heterogeneous catalysis design” to “enables a more accurate prediction and design of heterogeneous catalysts”.*

*We will address the referee’s other constructive comments below, including providing a series of examples regarding the generality of the strain effects on catalytic activity. We hope the referee has found the revised manuscript merits publication in Nature now.*

**Q: 1) On the second page of the manuscript, the authors correctly state that the "cleavage of bulk metal ... leads to attractive interactions between surface atoms". However, I would have expected that the authors explain at least in one sentence why the cleavage leads to attractive interactions.**

*Response: We thank the referee for the constructive suggestion. We now have split the sentence into two sentences, along with the addition of an explanatory phrase. The revised sentences are as following: “Cleavage of bulk metal ... leads to a reduction in the number of the bonds of surface atoms and consequent charge redistribution. More specifically, such a process results in an increase in the charge density of surface atoms, which screens the electrostatic repulsion and induces a net attractive interaction between surface atoms.”*

**Q: 2) The authors estimate that the "surface pressure" on Pt(111) corresponds to a "huge" pressure of  $2 \times 10^5$  atm. I do not consider it appropriate to compare gas pressure to interatomic interactions. On the atomistic level, chemistry is based on electrostatic interactions which is 40 orders of magnitude stronger than the gravitational interaction, so it is no surprise that forces based on interatomic interactions are much stronger than forces corresponding to atmospheric pressure.**

*Response: We have removed the word “huge” and left the judgment for readers. While we agree on referee’s statement in general, we also would like to note that such surface pressure is about 10% of the bulk modulus. We have added this note in the revised version.*

**Q: 3) On page 7, the authors state that their "results additionally suggest that the catalytic activity of stepped surfaces is significantly more complex than what is implied by the widespread assumption that reactivity is identical for all terrace atoms. Specifically, as perfect Pt(111) single crystal surfaces are well known to bind too strongly to reaction intermediates for common electrocatalytic reactions, such as ORR, large."**

**I do not think that there is indeed a "widespread assumption that reactivity is identical for all terrace atoms", as there have already been DFT studies of adsorption energies across step edges and adjacent terraces. Furthermore, the second sentence cited above saying that Pt(111) binds too strongly appears strange considering that Pt is still considered to be the best ORR catalyst. Following this line of thought, it should rather be said that all other catalysts bind too strongly as their ORR activity is less than the one of Pt.**

*Response: We have removed the word “widespread” and left the judgment for readers. We note that, while we have been in the field so many years, we have not noticed any DFT studies of adsorption energies across step edges and adjacent terraces as we presented in the current work. So, we would be happy to cite them if the referee can provide us with the corresponding references that we have inadvertently neglected.*

*Regarding our statement of “Pt(111) binds too strongly”, we agree with the referee that Pt is the most active monometallic ORR catalyst and all other monometallic catalysts bind more strongly than that Pt. However, the comparison in our paper is not with respect to those monometallic catalysts, but “optimal catalysts” on volcano plots, i.e., those with a binding energy that is  $\sim 0.1$  eV weaker than that on Pt(111). Thus, in comparison with “optimal catalysts”, Pt(111) binds indeed still too strongly. In order to make this point clear, we have emphasized such a comparison, as highlighted in the revised version.*

**Q: 4) At the same page, the authors state for the first time in the article that close to the steps there is "an enhancement factor of  $\sim 50$  times compared to that of perfect Pt(111)". However, the reader does not have any chance to comprehend why there is an alleged enhancement of 50 times as no information is given how this enhancement is derived. Only when reading the methods section on page 18 of the manuscript, it becomes clear how this factor is derived. I understand that the full derivation given in the methods section should not be part of the main text. However, the authors should at least briefly explain how this factor is derived.**

*Response: We thank the referee for pointing out this confusion. We have added the following sentence before the statement “an enhancement factor of  $\sim 50$  times”, including directing readers to the method section for details: catalytic activity depends on the binding energy of reaction intermediates exponentially (see method section for more details). We hope it is helpful in reducing the confusion.*

**Q: 5) An enhancement factor of 50 sounds to be large. However, on the other hand the authors state on page 5/6 that "the maximum reduction in binding strength ... is in the range of 0.06-0.11 eV", which appears to be rather small. The factor 50 simply results from the fact that the change of at most 0.1 eV simply enters exponentially in the activity. In my opinion it is only fair to admit this fact. Changes in the adsorption energy by about 0.1 eV through some manipulation are usually not considered to be really large. It appears that by emphasizing the factor 50 the authors somehow exaggerate the strength of the change they observe close to the step sites.**

*Response: We have admitted and highlighted that an enhancement factor of 50 in ORR activity is due to a weakening of OH binding energy  $\sim 0.1$  eV in the revised version. We also have clarified that such a correlation is due to that ORR activity depends on the binding energy of reaction intermediates exponentially. We established such a correlation because ORR activity, rather than the binding energy of reaction intermediates, is what was measured experimentally and what we would like to compare with.*

*We also would like to explain why we care about a maximum weakening in OH binding energy of  $\sim 0.1$  eV and a maximum ORR enhancement of  $\sim 50$  times. First, we fully agree with the referee that changes in the adsorption energy by about 0.1 eV are usually not considered to be really large. Moreover, it is essentially the maximum change in adsorption energy observed in the current work, i.e. we are dealing with changes in adsorption energy even smaller than 0.1 eV. On the other hand, in many studies, such as references 7, 8, 11 and 12 cited in the current work which studied the change in adsorption energy versus the coordination number of surface atoms, even the minimum absolute errors (MAE) for the binding energy are similar to the maximum changes in the current work (i.e., both are on the order of 0.1 eV, see Figure R1), and the maximum absolute errors (MAX) are even much larger (i.e., on the order of 0.4 eV, see Figure R1). Those MAE and MAX imply uncertainties of 50 times and 6 orders of magnitude in predicted catalytic activity at room temperature. It is worth noting that the above examples cited only involve monometallic Pt atoms with different coordination numbers. If a change in elements and composition of catalysts is*



considered, the error bars in adsorption energy and the uncertainties in catalytic activity would be even larger.

Those large uncertainties lead to very low precision in predicted activity. The low precision in predicted activity is one important reason that the active sites for ORR on the stepped Pt(111) surfaces have not been identified over the last two decades: the differences in ORR activity between those surfaces are usually much smaller than 50 times. In order to identify the active sites, we need to reduce the error bar to a value much smaller than 0.1 eV in adsorption energy and increase the precision in predicted activity with uncertainty much smaller than 50 times. To achieve this goal, in the current work, we essentially eliminate the error bars and uncertainties by considering the activity of each individual atom, and their subtle geometric and electronic effects induced by the cooperative interactions between the various surface features, i.e., stress release induced by the presence of monoatomic steps and resulting atomic site-specific strain. As a consequence, we found that a cluster of atoms on terrace sites near the step edges are highly active atomic sites for ORR.

In summary, we correlated the weakening in OH binding energy with the ORR activity because catalytic activity is what was measured experimentally and what we needed to compare with. We considered small changes in the adsorption energy because high precision in predicted activity is desired to identify active sites for ORR on stepped Pt(111) surfaces.

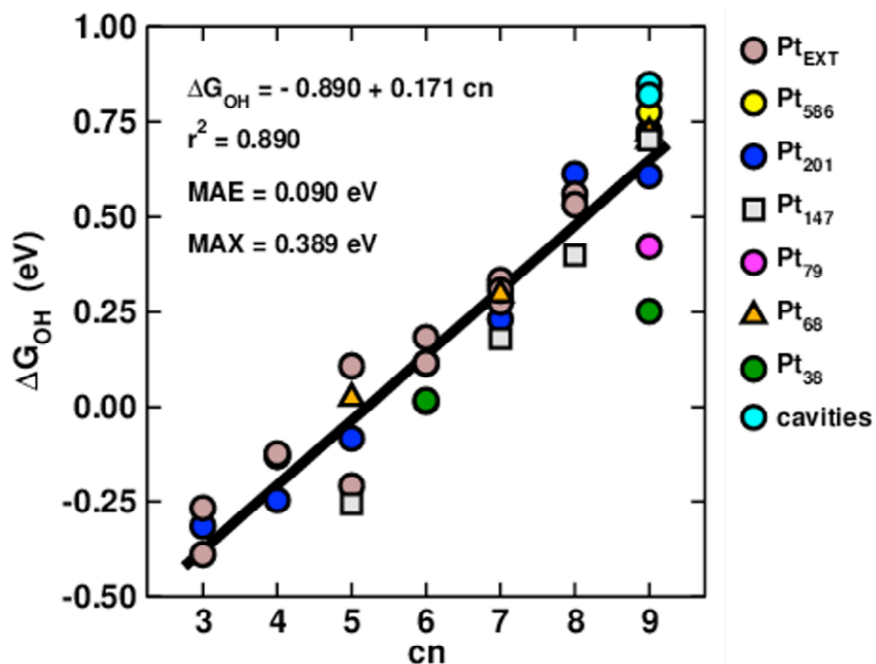


Figure R1. Adsorption energies of \*OH on various sites on Pt extended surfaces, Pt<sub>586</sub>, Pt<sub>201</sub>, Pt<sub>147</sub>, Pt<sub>79</sub>, Pt<sub>68</sub>, Pt<sub>38</sub>, and cavities plotted as a function of conventional coordination numbers, reported by Calle-Vallejo, F. et al. in Science 350 (2015) 185-189.

**Q: 6)** As mentioned above, only when carefully reading the theoretical methods section, it becomes clear where the enhancement factor comes from. It is based on the sentence:

"For Pt(111) surface, the potential-determining step is OH\* protonation to produce H<sub>2</sub>O, in which U<sub>4</sub> (Delta G<sub>4</sub> (U<sub>4</sub>) = 0) is the maximum potential". This means that the catalytic activity of the ORR on Pt depends on one single adsorption energy. However, the authors do not give any reference for this central statement. It is based on the well-known scaling relations. As Christensen et al., JPCC 120, 24910 (2016) put it:

"Based on the scaling relation, it is possible to use adsorption free energies as predictors for catalyst activity. For ORR, the adsorption free energy of OH\* can be used as predictor with the optimum at (4.92 eV - 3.2 +/- 0.2 eV)/2 = 0.9 +/- 0.1 eV. Catalysts which adsorb OH\* slightly (~0.1 eV) weaker than Pt have been found to display improved activity over Pt."

Response: *We thank the referee for reminding us of this paper. This paper and our current paper essentially used the same methods, including the well-known scaling relations and the volcano plots, which predict an OH binding energy that is ~0.1 eV weaker than that on Pt(111) for catalysts with optimal ORR activity. This is also the reason that we consider and focus on a weakening in OH binding energy within 0.1 eV. However, we did not refer to this paper per se. The current work is a succession of our previous ORR work published in Nano Energy (2016, 29, 369), Nano Letters (2017, 17, 3391), ACS Catalysis (2018, 8, 35), Science (2019, 363, 870) which did refer to JPCB (2004, 108, 17886), nchem (2009, 1, 466), ChemCatChem (2011, 3, 1159). Those references also have been cited in the above JPCC paper. We have cited those references and clarified it in the revised version.*

**Q: However, this is an exception rather than the rule. Typical catalytic activities depend on more than one adsorption energy. For example, activation barriers correspond to the difference between the energy of the system in the transition state and in the initial state. Now a lattice expansion of a late transition metal typically leads to stronger binding according to the d-band model. However, the stronger binding in the initial, the transition and the final state can all be different so that it cannot be predicted whether any activation or any reaction energies increases or decreases as a function of the lattice strain. Therefore in principle no general trends in the catalytic activity as a function of the lattice strain can be really predicted which is why the studies of Schlogl et al. mentioned above did not reveal any general trend.**

Response: *We agree with the referee that typical catalytic activities depend on more than one adsorption energy. We also agree with the referee regarding the above example in response to a lattice expansion (tensile strain), i.e., the stronger binding in the initial, the transition and the final state can all be different. We further agree with the referee that the studies of Schlogl and coworkers did not show general trends in the catalytic activity as a function of the lattice strain, because of the complexity and ill-defined nature of catalysts used in their experiment, as discussed in the above response (i.e., a wide size distribution of catalyst nanoparticles, faults and twins in catalysts, and the contribution from catalyst/support interfaces).*

*It is worth noting that while Schlogl and coworkers' papers did not show general trends in the catalytic activity as a function of the lattice strain, it has been demonstrated by the very first strain-activity paper published in 1998 by Mavrikakis, Hammer, and Nørskov (Phys. Rev. Lett. 1998, 81, 2819), and many other papers. For example, this paper showed that CO dissociation barriers on Ru(0001) decrease with increasing tensile strain and increasing binding of both the initial and the final state (Figure R2). It is understandable based on the bond order conservation principle as explained below. For CO dissociation CO\*+\* → C\*+O\**

under tensile strain, while the magnitude of the increasing binding of the initial state (i.e.,  $\text{CO}^*$ ) and final state (i.e.,  $\text{C}^*+\text{O}^*$ ) are different, they are ordered. This ordering is because the adsorption of atomic C and O with fully unsaturated bonds is much stronger than the adsorption of molecular CO with partially saturated bonds (see Figure R2). Also, there are two adsorbates at the final state (i.e.,  $\text{C}^*+\text{O}^*$ ) but only one adsorbate at the initial state (i.e.,  $\text{CO}^*$ ). As a consequence, while tensile strain leads to an increase in the binding of both the initial state and final state, the latter is much more pronounced, which consequently leads to more exothermic reaction energy. Based on the Brønsted–Evans–Polanyi (BEP) relationship (e.g, *Journal of Catalysis* 224 (2004) 206), more exothermic reaction energy would correspond to a lower reaction barrier, as exactly observed in this paper (Figure R2). As each elementary step may either lead to the break or the formation of chemical bonds of reactants, it would produce either more or less unsaturated bonds, which would result in either more or less exothermic reaction energy, and consequently either lower or higher reaction barrier in response to tensile strain. Thus, a general trend (i.e., increase or decrease) of both reaction energy and activation energy can be predicted as a function of lattice strain, though searching for exceptions is also part of the research.

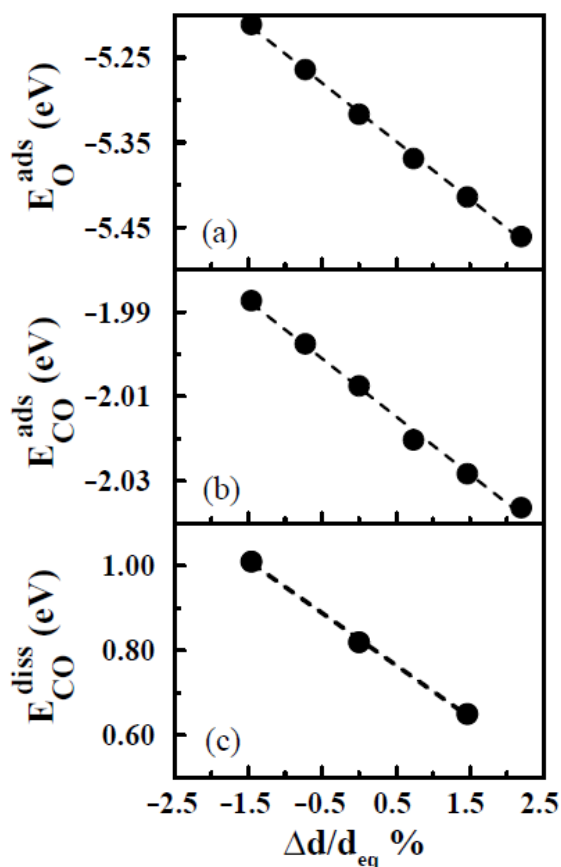


Figure R2 Effect of surface strain of Ru(0001) on the (a) binding energy of atomic oxygen ( $E_{\text{O}}^{\text{ads}}$ ) (top panel), (b) binding energy of molecular CO ( $E_{\text{CO}}^{\text{ads}}$ ) (middle panel), and (c) CO dissociation barrier ( $E_{\text{CO}}^{\text{diss}}$ ), referenced to a zero of the clean surface plus a gas phase CO molecule (bottom panel). This figure is adapted from Mavrikakis, Hammer, and Nørskov, *Phys. Rev. Lett.* 1998, 81, 2819.

As mentioned above, many other papers also have shown general trends in the catalytic activity as a function of the lattice strain using more well-defined systems and model reactions, in comparison with

Schlogl and coworkers. Among them, the ORR may be the most well-studied one for the strain effects, due to its importance for the hydrogen fuel cells. As shown in Figure R3, multiple experimental studies have unambiguously shown that compressive strain enhances ORR activity, while tensile strain decreases ORR activity. Such a trend also has been predicted by theory, including our own work (e.g., *Nano Lett.* 2017, 17, 3391; *ACS Catal.* 2018, 8, 35; *Science* 2019, 363, 870). Thus, there is a general trend in ORR activity as a function of the surface strain.

The hydrogen evolution reaction (HER) is another well-studied one for the strain effect. For the alkaline HER, it has been observed that, opposite to the ORR, compressive strain reduces activity and tensile strain increases activity with the maximum activity at ~2.8% strain, i.e., there is a volcano shape for activity versus surface strain (Figure R4). Thus, there is also a general trend in HER activity as a function of the surface strain.

*In addition to ORR and HER, a general trend in catalytic activity in response to surface strain has been observed for more complex reactions, such as the methanol oxidation reaction (see Figure R5) in which one single adsorption energy cannot be used as a descriptor for the catalytic activity (see Rossmeisl, Ferrin, Tritsarlis, Nilekar, Koh, Bae, Brankovic, Strasser, Mavrikakis, Bifunctional anode catalysts for direct methanol fuel cells. *Energy Environ. Sci.* 2012, 5, 8335). All these examples have demonstrated that, while Schlogl and coworkers were not able to show in their experiments using ill-defined catalysts, general trends in the catalytic activity as a function of the surface strain do exist for model reactions on more well-defined catalysts.*

*We have added the following statement in the revised version along with the related references. “We note that, in addition to ORR, general trends in catalytic activity in response to surface strain have been observed for chemical reactions that are either simpler or more complex than the ORR, including those in which one single adsorption energy cannot be used as a descriptor for the catalytic activity.”*

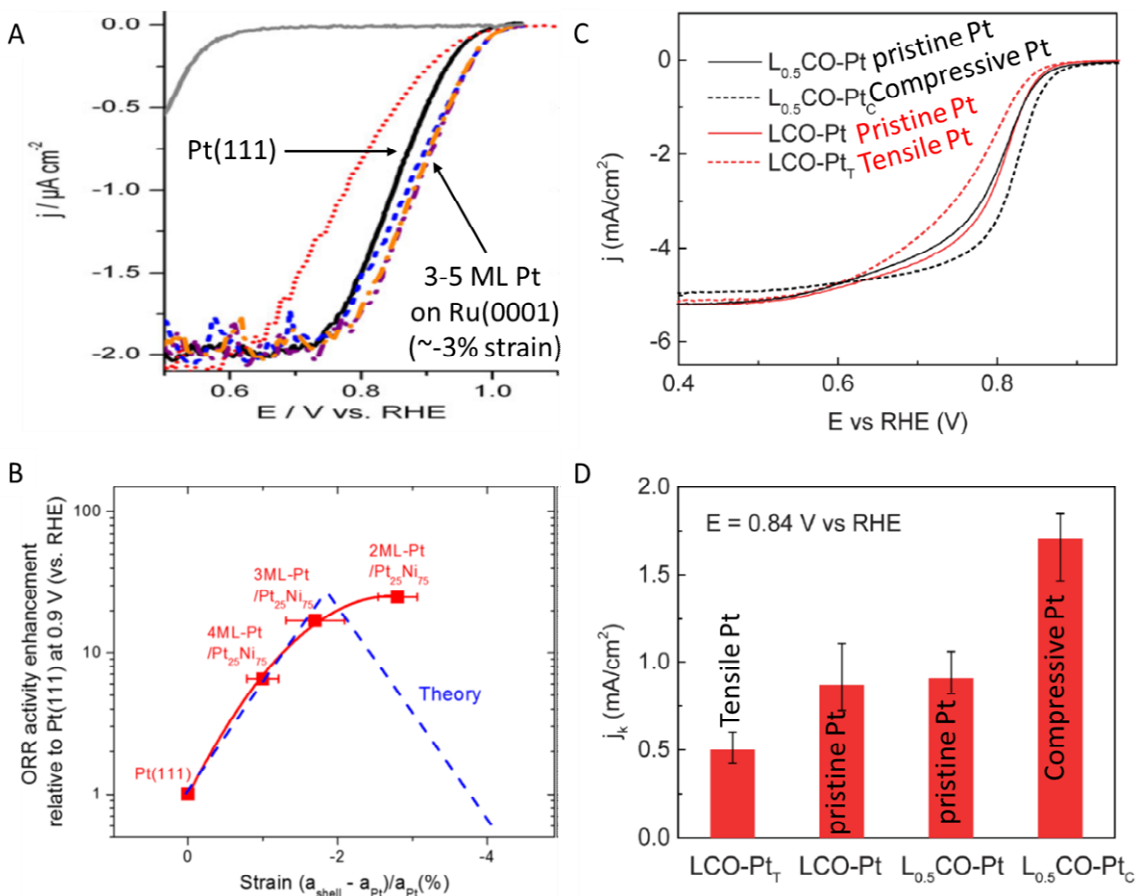


Figure R3 Measured ORR activity as a function of surface strain. These measurements show that compressive strain can enhance ORR activity, while tensile strain can decrease ORR activity. A: Brimaud, S.; Engstfeld, A. K.; Alves, O. B.; Hoster, H. E.; Behm, R. J., Oxygen Reduction on Structurally Well Defined, Bimetallic PtRu Surfaces: Monolayer  $\text{Pt}_x\text{Ru}_{1-x}/\text{Ru}(0001)$  Surface Alloys Versus Pt Film Covered Ru(0001). *Top. Catal.* 2014, 57, 222; B: Asano, M.; Kawamura, R.; Sasakawa, R.; Todoroki, N.; Wadayama, T., Oxygen Reduction Reaction Activity for Strain-Controlled Pt-Based Model Alloy Catalysts: Surface Strains and Direct Electronic Effects Induced by Alloying Elements. *ACS Catal.* 2016, 6, 5285; C,D: Wang, H.; Xu, S.; Tsai, C.; Li, Y.; Liu, C.; Zhao, J.; Liu, Y.; Yuan, H.; Abild-Pedersen, F.; Prinz, F. B.; Nørskov, J. K.; Cui, Y., Direct and continuous strain control of catalysts with tunable battery electrode materials. *Science* 2016, 354, 1031.

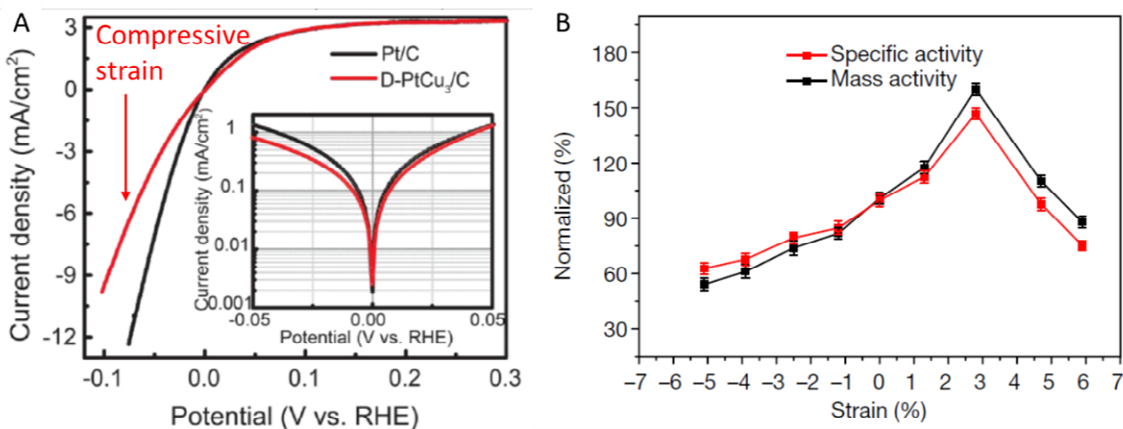


Figure R4 Influence of surface strain on alkaline HER. Compressive strain reduces HER activity, while tensile strain increases HER activity with a maximum at 2.8% strain. A: Jiao, L.; Liu, E.; Hwang, S.; Mukerjee, S.; Jia, Q., Compressive Strain Reduces the Hydrogen Evolution and Oxidation Reaction Activity of Platinum in Alkaline Solution. *ACS Catal.* 2021, 11, 8165; B: He, T.; Wang, W.; Shi, F.; Yang, X.; Li, X.; Wu, J.; Yin, Y.; Jin, M., Mastering the surface strain of platinum catalysts for efficient electrocatalysis. *Nature* 2021, 598, 76.

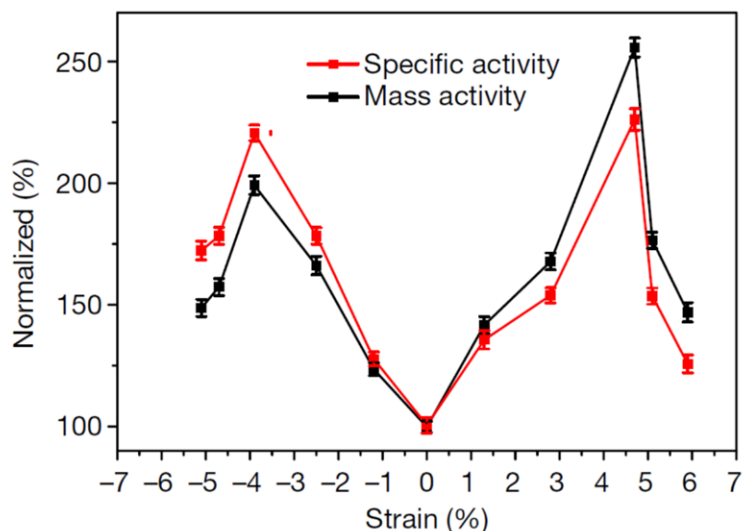


Figure R5 Influence of surface strain on the methanol oxidation reaction. This figure is adapted from He, T.; Wang, W.; Shi, F.; Yang, X.; Li, X.; Wu, J.; Yin, Y.; Jin, M., Mastering the surface strain of platinum catalysts for efficient electrocatalysis. *Nature* 2021, 598, 76.

**Q:** The authors of the present study consider a particular system in which one single adsorption energy can be used as a descriptor for the catalytic activity. However, again, this is an exception rather than a rule. Therefore the results of this particular study do not create "a new paradigm for heterogeneous catalyst design" and the manipulation of surface stress does not correspond to a "powerful strategy for control of catalytic activity" in general activity. In my opinion, this is the most critical point about the present study. Hence this paper is only suitable for a more focussed journal, but only once the special

**nature of the ORR on Pt(111) with respect to its dependence on one single adsorption energy is properly acknowledged in the manuscript.**

*Response: We understand that the referee is critical regarding whether surface strain affects catalytic activity in general. As shown above, there are indeed general trends of catalytic activity as a function of the surface strain for the ORR and the reactions that are either simpler or more complex than the ORR, in which one single adsorption energy cannot be used as a descriptor for the catalytic activity.*

*To further discuss the generality and limitation of the strain effect, we would like to put the strain effect in perspective: the strain effect is only one of those effects proposed in catalysis research. As the referee may know, other well-known effects include the ligand effects (or so-called electronic effects), the coordination effects (i.e. the effects of local coordination environments), and the composition effects (i.e., the effects of different chemical elements), among others. All of them have been frequently demonstrated to be able to affect catalytic activity in general (see National Science Review 2015, 2, 140 for a comprehensive review). But none of them are omnipotent, i.e., none of them are able to be applied to every single reaction, regardless of a simple or a complex reaction, but to those reactions sensitive to the corresponding effects. It should also be the case for the strain effect.*

*With these clarifications, we hope the referee has found that revealing atomic site-specific strain at the vicinity of the step edge induced by surface stress release and its impact on ORR activity enhancement provides an **effective strategy to tune catalytic activity of chemical reactions that are sensitive to surface strain**. We also have changed our statement correspondingly, from “powerful strategy for control of catalytic activity” to “**effective strategy to tune catalytic activity of chemical reactions that are sensitive to surface strain**.”*

*Also, based on referees’ comments, we have revised our statement from “creates a new paradigm for heterogeneous catalysis design” to “**enables a more accurate prediction and design of heterogeneous catalysts**”. We hope the referee has found the revised statement more accurate now. We also hope this statement appropriately describes the contribution and influence of our work to the field.*

**Referee #3 (Remarks to the Author):**

**Q:** In the present submission, Liu et al. aims at revealing an underestimated, more precisely not accounted for, influence of monoatomic step on the resulting strain experienced by the atoms at the vicinity of the steps, and the resulting influence of it on the catalytic activity of the whole surface. The oxygen reduction reaction has been chosen as model reaction, but the finding of the authors should be generalizable to any catalytic reactions.

*Response: We thank the reviewer for the positive comments regarding the originality of our work and the generality of our findings.*

**Q:** Formally, the effect of tensile/compressive strain on adsorption and (electro-)catalytic transformations with planar periodically ordered surfaces is already well documented in the literature, both computationally and experimentally (see e.g. works published by A. Gross and R.J. Behm). The authors, focusing on such effect induced by the presence of monoatomic step on the surface, bring the topic to a step further towards the direction of more realistic catalytic surfaces such as those employed into practical application, which are highly defective. Albeit the claim of the authors that it offers a new paradigm and design strategies for practical materials is in my view overstated, revealing and detailing effects that would allow for a better definition of the approximations applied in computational modelling is of critical importance to enable more accurate predictive capabilities. Furthermore, the search for the effect driving the rate of the catalytic reactions down to the atomic scale level is as old as the research in the catalysis field. In that sense, the approach undertaken by the authors is highly valuable.

*Response: We appreciate the reviewer's objective and positive comments. We are pleased to know that the reviewer has found our work highly valuable. Based on the reviewer's comments, we have changed our claim of "creates a new paradigm for heterogeneous catalysis design" to "enables a more accurate prediction and design of heterogeneous catalysts". We will address the reviewer's other constructive comments below.*

**Q:** At first glance, the manuscript proposed by the authors is quite appealing. It is well structured and well written. Methodology/approximation employed for the computational modelling, description of the catalytic reaction and experimental methods correspond to the state of the art and are well described. Nevertheless, a comparison of the findings/claims with literature records reveals some issues impeding the publication of this manuscript.

*Response: We are pleased to know the reviewer has found our manuscript appealing, and our computation and experiment state-of-the-art. We have thoroughly addressed the reviewer's constructive comments below. We hope the reviewer has found the manuscript suitable for publication now.*

**Q:** According to the results previously published by the Feliu's group (Electrochim. Acta 334 (2020) 135452) very (very) little influence of the step density is observed experimentally for the ORR kinetics on Pt[(111)x(110)] stepped surfaces in perchloric acid solutions with respect to Pt(111) (the surfaces modelled in the present submission). On the other hand a much more pronounced influence can be observed for Pt[(111)x(100)] (op. cit.) stepped surfaces, being furthermore non-monotonic. This raises two questions/comments regarding the claim of the authors:



- If the effect of stress release at the step vicinity in determining the final performances of the catalytic surface is of outstanding importance as claimed by the authors for these modelled surfaces, why an enhancement of the reaction rate is hardly detected experimentally?

Response: Below we will explain a possible reason for the negligible enhancement of the reaction rate in this specific experiment and demonstrate that the effect of stress release at the step vicinity is indeed important in determining the final performances of each surface for ORR. We have cited the paper published by the Feliu's group in 2007 (*Journal of Electroanalytical Chemistry* 599 (2007) 333), which compared the ORR activity of Pt[n(111)x(110)] surfaces in 0.1 M HClO<sub>4</sub> with respect to Pt(111). The surfaces studied and experimental conditions are essentially the same as those used in the above 2020 *Electrochimica Acta* paper mentioned by the reviewer, except the authors conducted the hydrogen peroxide reduction reaction before the ORR in the *Electrochimica Acta* paper. While very (very) little influence was observed in that *Electrochimica Acta* paper, a much larger influence was observed in the 2007 paper (e.g., up to 50 meV difference in the potential at a current density of a half diffusion limiting value, see Figure R6). It is worth noting that a similar large influence was also observed by other groups, such as Hoshi and co-workers (*Electrochimica Acta* 112 (2013) 899, see Figure R7). The consistency between the results in these two publications and that in our current work (both predictions and experience) is the reason that we have inadvertently neglected the paper mentioned by the referee and the discrepancies between these papers. We suspect that the hydrogen peroxide reduction reaction may have induced surface reconstruction, which leads to lower ORR activity in the *Electrochimica Acta* paper. We will explain this possibility below.

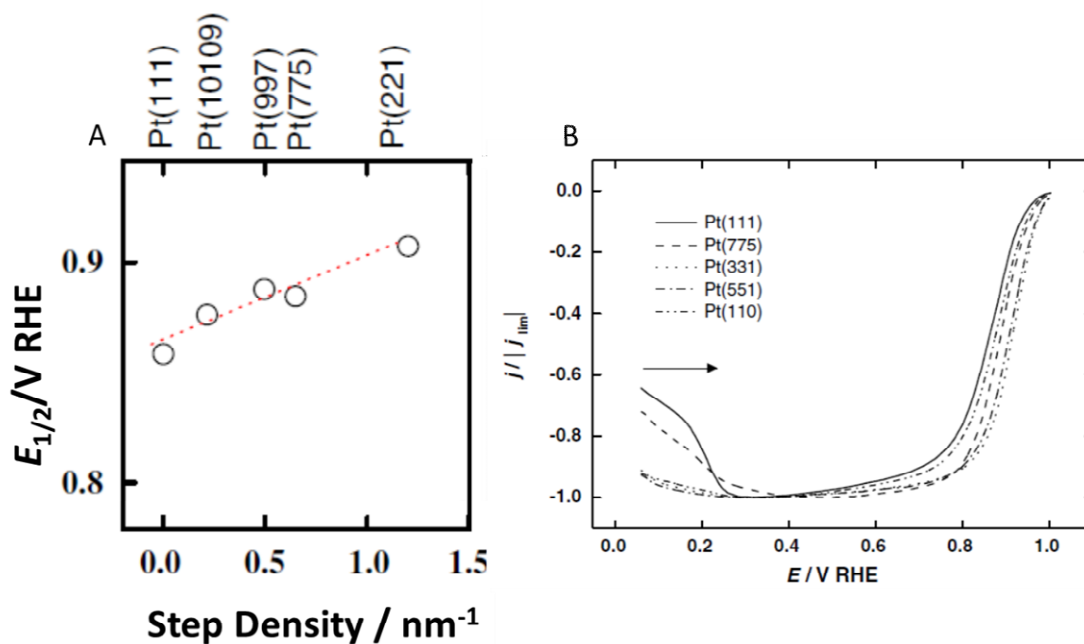


Figure R6. The influence of step density on the ORR activity of Pt[n(111)-(110)] reported by the Feliu group in the *Journal of Electroanalytical Chemistry* 599 (2007) 333. (A) the potential at a current density of a half diffusion limiting value, which increases up to 50 meV with the increasing step density. (B) typical polarization curves.

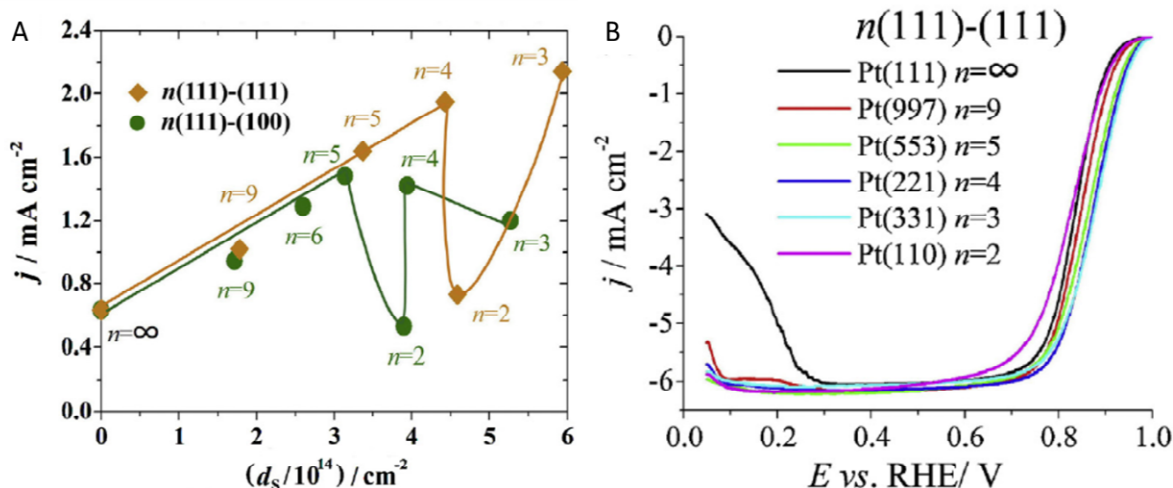


Figure R7. The influence of step density on the ORR activity of Pt[n(111)-(111)] (i.e., Pt[(n-1)(111)-(110)]) and Pt[n(111)-(100)] reported by Hoshi and co-workers in *Electrochimica Acta* 112 (2013) 899. (A) Cathodic current density  $j$  of the ORR at 0.90 V (RHE) plotted against the step atom density  $d_s$  in 0.1 M HClO<sub>4</sub>. (B) Typical polarization curves of Pt[n(111)-(111)].

To further understand the causes for the negligible enhancement reported by the Feliu group in the 2020 *Electrochimica Acta* paper, we have dug into the literature, especially the other papers published by the Feliu's group. We have found that, in addition to the above papers using stepped surfaces with relatively narrow terraces (3-20 atom wide) and large enhancement in predicted ORR activity, the Feliu's group also studied stepped surfaces with wider terraces (with 20-50 atom side, see *Catalysis Today* 244 (2015) 172) and small enhancement in predicted ORR activity. Consistent with our prediction, those surfaces with wider terraces indeed have relatively small enhancements in measured ORR activity. It is worth noting that the ORR enhancements on surfaces with wide terraces are similar to the ORR enhancements on surfaces with narrow terraces pre-treated by the hydrogen peroxide reduction reaction (see Figure R8). Such a similarity implies the possibility of surface reconstruction of those surfaces from narrow terraces to wide terraces induced by the hydrogen peroxide reduction reaction in the 2020 *Electrochimica Acta* paper.

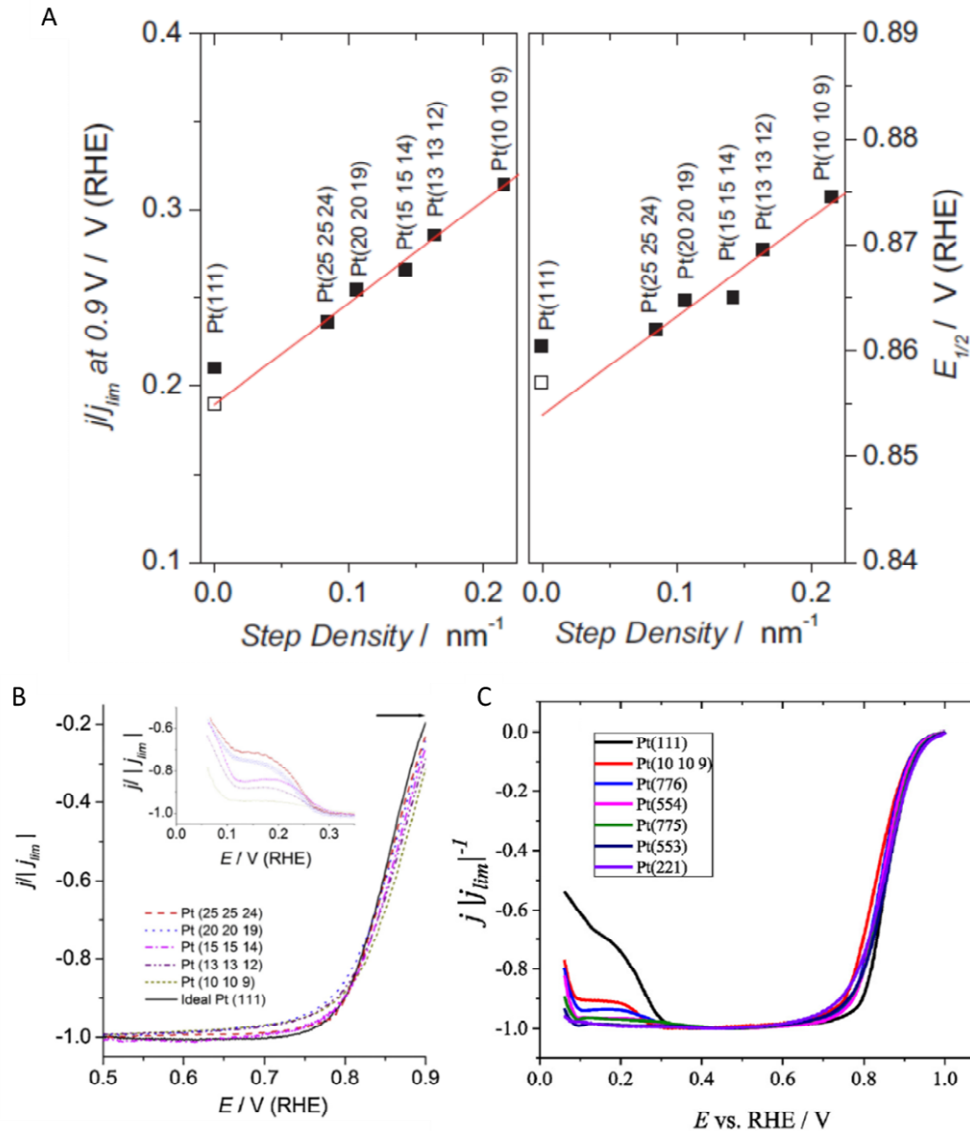


Figure R8. The influence of step density on the ORR activity of Pt[n(111)-(110)] reported by Feliu's group. (A, B) measurement on the wide terrace (with 20-50 atom side) reported in Catalysis Today 244 (2015) 172. (C) measurement on the narrow terrace (3-20 atom wide) after hydrogen peroxide reduction reaction reported in Electrochim. Acta 334 (2020) 135452.

Thus, we conclude that the effect of stress release at the step vicinity is indeed important in determining the final ORR activity of each surface. This is supported by our own experience and all observation in the literature except the one mentioned by the reviewer. We have cited the Feliu group's those additional papers to support such an argument. We also have added a note in the revised version regarding the exception: "Such a trend is in excellent agreement with the terrace width dependent ORR activity reported in the literature, except the one preceded by the hydrogen peroxide reduction reaction. We suspect the latter may have undergone surface reconstruction, as indicated by the similar activity to those with much wider terraces."

**Q: • Within the frame defined by the authors, how the symmetry of the step (either (110) or (100)) influences the stress release at the vicinity of the steps in the model of the authors to cope with the experimental observations where the enhancement of the ORR with the step density present different magnitude depending on the symmetry of the atomic step?**

*Response: In order to address the reviewer's comment, we have studied a new series of surfaces with (100) type steps, including the stress release at the vicinity of the steps, site-specific strain and their influence on the ORR activity. Before comparing the influence of symmetry ((110) vs (100)) on those predicted properties, we would like to first summarize our response to the reviewer's last comment: both our own experiment and all measurements in the literature, except the one mentioned by the reviewer, showed a large effect of stress release in determining the final ORR activity of surfaces with (110) type steps, e.g., up to 50 meV in the potential at a current density of a half diffusion limiting value  $E_{1/2}$  (see Figure R6 and Figure R7). Furthermore, although the effect is pronounced for surfaces with (100) type steps as indicated by the reviewer (i.e., up to 40 meV at  $E_{1/2}$ , see Figure R9), it is actually smaller than that on (110) type of steps. The differences in ORR activity between these two types of steps also can be seen from the cathodic current density at 0.9  $V_{RHE}$  (see Figure R7), i.e., a larger current for surfaces with the same terrace width but (110) type steps, in comparison to those with (100) type steps.*

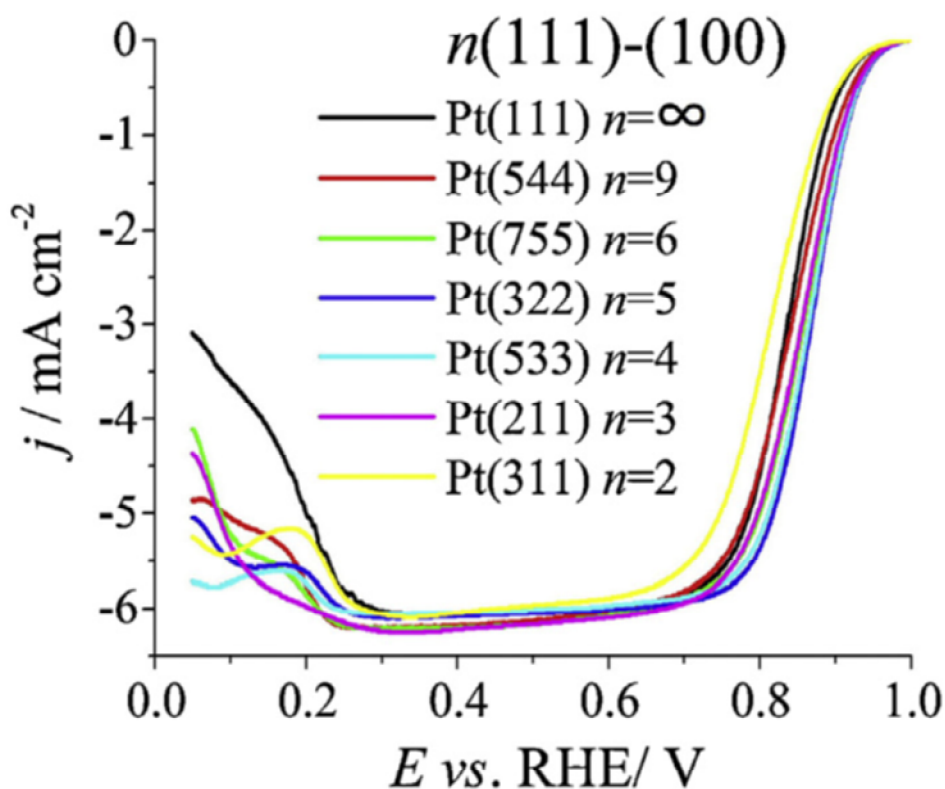


Figure R9. The influence of step density on the ORR polarization curves of Pt[n(111)-(100)] reported by Hoshi and co-workers in *Electrochimica Acta* 112 (2013) 899.

Now, we compare the influence of symmetry ((110) vs (100)) on the predicted stress release, site-specific strain, and ORR activity. As shown in Figure R10, in comparison with stepped Pt(111) surfaces with (110) type of steps, surfaces with (100) type steps have a smaller effect on the stress release and atomic-site specific strain, and consequently a smaller effect on the enhancement of the ORR activity. Such consistency between the prediction and the above experimental results in ORR activity further confirms the crucial role of stress release and atomic site-specific strain in the enhancement of ORR activity. Such results also verify the generality of the influence of stress release and atomic site-specific strain on the ORR activity. We discussed the differences in the main text and added the results of (100) type steps into extended data figures, along with a note in the main text: “We find that the above correlation between terrace width dependent stress release, atomic site-specific strain and ORR activity is applicable to stepped Pt(111) surfaces with (100) type steps, though the magnitude is smaller in comparison to surfaces with the same terrace width but (110) type steps (Extended Data Fig. 6, Extended Data Fig. 7 and Extended Data Fig. 8). Such a dependence on the symmetry of the steps is consistent with that observed in the previous experiment, which further confirms the crucial role of stress release and atomic site-specific strain played in the enhancement of ORR activity.”

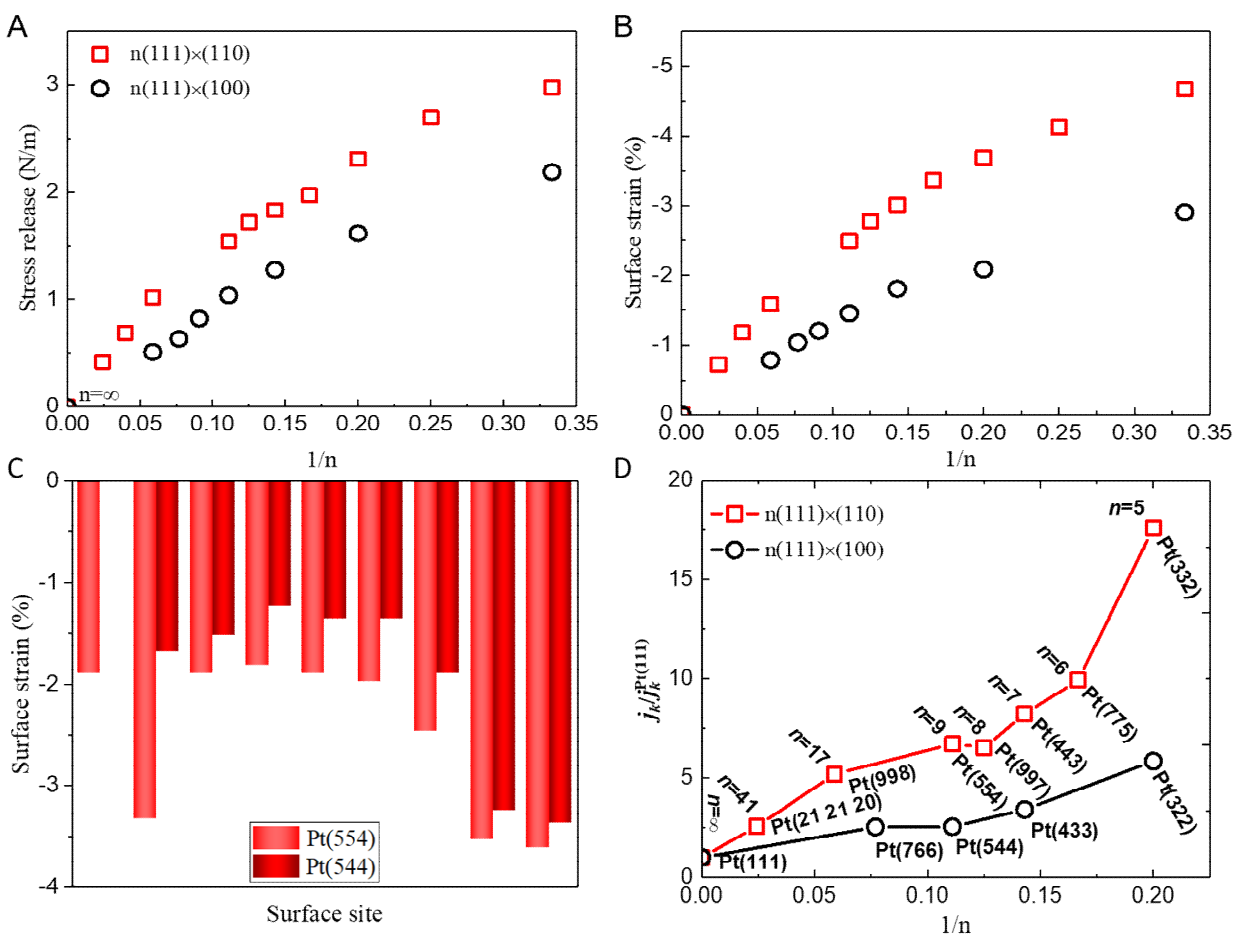


Figure R10. The influence of step type on surface stress, surface strain and ORR activity. (A, B) The correlation of stress release and surface strain with respect to atomic row  $n$ . (C) Atomic site-resolved surface strain of Pt(554) and Pt(544) surfaces with terrace width  $n=9$ . (D) The predicted relationship between terrace width and step type of stepped surfaces and ORR activity.

**Q: To support the generality of their finding, the authors partially covered a Pt stepped surface in a systematic fashion with Au adatoms, and probed the resulting enhancement on the ORR. Very little influence of the Au coverage is observed up to ca. 0.5 ML on the ORR activity, followed by a significant increase for higher Au coverage. Interestingly, earlier report from Behm's group (J. Electroanal. Chem. 716 (2014) 71-79) on Pt<sub>x</sub>Au<sub>1-x</sub>/Pt(111) surface alloys showed an almost completely suppressed hydroxyl adsorption for Au content higher than 50%, and suggesting that the size of atomic ensembles is larger than Pt<sub>3</sub> for the hydroxyl adsorption. Thus, the experimental results of the authors could be as well explained by an atomic ensemble effect, being too small at high Au coverage and leading to the destabilisation of the hydroxyls on the Pt surfaces. This would result as well into an enhancement of the ORR activity of the non-covered Pt surface. Thus, the strain/strain might not be the root cause of the enhancement of the ORR activity at high Au coverage.**

*Response: We thank the reviewer for reminding of us this paper from Behm's group. For Pt<sub>x</sub>Au<sub>1-x</sub>/Pt(111) surface alloys, there was no noticeable enhancement of ORR activity regardless of the Au content and the distribution of atomic ensembles. Such a result implies that ensembles of Pt atoms cannot enhance the ORR activity. In other words, the enhancement of ORR activity in our own Au/Pt experiment is not because of a change in the distribution of atomic ensembles, but something else. The linear correlation between Au coverage-dependent stress release and strain generation, and the relationship between surface strain and ORR activity suggest that stress release and extra strain would indeed be the root cause of the enhancement of the ORR activity.*

*It is worth noting that Au deposition not only releases residual stress and generates additional compressive strain, it also reduces surface sites with small strain. The latter may be the cause of a more notable activity enhancement at the Au coverage around 0.5ML, i.e. the disappearance of terrace sites with small strain. Such an effect is similar to that with decreasing terrace width of the stepped surfaces, as evidenced by the predicted ORR activity profile versus terrace width  $n$ , i.e. there is a more notable activity enhancement at the terrace width of  $n \leq 8$  (Figure R11). Such an activity profile is very similar to that versus Au coverage in Figure 3c, which confirms that strain is the root cause of the enhancement in ORR activity. We have added the following statement in the revised version: "A notable activity increase is observed when the Au coverage increases to 4/9 ML and higher coverages due to increasing strain in exposed Pt sites and disappearing terrace sites with small strain. The latter is similar to the effect of decreasing terrace width of the stepped surfaces, as evidenced by the predicted ORR activity profile versus terrace width  $n$ , i.e. there is a more substantial activity enhancement at the terrace width of  $n \leq 8$ ." We also have added Figure R11 to Extended Data Fig. 5. This analysis further demonstrates that stress release and strain are the root cause of the enhancement of the ORR activity at high Au coverage.*

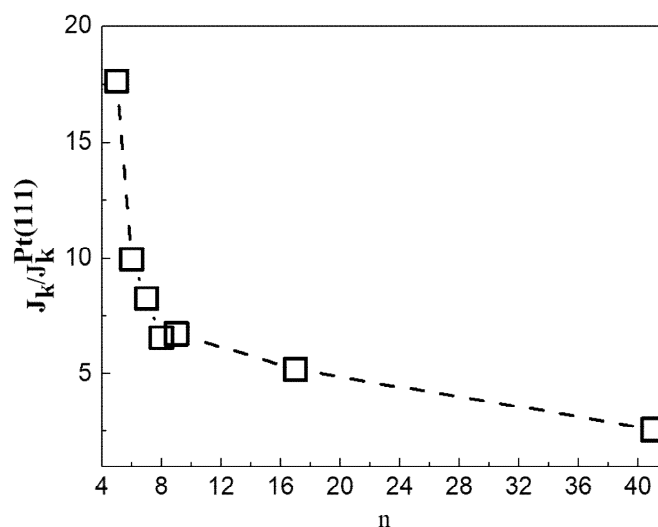


Figure R11. Predicted ORR activity of Pt[n(111)-(100)] with respect to the terrace width  $n$ .

**Q:** Since the authors claim that accounting for the modified surface stress at the vicinity of the atomic step ‘resolve’ long-standing issues related to the identification of the catalytic site for the ORR, I believe that a simple graphical representation would be helpful for the reader to track progresses and impact in detailing catalysis down to the atomic scale level. For example, showing the mismatch between predictions and measurements of the kinetic current density, accounting or not for such effect, would be valuable from a quantitative perspective. Comparing Fig. 3c and Fig. 4b, the computational model proposed by the authors seems to overestimate by one order of magnitude the enhancement of the ORR rate.

*Response:* We thank the reviewer for reminding of us the quantitative differences (i.e., overestimation by a factor of ~5 times, more precisely) between the predicted enhancements in Fig. 3c and the measured ORR activity and enhancements in Fig. 4b. Below, we will explain why there was a large overestimation in the predicted enhancements and how we can reduce it. First of all, lowering the mismatch between theory and experiment so as to achieve quantitative agreement is definitely our ultimate goal and the goal of the entire computational community, but remains a formidable task for catalytic reactions on surfaces, especially under electrochemical environments. Currently, the absolute errors between the predicted activity and measured activity are usually orders of magnitude. By taking advantage of normalization, however, we may be able to achieve a semi-quantitative agreement, i.e., within one order of magnitude. For example, by using Pt(111) as the reference, the predicted ORR enhancement of Pt(554) is 6.7 times, in comparison with that on Pt(111). Compared with the measured enhancement factor of 2.7, the overestimation factor is 2.5 times. For Au/Pt(554), if we still use Pt(111) as the reference, such an overestimation factor would enter the enhancement factor induced by Au, and magnify the relative error. This is precisely the reason for a large overestimation factor of ~5 in the predicted enhancements in Figure 3c.

To reduce such a large overestimation factor and at the same time highlight the impact of Au deposition, we can normalize the currents to Pt(554), rather than Pt(111), for the enhancement factor of Au/Pt(554). As shown in Figure R12, with such a change in the reference, we can reduce the overestimation factor from



$\sim 5$  to  $< 2$ . We also have updated Figure 3c correspondingly. To further reduce the overestimation factor, it would be necessary to take into account more factors, for example, beyond the current Sabatier analysis and more importantly a higher accuracy in the theoretical calculations. As a concept paper, instead of manipulating a quantitative agreement, which current DFT calculations are not able to achieve, we would rather live with an overestimation factor of  $\sim 2$  and emphasize the semi-quantitative agreement in the enhancement factors between the predicted and measured ORR activity both in the presence of step type defects and in the presence of Au with various coverage at the step edge. For the same reason, we would refrain from drawing a graphical representation to show the quantitative mismatch between predictions and measurements of the kinetic current density, accounting or not for the effect of stress release, though we appreciate such a suggestion.

We have replaced Fig. 3c with Figure R12A, along with the addition of the following note: "to reduce the errors induced by reference states and at the same time highlight the impact of Au deposition, we normalize the enhancements to Pt(554)."

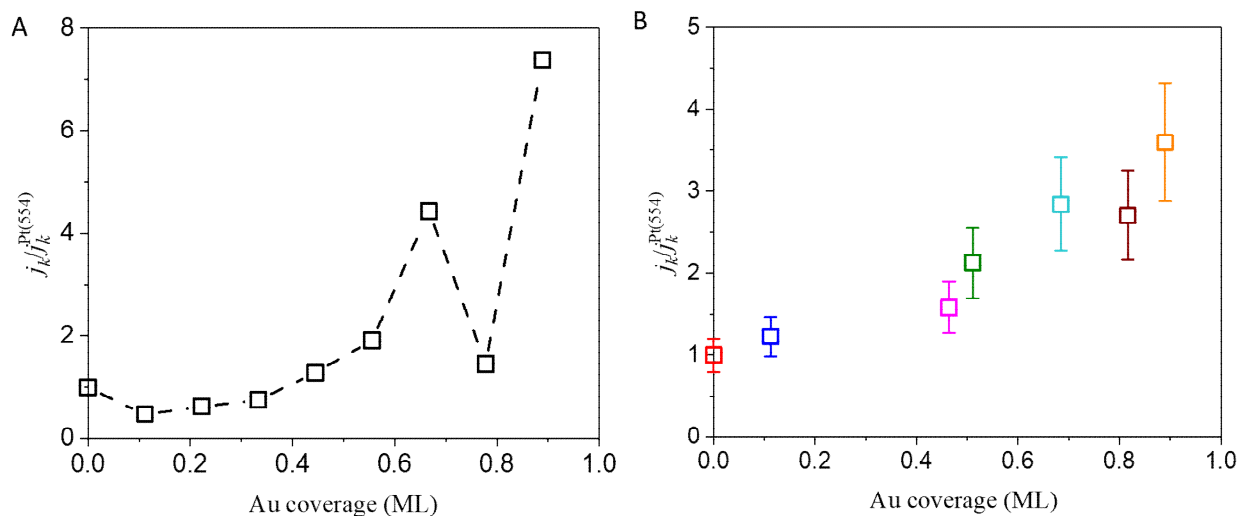


Figure R12. Predicted and measured ORR activity of Au/Pt(554) with respect to that of Pt(554).

**Q:** In summary, the modification of the strain experienced by atoms at the vicinity of atomic steps/defects is likely to occur. These atoms will indeed present different properties for the adsorption of species, and consequently different catalytic activity. Yet, it is in my view not demonstrated that i) the magnitude of this effect rationalizes the changes of the catalytic activity for the whole surface and ii) accounting quantitatively for this effect lowers significantly the mismatch theory/experiment.

*Response:* We thank the reviewer for affirming the qualitative validity of our key findings. We also would like to thank the reviewer for reminding of us those quantitative differences. By addressing the above two key questions as thoroughly as we are able to, we hope the reviewer has found the manuscript suitable for publication now. We would like briefly summarize our efforts below.

i) By comparing the predicted and measured ORR activity with respect to the terrace width for stepped (111) surfaces with both (110) type and (100) type step edges, we hope we have convinced the reviewer that taking into account stress release and atomic site-specific strain can rationalize the changes of the catalytic activity for the whole surface not only with respect to the terrace width but also the symmetry.



II) While exactly matching experimental results would require an error bar much smaller than the chemical accuracy, which is inaccessible for the current DFT calculations, we have achieved semi-quantitative agreement between predicted and measured ORR activity, by taking advantage of normalization.

Rather than a semi-quantitative agreement, we would like to highlight the uncertainty we reduced, the precision we achieved, and ultimately the active sites we revealed in the current work by taking into account the stress release and atomic site-specific strain. As shown in Figure R13, the minimum absolute errors (MAE) and the maximum absolute errors (MAX) for the binding energy of OH adsorption on Pt with various coordination numbers are in the order of 0.1 eV and 0.4 eV, which imply uncertainties of 50 times and 6 orders of magnitude, respectively, in ORR activity. By taking into account atomic site-specific strain induced by stress release, the current work eliminates such uncertainties and achieves precise prediction of atomic site-specific catalytic activity. Although the predicted activity is overestimated by a factor of  $\sim 2$  in comparison with the experimental values, it still unambiguously reveals the active sites for ORR on stepped Pt(111) surfaces, which provides a strategy to tune the overall surface reactivity, as demonstrated in the current work.

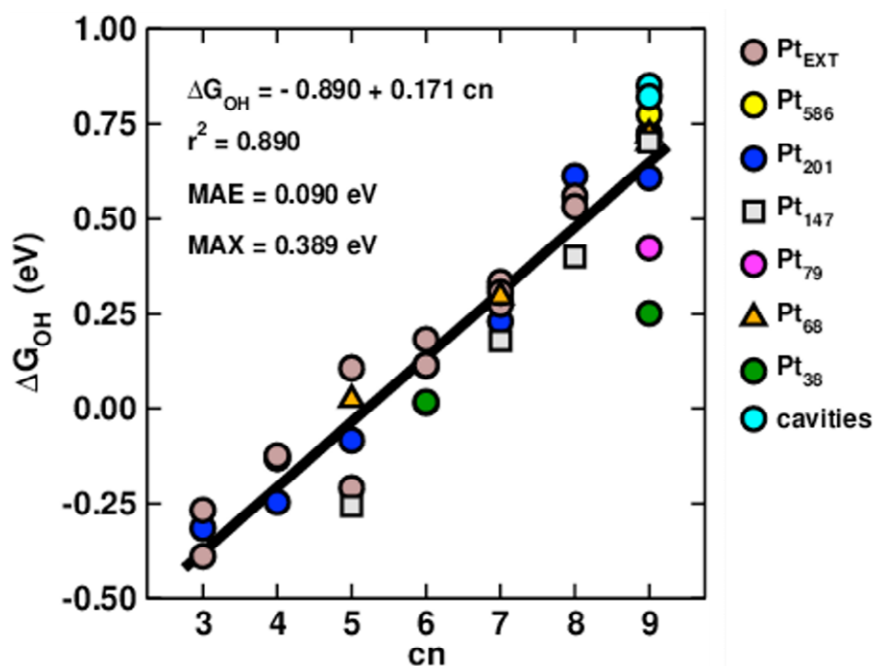


Figure R13. Adsorption energies of  $*OH$  on various Pt sites as a function of coordination numbers, reported by Calle-Vallejo et al. in Science 350 (2015) 185.

## Reviewer Reports on the First Revision:

----- Referees' comments -----

Referee #1 (Remarks to the Author):

I supported publication of this work in my first review, and I am pleased to see that the matters raised by the other two reviewers and myself have been addressed in the revised manuscript. Those improvements will further help conveying the key messages to a larger audience, as desirable for Nature readers.

I appreciate the argument that strain effects on catalytic activities are in themselves not a new phenomenon. The beauty in this work is the quantification and validation of this effect at chemically simple surfaces with a deeper dive into the actual atom positions/local lattice parameters and the resulting electronic structure.

In summary, I still support publication of this work, and I do so even more for the revised version.

Referee #2 (Remarks to the Author):

The authors have replied in very much detail to the criticism raised by the referees which I really appreciate. And certainly, the manuscript represents an interesting and competent work. Still I continue to be not convinced that this manuscript represents "an advance in understanding likely to influence thinking in the field", as is the prerequisite for publication in Nature, and therefore I recommend publication of this nice work in a more focused journal. Below I will respond in detail to the reply of the authors using the original numbering of my first report.

1) In response to my first point, the authors revised the text to "Cleavage of bulk metal ... leads to a reduction in the number of the bonds of surface atoms and consequent charge redistribution. More specifically, such a process results in an increase in the charge density of surface atoms, which screens the electrostatic repulsion and induces a net attractive interaction between surface atoms."

I appreciate that the authors have followed my advice to explain why cleavage leads to attractive interactions. However, I am not satisfied with their explanation. The authors explain the attractive interaction by the increased charge density. Yet, an increased charge density does not necessarily imply higher interactions. This is for example reflected in the construction of the Embedded-Atom-Method (EAM) by Daw and Baskes, the same idea also enters the Effective Medium Theory (EMT) by Norskov et al. Both methods include a charge density embedding term which exhibits a maximum binding for an optimal charge density. For a further increase of the charge density, the interaction becomes less attractive again. Hence there is no monotonic dependence of the net attractive interaction between surface atoms on the charge density.

The tensile strain of metal surfaces is much more naturally explained by bond-order arguments saying that the reduced coordination of the surface atoms compared to bulk atoms leads to a stronger binding between the metal surface atoms.

2) response okay

3) The authors state that in their response that they "have not noticed any DFT studies of adsorption energies across step edges and adjacent terraces as ... presented in the current work" in spite of the fact that they "have been in the field for so many years". Now referee #3 explicitly mentions the work by A. Gross and R.J. Behm. Hence the authors might want to have a look at

Electrocatal. 8, 530 (2017), DOI:10.1007/s12678-017-0354-1 , where exactly such a DFT study of adsorption energies across a step and a terrace has been presented.

4-5) response okay

6) In their response, the authors use an example taken from the seminal paper by Mavrikakis about strain effects on surfaces, here particularly the reduction of the CO dissociation barrier for increasing surface strain. They argue that bond-breaking processes lead to an exothermic reaction energy which is then connected to a lowering of the reaction barrier invoking the Bronsted-Evans-Polanyi relationship. I accept the argument with the BEP relationship, however, I do not think that the general statement is true that dissociative reactions on surfaces are in general exothermic, in particular when the initial product might be a radical. An example is the dissociation of methoxy into formaldehyde and hydrogen on a catalyst surface which occurs in the methanol oxidation. This reaction is typically strongly endothermic, and it might be the reason for the non-uniform influence of surface strain on the methanol oxidation reaction shown in Fig. R5 in the reply. The authors might also want to consider J. Catal. 231, 420 (2005), Catal. Lett. 127, 113 (2009) and J. Mol. Catalysis A 393, 296 (2014) where strain effects in the methanol oxidation on metal surfaces have been considered by DFT calculations.

Furthermore, many catalytic processes usually include both bond-breaking and bond-making steps, and then it would depend on the rate-limiting step whether the reaction is promoted or suppressed upon applying lattice strain. To me, these are strong arguments that it cannot be predicted whether surface reactivity in general is enhanced or lowered as a function of lattice strain.

In principle, the seminal paper by Mavrikakis et al. mentioned by the authors has shown that surface strain influences the energetics on surfaces. Hence since the publication of this paper in 1998 it is no surprise that surface strain, for example generated at stepped Pt surfaces, modifies the reaction and activation energies of surface reactions. Hence I cannot endorse that the authors have made a "discovery", as written in the abstract.

I would like to add a final point in this respect. In their abstract the authors claim that their "discovery provides a new perspective for both fundamental understanding of catalytically active atomic sites and the rational design of heterogeneous catalysts." As far as the fundamental understanding is concerned, I already argued above that strain effects in the interaction of adsorbates with surfaces have been studied for 25 years, and in my opinion the otherwise very nice study of the authors does hardly add anything to this fundamental understanding. Second, I like to question whether the results of this study will really provide new routes for the "rational design of heterogeneous catalysts". Commercial catalysts are typically not made of single crystals, but rather consist of supported nanoparticles that naturally have a high defect and step density. It is unclear how the authors want to "control ... reactivity by either varying terrace widths or controlling external stress" for such catalysts, as they write in the abstract. Hence I wonder how the insights gained in this study will enter the design of such catalysts.

Referee #3 (Remarks to the Author):

With the revised version of their manuscript, the authors provided detailed point-by-point answers to the comments made by my-self and by Reviewer#2. In my view, the arguments developed by the authors, largely supported by references, together with the revisions applied on the manuscript lift-up the concerns raised in the first round of review.

I am particularly happy to see that the results in the 2020 paper from the Feliu's group were in fact an outlier when compared to a larger set of experimental data on Pt[(111)x(110)]. The

additional calculations on Pt[(111)x(100)], qualitatively consistent when experimental data gained on the two types of step geometries are compared, provide additional strength to the claim of the authors.

I do not have further technical comments, the article and the findings are very fine, only one of more semantic nature for the general positioning of the manuscript. The authors wrote the following:

- ‘...provides new perspective for both fundamental understanding of catalytically active atomic sites and the rational design of heterogeneous catalysts’ introductory section, page 2, l.31.
- ‘...enables a more accurate prediction and design of heterogeneous catalysts’, page 3, l.50

It is in my view more than optimistic to consider that the present work could find a straight way for preparation of practical nanostructured catalysts materials. I mentioned in the first round of review, that this is a ‘step towards the direction of more realistic catalytic surfaces such as those employed in practical application’. The way is however quite long from extended single crystals to practical supported catalysts. The ‘catalyst-by-design’ approach at this scale will remain complicated since:

- most of the preparation methods for the preparation of catalyst are colloidal syntheses where numerous forces takes place in establishing the final catalyst particulates;
- the strain release might be counter-balanced by the compressive strain taking place in nanostructured catalysts;
- the industrial constrains where production costs and production rate will be balanced against potential gains in catalytic reactivity and durability of these gain of performances over time.

I understand that the authors wish to bind their works to a potential practical application and this comment on the perspective for the preparation of catalyst should not be received as minoring the impact of the findings presented by the authors. A fundamental understanding, unveiling critical effects not accounted for, enabling the resolution/description of the catalytic site down to the atomic scale-level driving the whole reaction rate observed experimentally, and nurturing a more accurate framework of approximations in computational chemistry/catalysis are my view a horizon more than sufficient. This is already quite a substantial achievement in the broad field of the catalysis (!), well suited for the readership of a journal like Nature. Here, I let the editor in charge of the manuscript and the authors to refine maybe a bit the final wording on this aspect.

Minor points:

- There is no ORR data in the Ref. 27. If you wish to cite works from the Behm’s group for the ORR on PtAu, you may want to prefer this one: J. Electroanal. Chem. 716 (2014) 71-79
- Page 10, l.172: ‘...Au is relatively inert for the ORR’: you could add ‘in acidic solutions’ to be more precise since the kinetics of the ORR on Au(100) and stepped Au single crystals in alkaline electrolytes is not that bad (see e.g. ancient Adzic’s works, likely published in the 80’s-early 90’s in J. Electroanal. Chem.).

I am in favour to make also available the reviews for the readers upon publication of the manuscript (of course if the authors and the other reviewers agree).

Beyond the scope of the present manuscript, I wonder if the strain release induced by the vicinity of an atomic step would be of sufficient magnitude to lead to a subtle revision/enrichment of the general model describing the factors governing the nanocrystal shapes (both Wulff equilibrium and kinetic shapes, see e.g. Claude R. Henry, Progresses in Surface Science 80 (2005) 92-116), since this model essentially relies on the surface tension of the nanocrystal facets. To make the things clear, I do not ask the authors to discuss this for the present manuscript, but it might be worth to have a look at it in future works.

Sylvain Brimaud

----- End of comments -----

## Author Rebuttals to First Revision:

1 Response to the referees' comments

2 General remark: We would like to thank the referees for their time and constructive  
3 comments, which have contributed significantly to the continual improvement of our  
4 manuscript. Now, we have thoroughly addressed all the comments and revised the  
5 manuscript accordingly. **The revisions are highlighted in the manuscript.** The point-by-  
6 point responses are listed below, with the referees' original comments shown in **bold**  
7 and our responses shown in *italics*.

8

9 Referee #1 (Remarks to the Author):

10 **I supported publication of this work in my first review, and I am pleased to see that**  
11 **the matters raised by the other two reviewers and myself have been addressed in**  
12 **the revised manuscript.**

13 **Those improvements will further help convey the key messages to a larger audience,**  
14 **as desirable for Nature readers.**

15 **I appreciate the argument that strain effects on catalytic activities are in themselves**  
16 **not a new phenomenon. The beauty in this work is the quantification and validation**  
17 **of this effect at chemically simple surfaces with a deeper dive into the actual atom**  
18 **positions/local lattice parameters and the resulting electronic structure.**

19 **In summary, I still support publication of this work, and I do so even more for the**  
20 **revised version.**

21 *Response to referee 1: We would like to thank the referee for taking the time to*  
22 *carefully review our revised manuscript and for the strong support of its publication in*  
23 *Nature.*

24

25 Referee #2 (Remarks to the Author):

26 **The authors have replied in very much detail to the criticism raised by the referees**  
27 **which I really appreciate. And certainly, the manuscript represents an interesting and**  
28 **competent work. Still I continue to be not convinced that this manuscript represents**  
29 **"an advance in understanding likely to influence thinking in the field", as is the**  
30 **prerequisite for publication in Nature, and therefore I recommend publication of this**  
31 **nice work in a more focused journal. Below I will respond in detail to the reply of the**  
32 **authors using the original numbering of my first report.**

33 *Response: We would like to first thank the referee for recognizing our efforts. We*  
34 *understand that the referee is still not convinced of the significance of the current work.*  
35 *To further clarify the value of our work, we would like to first quote words from the*  
36 *other two referees and then add a few additional words.*

37 *The third referee explained why the findings in the current work can influence thinking*  
38 *in the field: it is "a fundamental understanding, unveiling critical effects not accounted*  
39 *for, enabling the resolution/description of the catalytic site down to the atomic scale-*  
40 *level driving the whole reaction rate observed experimentally, and nurturing a more*  
41 *accurate framework of approximations in computational chemistry/catalysis". The first*  
42 *referee gave a similar comment: "The beauty in this work is the quantification and*  
43 *validation of this effect at chemically simple surfaces with a deeper dive into the actual*

44 *atom positions/local lattice parameters and the resulting electronic structure". The*  
45 *third referee give the following overall assessment: "quite a substantial achievement*  
46 *in the broad field of the catalysis, well suited for the readership of a journal like Nature".*

47 *Thus, for "an advance in understanding likely to influence thinking in the field", it is the*  
48 *following findings: the presence of small imperfections, such as step-type defects, can*  
49 *break the symmetry and lead to the release of the surface stress, relaxation of surface*  
50 *atoms, and generation of inhomogeneous strain fields that may span multiple*  
51 *nanometers on transition metal surfaces. The associated electronic and geometric*  
52 *effects lead to atomic site-specific reactivity, which results in orders of magnitude*  
53 *differences in catalytic activity even for atoms with identical local environments. This*  
54 *phenomenon in catalytic activity resolves longstanding puzzles about the nature of the*  
55 *active site and structure sensitivity of the ORR in the literature, among others. While*  
56 *each individual effect or phenomenon may have already been known, understanding*  
57 *their synergistic interaction is an advance likely to influence thinking in the field.*

58 *So, along with the detailed response below, we hope the referee has found the revised*  
59 *version suitable for publication in Nature now.*

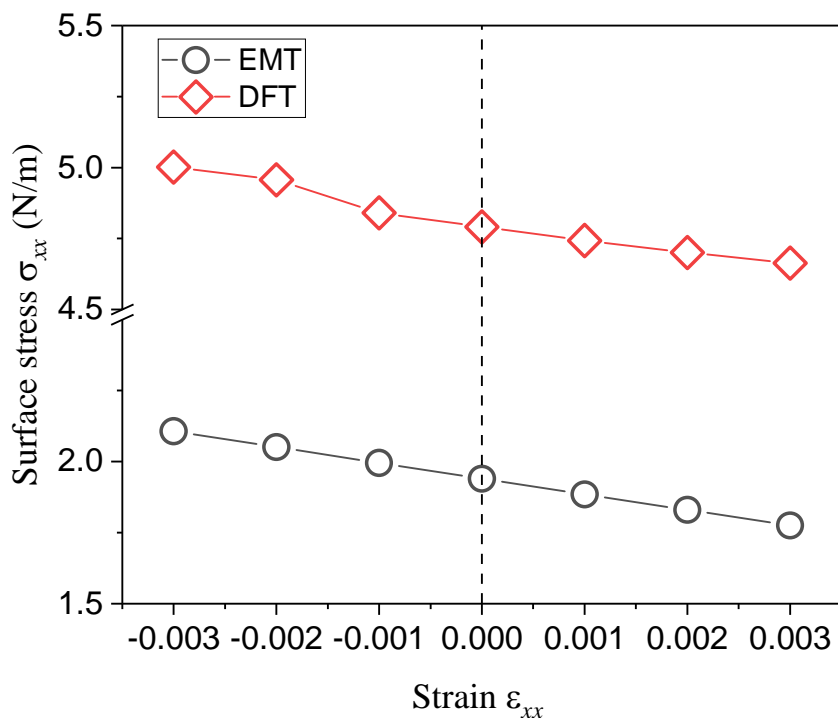
60

61 **1) In response to my first point, the authors revised the text to "Cleavage of bulk**  
62 **metal ... leads to a reduction in the number of the bonds of surface atoms and**  
63 **consequent charge redistribution. More specifically, such a process results in an**  
64 **increase in the charge density of surface atoms, which screens the electrostatic**  
65 **repulsion and induces a net attractive interaction between surface atoms." I**  
66 **appreciate that the authors have followed my advice to explain why cleavage leads**  
67 **to attractive interactions. However, I am not satisfied with their explanation. The**  
68 **authors explain the attractive interaction by the increased charge density. Yet, an**  
69 **increased charge density does not necessarily imply higher interactions. This is for**  
70 **example reflected in the construction of the Embedded-Atom-Method (EAM) by**  
71 **Daw and Baskes, the same idea also enters the Effective Medium Theory (EMT) by**  
72 **Norskov et al. Both methods include a charge density embedding term which**  
73 **exhibits a maximum binding for an optimal charge density. For a further increase of**  
74 **the charge density, the interaction becomes less attractive again. Hence there is no**  
75 **monotonic dependence of the net attractive interaction between surface atoms on**  
76 **the charge density.**

77 **The tensile strain of metal surfaces is much more naturally explained by bond-order**  
78 **arguments saying that the reduced coordination of the surface atoms compared to**  
79 **bulk atoms leads to a stronger binding between the metal surface atoms.**

80 *Response: we would like to thank the referee for reminding us of the role of the reduced*  
81 *coordination on surface stress. While we emphasized the role of charge redistribution*  
82 *on surface stress, we did not intend to exclude the role of reduced coordination. For*  
83 *DFT calculations, both contributions are included simultaneously. To further illuminate*  
84 *this point, we now have performed EMT calculations on Pt(111), as a case study, to*  
85 *evaluate the contribution of reduced coordination. Surface stress from the EMT*  
86 *calculation is 1.94 N/m, which is about 40% of surface stress from the DFT calculation*

87 (see Figure R1). This result implies that electronic structure effects, which are  
 88 accounted for in the DFT calculations, also influence the stress, and we can conclude  
 89 that both reduced coordination and charge redistribution contribute to the tensile  
 90 surface stress. As the total surface stress and its release are the driving forces of atomic  
 91 site-specific strain, we will not emphasize each individual contribution. So, we have  
 92 revised the manuscript as follows: "Cleavage of bulk metal to create surfaces, which  
 93 leads to a reduction in the coordination of surface atoms and consequent charge  
 94 redistribution, usually induces an attractive interaction between surface atoms".



95

96 Figure R1 surface stress of a 6ML Pt(111) slab calculated with EMT and DFT. Surface  
 97 stress is evaluated with the formula  $\sigma_{xx} = \frac{1}{A} \frac{\partial(\gamma A)}{\partial \epsilon_{xx}}$  and interpolated to 0 strain.

98 2) response okay

99

100 3) The authors state that in their response that they "have not noticed any DFT  
 101 studies of adsorption energies across step edges and adjacent terraces as ...  
 102 presented in the current work" in spite of the fact that they "have been in the field  
 103 for so many years". Now referee #3 explicitly mentions the work by A. Gross and R.J.  
 104 Behm. Hence the authors might want to have a look at *Electrocatal.* 8, 530 (2017),  
 105 DOI:10.1007/s12678-017-0354-1, where exactly such a DFT study of adsorption  
 106 energies across a step and a terrace has been presented.

107 *Response: We would like to thank the reviewer for reminding us of this insightful paper.*  
 108 *A. Gross and R.J. Behm are two pioneers in the field, and we apologize for inadvertently*  
 109 *neglecting their impactful work. It is worth noting that the trend in atomic site-specific*

110 hydrogen adsorption reported in the paper can be explained by the stress release,  
111 strain generation, and associated effects on surface reactivity revealed in our work.  
112 Now, we have cited this paper in the revised version as we have promised, along with  
113 the following statement: *It is worth noting that the above results also can explain the*  
114 *site specific hydrogen adsorption on Pt monolayer island modified Ru(0001) surfaces.*

115  
116 4-5) response okay

117  
118 **6) In their response, the authors use an example taken from the seminal paper by**  
119 **Mavrikakis about strain effects on surfaces, here particularly the reduction of the CO**  
120 **dissociation barrier for increasing surface strain. They argue that bond-breaking**  
121 **processes lead to an exothermic reaction energy which is then connected to a**  
122 **lowering of the reaction barrier invoking the Bronsted-Evans-Polanyi relationship. I**  
123 **accept the argument with the BEP relationship, however, I do not think that the**  
124 **general statement is true that dissociative reactions on surfaces are in general**  
125 **exothermic, in particular when the initial product might be a radical. An example is**  
126 **the dissociation of methoxy into formaldehyde and hydrogen on a catalyst surface**  
127 **which occurs in the methanol oxidation. The authors might also want to consider J.**  
128 **Catal. 231, 420 (2005), Catal. Lett. 127, 113 (2009) and J. Mol. Catalysis A 393, 296**  
129 **(2014) where strain effects in the methanol oxidation on metal surfaces have been**  
130 **considered by DFT calculations.**

131 **Furthermore, many catalytic processes usually include both bond-breaking and**  
132 **bond-making steps, and then it would depend on the rate-limiting step whether the**  
133 **reaction is promoted or suppressed upon applying lattice strain. To me, these are**  
134 **strong arguments that it cannot be predicted whether surface reactivity in general is**  
135 **enhanced or lowered as a function of lattice strain.**

136 *Response: First, we note that there is a misunderstanding between us and the referee*  
137 *regarding the word “exothermic”. In our first response, we stated that “while tensile*  
138 *strain leads to an increase in the binding of both the initial state and final state, the*  
139 *latter is much more pronounced, which consequently leads to more exothermic*  
140 *reaction energy”. We apologize that this terminology was not clear. We simply meant*  
141 *that a reduction in the reaction energy (stabilization) is generally correlated with a*  
142 *reduction in the activation barrier. This statement of the BEP principle holds for both*  
143 *endothermic and exothermic reactions We hope that this explanation resolves the*  
144 *misunderstanding.*

145 *Concerning the referee’s comments about the generality of strain effects: we fully*  
146 *agree that surface strain does not have the same effect on all reactions. In fact,*  
147 *reaction rates may be either increased or decreased by strain, depending upon the*  
148 *details of the chemical reaction and the catalytic mechanism. Further, it is quite*  
149 *possible that certain magnitudes of strain may promote a reaction, while excessive*  
150 *strain can impede the reaction (for example, for ORR on Pt, while we and others state*  
151 *that compressive strain promotes ORR, there are subtleties as well, i.e., the effect may*  
152 *reverse and lead to suppression in the ORR when strain is beyond a critical value). Thus,*



153 *it would be too arbitrary to generalize the effect without a fundamental understanding*  
154 *of the rate-limiting steps (potential-limiting steps), and their sensitivity toward surface*  
155 *strain. Indeed, for this very reason, we sought a fundamental understanding of the*  
156 *rate-limiting steps (potential-limiting steps) in the ORR, and their sensitivity toward*  
157 *surface strain in our previous studies(Nat Chem 2, 454-460 (2010), Nano Lett. 17, 3391-*  
158 *3395 (2017), ACS Catal. 8, 35-42 (2018), and Science 363, 870-874 (2019)). In general,*  
159 *strain can certainly influence catalytic reactions, but for the above reasons, it is not our*  
160 *intention to generalize trends beyond those reported in the literature, but to show a*  
161 *concrete case in fundamental understanding of the causality of surface stress release*  
162 *and the activity sites for the ORR.*

163

164 **In principle, the seminal paper by Mavrikakis et al. mentioned by the authors has**  
165 **shown that surface strain influences the energetics on surfaces. Hence since the**  
166 **publication of this paper in 1998 it is no surprise that surface strain, for example**  
167 **generated at stepped Pt surfaces, modifies the reaction and activation energies of**  
168 **surface reactions. Hence I cannot endorse that the authors have made a "discovery",**  
169 **as written in the abstract.**

170 **I would like to add a final point in this respect. In their abstract the authors claim**  
171 **that their "discovery provides a new perspective for both fundamental**  
172 **understanding of catalytically active atomic sites and the rational design of**  
173 **heterogeneous catalysts." As far as the fundamental understanding is concerned, I**  
174 **already argued above that strain effects in the interaction of adsorbates with**  
175 **surfaces have been studied for 25 years, and in my opinion the otherwise very nice**  
176 **study of the authors does hardly add anything to this fundamental understanding.**  
177 **Second, I like to question whether the results of this study will really provide new**  
178 **routes for the "rational design of heterogeneous catalysts". Commercial catalysts are**  
179 **typically not made of single crystals, but rather consist of supported nanoparticles**  
180 **that naturally have a high defect and step density. It is unclear how the authors want**  
181 **to "control ... reactivity by either varying terrace widths or controlling external**  
182 **stress" for such catalysts, as they write in the abstract. Hence I wonder how the**  
183 **insights gained in this study will enter the design of such catalysts.**

184 *Response: We realize that there is a misunderstanding between us and the referee*  
185 *regarding the definition of "this discovery". First of all, we did not claim that we*  
186 *discovered the strain effects, i.e., surface strain influences surface reactivity and*  
187 *consequently ORR activity. What we have discovered is that the presence of small*  
188 *imperfections, such as step-type defects, can break the symmetry and lead to release*  
189 *of the surface stress, relaxation of surface atoms, and generation of inhomogeneous*  
190 *strain fields that may span multiple nanometers on transition metal surfaces. The*  
191 *associated electronic and geometric effects lead to atomic site-specific reactivity,*  
192 *which results in orders of magnitude differences in catalytic activity even for atoms*  
193 *with identical local environments. This phenomenon in catalytic activity resolves*  
194 *longstanding puzzles about the nature of the active site and structure sensitivity of the*  
195 *ORR in the literature, among others.*

196 We summarize the conceptual correlations in our work as follows: imperfections  
197 (defects) → surface stress release → the relaxation of surface atoms →  
198 inhomogeneous strain fields → atomic site-specific electronic structure → atomic site-  
199 specific reactivity → high ORR activity for atoms at the vicinity of the steps → large  
200 variations in ORR activity with terrace widths. We agree with the referee that many of  
201 these individual phenomena are very fundamental and have been described in previous  
202 literature. The major impact of our work, then, is the synthesis of these concepts to  
203 identify a powerful connection between stress release induced by surface defects and  
204 overall catalytic properties. To clarify this point, we have changed “this discovery” to  
205 “*the discovery of the above synergy*”.

206 Regarding the “rational design of heterogeneous catalysts” and “control ... reactivity  
207 by either varying terrace widths or controlling external stress”, we do acknowledge  
208 that it is challenging to do so in experiment. At the same time, we would like to point  
209 out that rational design and controlled synthesis of nanocatalysts (e.g., nanoparticles)  
210 have been studied for decades, and tremendous progress has already been made, such  
211 as shape control, size control and structure control, among others. Our current work is  
212 to provide a rationale, foundation or principle for introducing additional controlling  
213 factors. However, to respect the referee’s comments, we will limit our discussion of  
214 “rational design” to “computational design” and “design principles”. So, we have made  
215 the corresponding changes for the following statements.

216 ‘rational design of heterogeneous catalysts’ →

217 ‘*design principles of heterogeneous catalysts*’

218 ‘...enables a more accurate prediction and design of heterogeneous catalysts’ →

219 ‘*...enables a more accurate prediction and computational design of heterogeneous*  
220 *catalysts*’.

221

222 Referee #3 (Remarks to the Author)

223 **With the revised version of their manuscript, the authors provided detailed point-**  
224 **by-point answers to the comments made by my-self and by Reviewer#2. In my view,**  
225 **the arguments developed by the authors, largely supported by references, together**  
226 **with the revisions applied on the manuscript lift-up the concerns raised in the first**  
227 **round of review.**

228 I am particularly happy to see that the results in the 2020 paper from the Feliu’s  
229 group were in facts an outlier when compared to a larger set of experimental data  
230 on Pt[(111)x(110)]. The additional calculations on Pt[(111)x(100)], qualitatively  
231 consistent when experimental data gained on the two types of step geometries are  
232 compared, provide additional strength to the claim of the authors.

233 I do not have further technical comments, the article and the findings are very fine,  
234 only one of more semantic nature for the general positioning of the manuscript. The  
235 authors wrote the following:

236 • ‘...provides new perspective for both fundamental understanding of catalytically  
237 active atomic sites and the rational design of heterogeneous catalysts’  
238 introductory section, page 2, l.31.

239 • ‘...enables a more accurate prediction and design of heterogeneous catalysts’,

240 page 3, l.50

241 It is in my view more than optimistic to consider that the present work could find a  
242 straight way for preparation of practical nanostructured catalysts materials. I  
243 mentioned in the first round of review, that this is a 'step towards the direction of  
244 more realistic catalytic surfaces such as those employed in practical application'. The  
245 way is however quite long from extended single crystals to practical supported  
246 catalysts. The 'catalyst-by-design' approach at this scale will remain complicated  
247 since:

- 248 • most of the preparation methods for the preparation of catalyst are colloidal  
249 syntheses where numerous forces takes place in establishing the final catalyst  
250 particulates;
- 251 • the strain release might be counter-balanced by the compressive strain taking  
252 place in nanostructured catalysts;
- 253 • the industrial constrains where production costs and production rate will be  
254 balanced against potential gains in catalytic reactivity and durability of these gain  
255 of performances over time.

256 I understand that the authors wish to bind their works to a potential practical  
257 application and this comment on the perspective for the preparation of catalyst  
258 should not be received as minoring the impact of the findings presented by the  
259 authors. A fundamental understanding, unveiling critical effects not accounted for,  
260 enabling the resolution/description of the catalytic site down to the atomic scale-  
261 level driving the whole reaction rate observed experimentally, and nurturing a more  
262 accurate framework of approximations in computational chemistry/catalysis are my  
263 view a horizon more than sufficient. This is already quite a substantial achievement  
264 in the broad field of the catalysis (!), well suited for the readership of a journal like  
265 Nature. Here, I let the editor in charge of the manuscript and the authors to refine  
266 maybe a bit the final wording on this aspect.

267 *Response: We thank the referee for recognizing our efforts and for such encouraging*  
268 *comments. We realized that there might be some misunderstanding regarding those*  
269 *two phrases pointed out by the referee, especially regarding the meaning of the word*  
270 *"design". Here we meant "computational design" and "design principles", such as*  
271 *controlling terrace width and introducing external stress, rather than experimental*  
272 *design, synthesis or control of nanostructured catalysts. We do understand there is a*  
273 *large gap between principles and practices. To emphasize the "principles" and*  
274 *"computational" nature of the current work, we have made the following changes to*  
275 *the above two sentences in the revised version.*

276 *'...provides new perspective for both fundamental understanding of catalytically active*  
277 *atomic sites and the rational design of heterogeneous catalysts' →*

278 *'...provides new perspective for both fundamental understanding of catalytically active*  
279 *atomic sites and design principles of heterogeneous catalysts'*

280 *'...enables a more accurate prediction and design of heterogeneous catalysts' →*

281 *'...enables a more accurate prediction and computational design of heterogeneous*  
282 *catalysts'.*

283

284 Minor points:

285 • **There is no ORR data in the Ref. 27. If you wish to cite works from the Behm's group**  
286 **for the ORR on PtAu, you may want to prefer this one: J. Electroanal. Chem. 716**  
287 **(2014) 71-79**

288 *Response: We are thankful for the reminder. This paper is certainly relevant to our*  
289 *current work, as we have discussed in the first round of review. We now have cited it*  
290 *in the revised version.*

291

292 • **Page 10, l.172: '...Au is relatively inert for the ORR': you could add 'in acidic**  
293 **solutions' to be more precise since the kinetics of the ORR on Au(100) and stepped**  
294 **Au single crystals in alkaline electrolytes is not that bad (see e.g. ancient Adzic's**  
295 **works, likely published in the 80's-early 90's in J. Electroanal. Chem.).**

296 *Response: We thank the referee for reminding us of the pioneering work from Adzic*  
297 *and workers for ORR on Au(100) in alkaline electrolytes, i.e., J. Electroanal. Chem. 364,*  
298 *265-269, (1994). Based on the referee's suggestion, We have added 'in acidic solutions'*  
299 *in the revised version to make our statement more precise.*

300

301 **I am in favour to make also available the reviews for the readers upon publication of**  
302 **the manuscript (of course if the authors and the other reviewers agree).**

303 *Response: We appreciate the reviewer's willingness and efforts. We are also in favor*  
304 *to make the reviews available for readers so as to show the constructive comments*  
305 *from reviewers and the detailed responses from us. We will let the editor know our*  
306 *willingness in the cover letter.*

307

308 **Beyond the scope of the present manuscript, I wonder if the strain release induced**  
309 **by the vicinity of an atomic step would be of sufficient magnitude to lead to a subtle**  
310 **revision/enrichment of the general model describing the factors governing the**  
311 **nanocrystal shapes (both Wulff equilibrium and kinetic shapes, see e.g. Claude R.**  
312 **Henry, Progresses in Surface Science 80 (2005) 92-116), since this model essentially**  
313 **relies on the surface tension of the nanocrystal facets. To make the things clear, I do**  
314 **not ask the authors to discuss this for the present manuscript, but it might be worth**  
315 **to have a look at it in future works.**

316 *Response: We are grateful for the referee's suggestion. It is certainly our plan to push*  
317 *our study toward site-specific reactivity of nanocrystals. Based on the referee's*  
318 *comments, we will take the nanocrystal shapes into consideration as well. At the same*  
319 *time, we hope our work also can motivate other scientists to join the efforts.*