nature portfolio

Peer Review File

Unraveling Oxygen Vacancy-Driven Catalytic Selectivity and Hot Electron Generation on Heterointerfaces using Nanostructured Platform

Corresponding Author: Professor Jeong Park

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
In this manuscript, G. Lee et. al. have studied the catalytic platform consisting CeOx nanowire arrays on the Pt film. They investigated the role of crystallinity and oxygen vacancy of CeOx nanowires on the partial oxidation selectivity by annealing CeOx in various environments. I have concerns in the methodology and conclusion of the manuscript. Also the organization of the manuscript needs major improvement. My comments are following:

1. The authors claimed that quantitative analysis of the crystallinity and oxygen vacancy concentration effects on the partial oxidation selectivity has been obtained. However, the crystallinity and oxygen vacancy concentration are not quantitatively characterized in my opinion. For example, Fig.2c is used to show crystallinity. The authors stated "a number of nanoscale grains with high crystallinity" (line 111, page 5). However, this is not a quantitative characterization of the crystallinity. Regarding oxygen vacancy concentration, the authors annealed the CeOx nanowires in various environments (vacuum, O2, Ar) and compared their XPS. However, this is also not a quantitative characterization of the oxygen vacancy concentration. In fact, the authors stated a few times of "high crystallinity" and "low oxidation state", which is apparently not a quantitative description. Since the quantitative analysis is the main argument in this manuscript, this point should be further investigated or elaborated.

2. The innovations in this manuscript, to me, are not significant in addition to their previous findings (Nature Communications 12, 40, (2021)). For example, in their previous paper, the nanowire/Pt platform has already been reported and the role of interface has been investigated. In the current manuscript, similar nanowire/Pt platform, nanofabrication method, electron generation through Schottky nanodiodes and partial oxidation selectivity are discussed, expect for the use of CeOx material (any advantages?) other than TiO2 and the quantitative analysis (discussed in my comment #1). In fact, the authors stated "we confirmed once again that the formation of the metal-oxide interfaces in CeOx/Pt enhanced partial oxidation selectivity, thereby exciting many more hot electrons compared to a bare Pt catalyst." (line 315, page 12), which is already reported in the above paper. Therefore, given my concerns about the quantitative analysis, the innovations in the manuscript should be further elaborated.

3. The organization of the manuscript needs major improvement. For example, if I am right, Fig.1 has never been referred in the manuscript. Also, supplementary Fig.1 appears to be "Supplementary Fig.".

4. Fig.4a is used to illustrate different pathways as a function of the oxygen vacancy concentration. However, if I interpret correctly, there is no difference in the schematics representing variations of oxygen vacancy concentration or MF/CO2 selectivity, expect for labels. Also, what are the red/yellow/blue/green balls representing?

5. The authors measured the I-V curve for the nanodiode comprising a Pt film on TiO2 without CeOx nanowire arrays, and obtained reasonable Schottky barrier height of 0.815 eV. Then they claimed all the CeOx/Pt Schottky nanodiodes exhibited a negligible difference in Schottky barrier height compared to nanodiode without CeOx nanowire arrays. What is the reason for this? This should be further elaborated. How about the barrier between Pt and CeOx nanowires?

6. minor issues regarding English:
Abstract: is crucial to achieve (line 5, page 2);
page 3, line 56: which gives well-formed...
page 3, line 30: a trade-off between ... (no relation)
page 5, line 98: that provide...

Reviewer #2

(Remarks to the Author)
The manuscript from Jeong Young Park et al presents a CeOx/Pt heterogeneous catalysts as a model platform to identify the key factor in governing the selectivity. In this well-defined heterostructures, the reaction-induced hot electron can directly be detected by unique Schottky nanodiode, which may be act as a real-time indicator for give feedback on the catalysts properties. The controlled and comparative experiments demonstrate that the improvements in selectivity are associated with the reduction of the activation barrier driven by a high fraction of oxygen vacancy in the Vac-CeOx/Pt, which leads to efficient charge transfer to reaction intermediates.

The main claim of the article, namely oxygen vacancy-driven catalytic selectivity and hot electron generation on CeOx/Pt heterointerfaces, is well documented by the experimental evidences and theoretical calculation presented in the manuscript. In my opinion, the findings are practically interesting, they constitute a relevant technological understanding. However, some key issues concerning the reliable assess the contribution of reaction parameters for selectivity and hot electron generation as well as relaxation dynamics should be addressed.

1.In Figure 2b, the nanowires treated in Ar show some remarked changes, such as fracture into shorter nanowires or random deformation. Could you give a more detailed discussion on the possible reasons? And this morphology variation may change the charge transport and/or injection efficiency, so complicate the resulting conclusion.
2.In the process of Fabrication of CeOx nanowire arrays on Pt film/TiO2 Schottky nanodiodes, the nanocrystalline non-stoichiometric CeOx nanowire arrays were transferred onto Pt film/TiO2 Schottky nanodiodes to construct the heterogeneous catalysts for evaluating MOR performance. As shown in main text, although the design array structure, the single nanowire within the array may show some differences from one to one, such as orientation, surface defect distribution and inter-distance of nanowire, those parameters may influence the charge transport, reaction pathway and thus the reaction selectivity. So in order to precisely probe and distinguish the contribution of each variable to catalytic performance, can you transfer single nanowire to form a heterogeneous catalysts on single-particle level, and then test the corresponding performances for identify the limiting factor and contribution. In this way, the single-particle device can decouple other impacting factors and minimize the average effects from nanowire array to investigate the resulting influence of single variable.
3.It is known to us that the strain (stress) play an important role in influencing and optimizing the catalytic performances. In the manuscript, the heterogeneous catalysts treated in vacuum, Ar, and O2 atmosphere may undergo different level of strain, which is most likely to impact the charge carrier dynamics and transport and the resulting catalytic performances. In other word, you should give relevant experiment evidence and associated discussion on the train effect on the selectivity in the heterogeneous catalysts.
4.In page 6, line 144, the exothermic reaction energy of MOR generates hot electrons through nonadiabatic electron excitation at metal-oxide interfaces. Could you give more information on the mechanism of how to generate hot electron, and they relax at the whole process, namely the hot electron relaxation dynamics.
5.The electron transfer rate is very sensitive to the energy barrier due to its exponential relationship with the barrier height. In page 7, line 160, you proposed that the flux of hot electrons is not governed by Schottky barrier height, could the Schottky barrier height has an effect on the hot electron injection?
6.In general, the hot carrier has a characteristic lifetime, beyond the timescale, the hot carriers become relaxed cold carriers. The evidence of hot electron generation based on the fact that the current density under the MOR condition exhibits an apparent enhancement compared to the non-reaction condition may not reliable, because the relaxed electron can also generate the current. Could you provide more evidences to show the hot electron generation.
7.The enhanced crystallinity and low oxidation state of Vac-CeOx/Pt plays a crucial role in enhancing selectivity and reaction-induced hot electron generation. Could you give a quantitative analysis in the threshold of vacancy contraction in influencing the selectivity and reaction-induced hot electron generation.

Reviewer #3

(Remarks to the Author)
My review for and comments to the authors' manuscript can be found attached.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have provided further elaboration and additional experiments to address my concerns. I believe the revised manuscript is now well-suited for publication in Nature Communications. Therefore, I recommend its acceptance.

Reviewer #2

(Remarks to the Author)
The authors have addressed the questions properly and I would like ti recommend its publication now.

Reviewer #3

(Remarks to the Author)
The authors have addressed my scientific concerns in a satisfactory manner. I have only a slight request: I would like to see the figure R2, showcasing the two competing reaction pathways, with Supplementary Table 3. The authors correct may correct me if I am wrong (and I apologise in advance in case I missed it) but the additional dehydrogenation reaction is never properly written down in the manuscript in contrast to the elementary reaction in the other pathway towards methylformate. So far this table comes out of nowhere which is a consequence of me asking for that but one way to put it into the context of the paper would be the following: Giving more details in Figure R2, i.e., just showing the abstraction of one H atom and then two arrows to CO2, which indicates a series of more elementary steps towards CO2 would, clarify the reaction that is investigated.

That is everything from my end. In my opinion, the paper can be subject to publication, and from my end, I do not need another round of review.

Replies to the reviewer's comments

Response to Reviewer 1

Reviewer comments #1-0:

In this manuscript, G. Lee et. al. have studied the catalytic platform consisting CeOx nanowire arrays on the Pt film. They investigated the role of crystallinity and oxygen vacancy of CeOx nanowires on the partial oxidation selectivity by annealing CeOx in various environments. I have concerns in the methodology and conclusion of the manuscript. Also the organization of the manuscript needs major improvement. My comments are following:

Author reply #1-0:

We appreciate the reviewer's detailed evaluation and valuable comments, which has enabled us to greatly improve our manuscript. The reviewer pointed out several valid concerns, especially in the methodology and conclusion. Therefore, we have made significant corrections in the revised manuscript, and the following are our point-by-point responses.

Reviewer comments #1-1:

The authors claimed that quantitative analysis of the crystallinity and oxygen vacancy concentration effects on the partial oxidation selectivity has been obtained. However, the crystallinity and oxygen vacancy concentration are not quantitatively characterized in my opinion. For example, Fig.2c is used to show crystallinity. The authors stated "a number of nanoscale grains with high crystallinity" (line 111, page 5). However, this is not a quantitative characterization of the crystallinity. Regarding oxygen vacancy concentration, the authors annealed the CeOx nanowires in various environments (vacuum, O2, Ar) and compared their XPS. However, this is also not a quantitative characterization of the oxygen vacancy concentration. In fact, the authors stated a few times of "high crystallinity" and "low oxidation state", which is apparently not a quantitative description. Since the quantitative analysis is the main argument in this manuscript, this point should be further investigated or elaborated.

Author reply #1-1:

We appreciate the reviewer's important comment regarding the quantitative characterization of crystallinity and oxygen vacancy concentration. We agree with the

reviewer's point that a TEM image cannot provide a quantitative characterization of crystallinity. In our work, the comparison between Pristine-CeO_x/Pt (without annealing) and others (annealed in O_2, Ar, and vacuum atmospheres) was utilized to evaluate the effects of crystallinity on selectivity and reaction-induced hot electrons. As shown in **Fig. 2d**, no significant differences in the XPD spectra (peak position or shape) were observed for the samples prepared under different annealing atmospheres. This is because all samples were annealed at the same temperature of 500 °C for 2 hours, which is sufficient to fully crystallize cerium oxide.[1] This result indicates that, in terms of the crystallinity of the heat-treated samples, the annealing temperature is more critical than the annealing atmosphere. Furthermore, CeO_x nanowire arrays were fabricated via e-beam evaporation, which usually deposits metal oxide materials in an amorphous state. This fabrication method allows for a direct comparison of the catalytic performance between amorphous (0% crystallinity) and fully crystalline (100% crystallinity) CeO_x nanowires.

We also agree with the reviewer that the deconvolution of XPS spectra into Ce (III) and Ce (IV) is not enough to provide the oxygen vacancy concentration quantitatively. However, the formation of oxygen vacancies intrinsically involves the reduction of Ce (IV) to Ce (III) due to charge compensation.[2] Since the only difference among O_2, Ar, and Vac.-CeO_x/Pt samples used in this study is the annealing environments, the ratio of Ce (III) to Ce (IV) confirmed through XPS peak deconvolution can represent the oxygen vacancy concentration. The ratio of Ce (III) to Ce (IV) is clearly determined as 25.22, 38.23, and 46.69% in each sample, respectively, allowing it to be considered a quantitative analysis.

If the quantitative analysis referred to by the reviewer means providing the absolute oxygen vacancy concentration, the XPS results that we exhibited may be insufficient. However, we can support that the relative difference in oxygen vacancy concentration can be precisely identified through the Ce (III) ratio, and these ratio differences are the parameters for quantitative analysis. Nevertheless, to address the reviewer's concerns, we conducted an additional analysis to verify and quantify the difference in oxygen vacancy concentration among samples using a new method other than XPS. The relative oxygen vacancy concentration can be compared by calculating the intensity ratio between the CeO_2 band at 460 cm^{-1} and the oxygen vacancy band at 546 cm^{-1} in the Raman spectra,[3] which also enables quantitative analysis. As shown in the Raman spectra (**Supplementary Fig. 3a**), the peaks originating from the substrate (417 cm^{-1} and 576 cm^{-1}) or the spectra around 510 cm^{-1} remain constant, while the intensity of the CeO_2 band (460 cm^{-1}) and the oxygen vacancy (O_v) band (546 cm^{-1}) vary significantly depending on the annealing conditions. The intensity ratio of the

O_v band to the CeO_2 band under different annealing conditions is plotted in **Supplementary Fig. 3b**. Notably, the trend of the O_v/CeO_2 intensity ratio achieved from Raman spectra aligns with the Ce (III) ratio obtained from the XPS analysis (**Fig. 2e**). Sample annealed under vacuum exhibited a higher O_v/CeO_2 ratio compared to those annealed under Ar or O_2 conditions, indicating a greater number of oxygen vacancies were generated in the CeO_x. This not only confirms that Raman spectroscopy, in addition to XPS, can also be used as a tool for quantitative analysis of oxygen vacancy concentration but also supports the accuracy of our previously reported results. In response to the reviewer's comment, the "Results" of the revised manuscript and Supplementary information were updated as follows to clarify the definition of quantitative analysis.

References

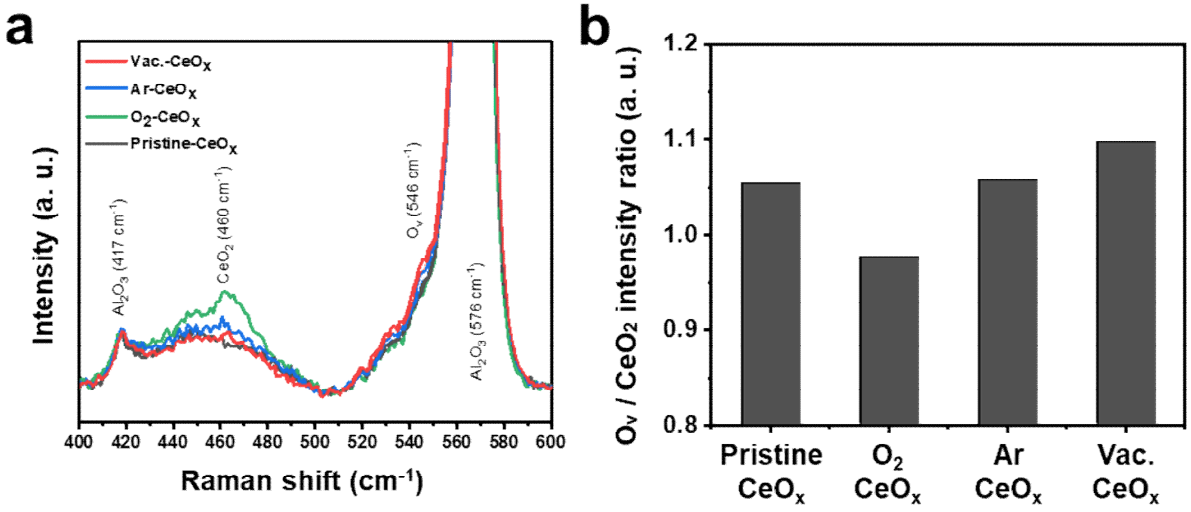
1 Chen, J. C. et al. Effect of calcination temperature on the crystallite growth of cerium oxide nano-powders prepared by the co-precipitation process. *J. Alloys Compd.* **496**, 364-369 (2010).

2 Bishop, S. R., Stefanik, T. S., & Tuller, H. L. Defects and transport in $Pr_xCe_{1-x}O_{2-\delta}$: composition trends. *J. Mater. Res.* **27**, 2009-2016 (2012)

3 Guo, M. et al. UV and Visible Raman Studies of Oxygen Vacancies inRare-Earth-Doped Ceria. *Langmuir* **27**, 3872-3877 (2011).

[Modifications in the manuscript]

(Supplementary information)



Supplementary Fig. 3 a Raman spectra of pristine CeO_x and CeO_x treated with various annealing conditions (vacuum, Ar, and O_2). The peaks located at 460 cm^{-1} and 546 cm^{-1} indicate CeO_2 band and oxygen vacancy band, respectively. The peaks at 417 and 576 cm^{-1} originate from the Al_2O_3 substrate. **b** Characterization of the relative oxygen vacancy concentration of pristine CeO_x and CeO_x treated with various annealing conditions (vacuum, Ar, and O_2) by calculating the intensity ratio between CeO_2 band and oxygen vacancy band.

(Results, page 6) "~ atmospheres: vacuum, Ar, and O_2. The temperature and time for the annealing process are sufficient to fully crystallize the CeO_x nanowires[36]. As shown in ~"
(Result, page 6) "As shown in **Fig. 2c**, the CeO_x nanowire treated with vacuum annealing was transformed to aggregates with a number of nanoscale grains in crystalline states."
(Results, page 7) "Thus, the influence of amorphous and fully crystalline states on catalytic performance can be elucidated by analyzing the difference between pristine and annealed CeO_x."
(Results, page 7) "The formation of oxygen vacancies accompanies the formation of electrons, which leads to a reduction in the oxidation state. Thus, the controlled oxidation states in each CeO_x sample, achieved through the formation and filling of oxygen vacancies[37,38], aimed at identifying the effects of the oxygen vacancy concentration on catalytic performance quantitatively."
(Results, page 7) "Moreover, we conducted an additional analysis to verify and support our XPS results using Raman spectroscopy. The relative oxygen vacancy concentration can be compared by calculating the intensity ratio between the CeO_2 band at 460 cm^{-1} and the oxygen vacancy band at 546 cm^{-1} in the Raman spectra[39]. As shown in the Raman spectra (**Supplementary Fig. 3a**), the intensity of the CeO_2 band (460 cm^{-1}) and the oxygen vacancy (O_v) band (546 cm^{-1}) vary significantly depending on the annealing conditions. The intensity ratio of the O_v band to the CeO_2 band under different annealing conditions is plotted in **Supplementary Fig. 3b**. Notably, the trend of the O_v/CeO_2 intensity ratio achieved from Raman spectra aligns with the Ce (III) ratio obtained from the XPS analysis (**Fig. 2e**)."
(Results, page 9) "Specifically, the crystalline state and low oxidation states in CeO_x nanowires led to a boost in hot electron generation."
(Results, page 11) "Thus, these results conclusively demonstrate that the modified CeO_x in a crystalline state and low oxidation state ~"
(Methods, page 18) "Raman measurements (Nanobase, XperRam S) were performed to investigate the oxidation states of the CeO_x nanowires and the Pt film using a laser wavelength

of 532 nm, with gratings of containing 1800 grooves per 1 mm. All Raman signals were collected using 50x microscope lens. I–V characteristics~”

Reviewer comments #1-2:

The innovations in this manuscript, to me, are not significant in addition to their previous findings (Nature Communications 12, 40, (2021)). For example, in their previous paper, the nanowire/Pt platform has already been reported and the role of interface has been investigated. In the current manuscript, similar nanowire/Pt platform, nanofabrication method, electron generation through Schottky nanodiodes and partial oxidation selectivity are discussed, expect for the use of CeOx material (any advantages?) other than TiO2 and the quantitative analysis (discussed in my comment #1). In fact, the authors stated "we confirmed once again that the formation of the metal-oxide interfaces in CeOx/Pt enhanced partial oxidation selectivity, thereby exciting many more hot electrons compared to a bare Pt catalyst." (line 315, page 12), which is already reported in the above paper. Therefore, given my concerns about the quantitative analysis, the innovations in the manuscript should be further elaborated.

Author reply #1-2:

We appreciate the reviewer’s valuable comment. As the reviewer pointed out, the nanodiode system (TiO_2/Pt Schottky nanodiode) and characterization methods used in this work resemble those in our previous paper. However, we want to emphasize that the previous paper only focused on the role of the heterogeneous interfaces between oxide and Pt film. It investigated the correlation between the interface and catalytic performance by modulating the heterogeneous interface density. In contrast, the distinguishing features of this study are summarized below, and the corresponding explanations for each are as follows:

(1) Elucidating the relation between physicochemical properties and catalytic performance

(2) Demonstrating TiO_2/Pt nanodiode as a basic system for evaluating catalytic performance

(1) Compared to previous paper, this manuscript takes it a step further by fixing the interface density and exploring the fundamental understanding of relation between oxygen vacancy and catalytic activity and hot electron transport. Specifically, controlling the oxygen vacancy concentration within CeO_x through varying the annealing atmospheres and elucidating its effects on catalytic selectivity while regulating other influential factors is a novel finding that has not been reported previously.

(2) Furthermore, in the previous study, TiO_2 was used as an oxide material participating in the reaction and as the composed material of nanodiode to detect hot electrons

simultaneously. However, in this study, we detect hot electrons generated through the interfaces between a new oxide material (CeO_x) and Pt film via the TiO_2/Pt Schottky barrier, demonstrating the potential for this nanodiode system to serve as a model platform for examining catalytic performance across various heterogeneous compositions. This and the reply to Reviewer comment #1-1 highlight a key research significance that overcomes the reviewer's concern regarding whether the only difference from the previous paper is simply the use of different materials. That is, the statement in line 315, page 12 refers to our reported results but does not imply that the claims of this study are similar to those of our earlier research. In response to the reviewer's comment, we added the statement on innovation in our work in the "Discussion" of the revised manuscript and removed the expression "*once again*" to reduce the possibility of misunderstanding from the revised manuscript.

[Modifications in the manuscript]

(Discussion, page 14) "Real-time detection of heterogeneous catalysis can be possible by observing the reaction-inducted hot electron directly in our unique Schottky nanodiode system. Furthermore, this TiO_2/Pt nanodiode successfully detects hot electrons generated through newly designed interfaces (CeO_x-Pt), demonstrating the potential to serve as a basic system for examining catalytic performance across various heterogeneous compositions. Our model platform ~"

Reviewer comments #1-3:

The organization of the manuscript needs major improvement. For example, if I am right, Fig.1 has never been referred in the manuscript. Also, supplementary Fig.1 appears to be "Supplementary fig.".

Author reply #1-3:

We are grateful to the reviewer for pointing out these errors and issues. Firstly, **Fig. 1** was designed to briefly explain the key concepts we aim to argue in this study and provide a guide for the contents to be discussed later. As the reviewer mentioned, **Fig. 1** was not referenced in the main text, and we have addressed this issue by adding an explanation of **Fig. 1** to the revised manuscript. Additionally, we meticulously reviewed and corrected errors in the revised manuscript beyond notation of "**Supplementary Fig. 1**".

[Modifications in the manuscript]

(Results, page 6) “We have integrated the CeO_x nanowire arrays with modulated physicochemical properties and Pt film as a model heterogeneous system to precisely elucidate their role on catalytic performance, especially MF selectivity toward MOR. Two different methods are utilized to evaluate the catalytic performance: sensing signal and electrical signal. Particularly, the Schottky barrier between TiO_2 and Pt was formed by fabricating this model system on top of the TiO_2 layer to detect reaction-induced hot electrons which enables real-time detection of catalytic performance, as depicted in **Fig. 1**. First, CeO_x nanowire arrays ~”

(Supplementary Information) “**Supplementary Fig. 2** X-ray photoelectron spectroscopy (XPS) spectra of the Ce 3d peaks on. **a** Pristine-CeO_x, **b** O_2-CeO_x, **c** Ar-CeO_x, and **d** Vac.-CeO_x.”

→ We would like to inform you that **Supplementary Fig. 1** was newly added during revision process and its number change to **Supplementary Fig. 2**.

(Main, page 3) “This trend is driven by the strong metal-support interaction (SMSI), which originates from charge transfer through metal-oxide interfaces, and acts as a catalytic promoter[20,21].”

(Main, page 4) “Therefore, these challenges propose the necessity of developing an ideal platform that provides both highly ordered structures and independent tunability of metal oxide properties.”

(Main, page 4) “Based on CeO_x nanowire arrays formed on Pt catalysts (CeO_x/Pt), the inherent contribution of modulated-CeO_x properties to both partial oxidation selectivity and chemically-induced hot electrons was estimated.”

(Result, page 6) “~ regardless of the conditions, maintaining the density of heterogeneous interfaces.”

(Result, page 8) “**Fig. 3b** visualizes the energy band diagram of the catalytic nanodiode and the designed working principles of hot electron generation under MOR conditions.”

(Results, page 9) “~ batch reactor, while reaction-induced hot electrons were measured using the Schottky nanodiodes.”

(Result, page 10) “Because the current signals from hot electron flux under reaction conditions are proportional to reaction activity[46], the chemicurrent density on CeO_x/Pt catalytic nanodiodes can be expressed as Eq. (1)”

(Result, page 12) “The energetics for reactions (1) and (2) were observed overall similarly, regardless of the presence of either ceria cluster itself or vacancies within the cluster, ~”

(Result, page 12) “For pure Pt, both C and O of CH_2O are bonded to the surface, whereas for ceria/Pt hybrid systems, only O of CH_2O is bonded to the surface, which thereby does not

require the breaking of metal-C bonding and facilitates the corresponding reaction."

(Result, page 13) "Indeed, in the AIMD result, the addition of more electrons to reactants tends to reduce the barriers by facilitating the O-C bond formation."

Reviewer comments #1-4:

Fig.4a is used to illustrate different pathways as a function of the oxygen vacancy concentration. However, if I interpret correctly, there is no difference in the schematics representing variations of oxygen vacancy concentration or MF/CO2 selectivity, expect for labels. Also, what are the red/yellow/blue/green balls representing?

Author reply #1-4:

The authors appreciate the reviewer's helpful and insightful comment. Based on the reviewer's comment, we updated **Fig.4a** to illustrate that the oxygen vacancy leads to the methyl formate formation compared to the formation of CO_2 in the revised manuscript. We also changed the colors of the balls to unify the colors in all Figures and labeled the balls with the sentence "The green, red, brown, and pink balls indicate Ce, O, C, and H, respectively" in **Fig. 4a** caption. The modifications are provided below:

[Modifications in the manuscript]

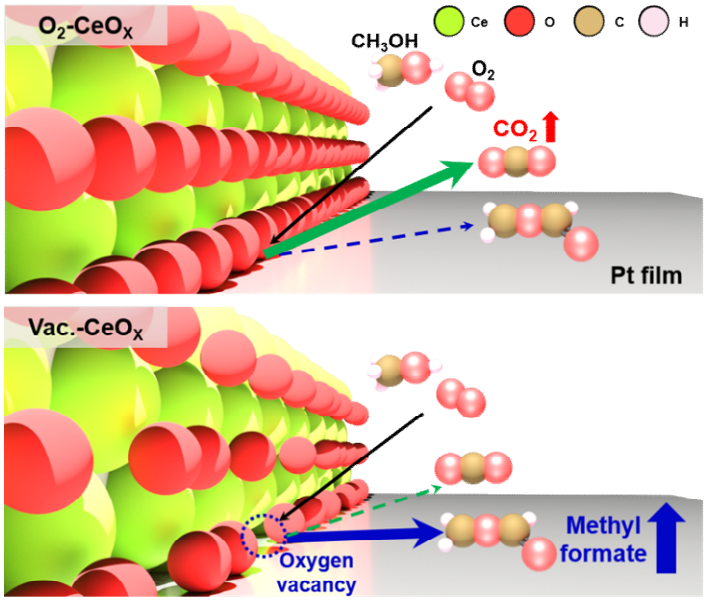


Fig. 4a Schematic illustration of O_2-CeO_x/Pt (upper image) and Vac.-CeO_x/Pt (below image). The high Ce (III) ratio induced by oxygen vacancy formation can control the selectivity of methanol oxidation reaction. The green, red, brown, and pink balls indicate Ce, O, C, and H, respectively.

Reviewer comments #1-5:

The authors measured the I-V curve for the nanodiode comprising a Pt film on TiO2 without CeOx nanowire arrays, and obtained reasonable Schottky barrier height of 0.815 eV. Then they claimed all the CeOx/Pt Schottky nanodiodes exhibited a negligible difference in Schottky barrier height compared to nanodiode without CeOx nanowire arrays. What is the reason for this? This should be further elaborated. How about the barrier between Pt and CeOx nanowires?

Author reply #1-5:

We appreciate the reviewer's valuable comment. In our study, due to the sensitive effect of the barrier height on hot carrier detection, we chose the Pt/TiO_2 nanodiode as a model system of the hot carrier detection and physically transferred CeO_x nanowires on the Pt film/TiO_2 nanodiode to preserve the Schottky barrier height at the interface of Pt/TiO_2, as illustrated in **Fig. 3a**. We assumed that the physical transfer of CeO_x nanowires would not affect the interface of Pt/TiO_2. Indeed, we obtained the Schottky barrier height of 0.8-0.9 eV for all CeO_x nanowires/Pt/TiO_2 nanodiodes, as shown in Fig. 3c and Supplementary fig. 5, corresponding to the Schottky barrier height of Pt/TiO_2 in other references[1,2]. From the result, we concluded that all the CeO_x/Pt/TiO_2 Schottky nanodiodes exhibited a negligible difference in Schottky barrier height compared to Pt/TiO_2 nanodiode without CeO_x nanowire arrays.

We agree with the reviewer that we need to provide more information to support our claim. We have fixed the following sentence: (Results, page 7 in the original manuscript) "Consequently, all the CeO_x/Pt Schottky nanodiodes exhibited a negligible difference in Schottky barrier height compared to nanodiodes without CeO_x nanowire arrays, confirming that the flux of hot electrons is not governed by Schottky barrier height (**Fig. 3c**, **Supplementary Fig. 5**)," in the revised manuscript to clarify our claim. Furthermore, we updated **Fig.3c** and **Supplementary Fig. 5** with additional sample data and error bars to enhance the data accuracy. Therefore, we updated all the values of the ideality factor and Schottky barrier height (e.g., Pt-TiO_2 as 1.35 and 0.835 eV, respectively) in the revised manuscript. The modifications are given below:

References

1 Schierbaum, K., Kirner, U., Geiger, J. & Göpel, W. Schottky-barrier and conductivity gas sensors based upon Pd/SnO2 and Pt/TiO2. *Sens. Actuators B: Chem.* **4**, 87-94 (1991).

2 Lee, S. W. et al. Intrinsic Relation between Hot Electron Flux and Catalytic Selectivity during Methanol Oxidation. *ACS Catal.* **9**, 8424-8432 (2019).

[Modifications in the manuscript]

(Results, page 8) "Both the ideality factor and Schottky barrier height in Pt-TiO_2 were obtained as 1.35 and 0.835 eV, respectively."

(Results, page 8) "As shown in **Fig. 3c** and **Supplementary Fig. 5**, all the CeO_x/Pt/TiO_2 Schottky nanodiodes exhibited a negligible difference in Schottky barrier height compared to nanodiode without CeO_x nanowire arrays, indicating that the deposition of CeO_x nanowires on Pt/TiO_2 nanodiode does not affect the interface at Pt/TiO_2 because the CeO_x was physically deposited on the surface of Pt film. Consequently, the results confirmed that, due to the intact interfacial junction at Pt/TiO_2, the negligible difference in Schottky barrier height does not influence the flux of hot electrons in this study. Furthermore, through XPS ~"

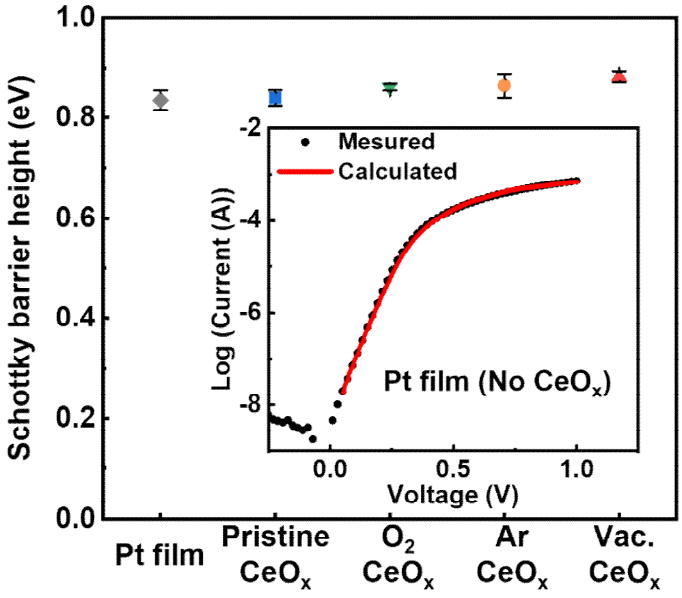
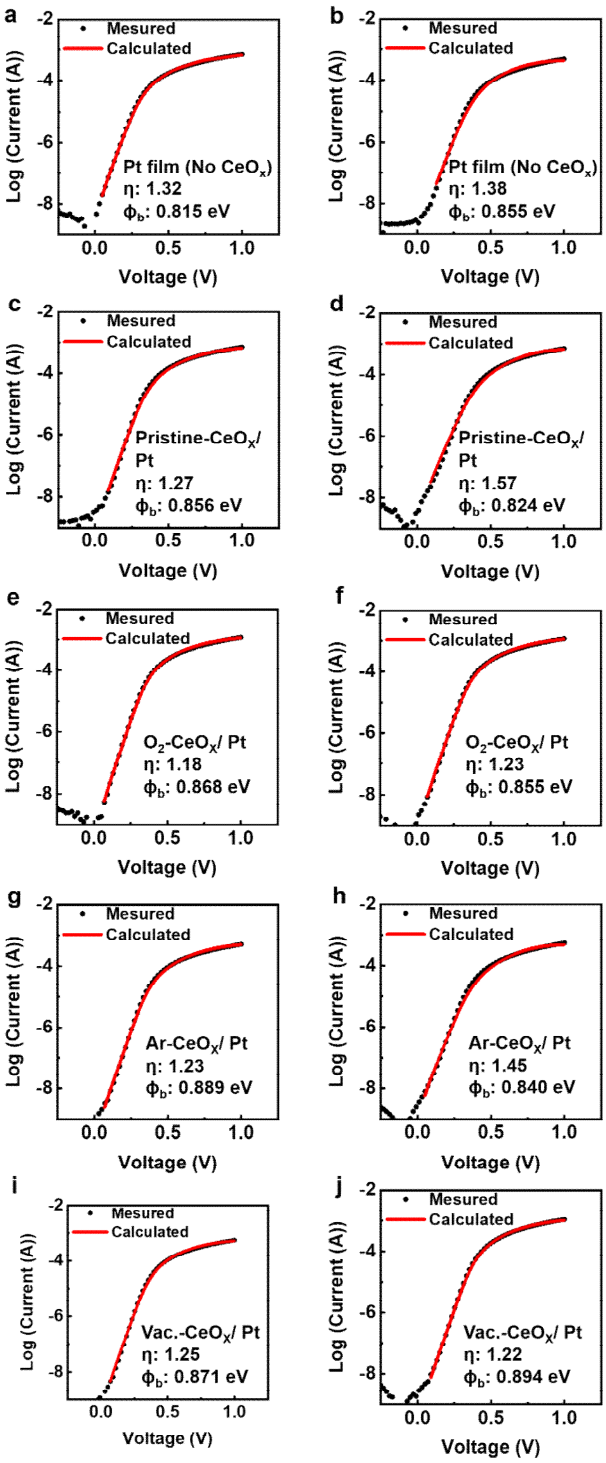


Fig. 3c Schottky barrier height of fabricated nanodiodes with independently modulated CeO_x nanowire arrays. The inset figure showed current-voltage curves of Pt-TiO_2. The red line means the curve that was calculated by the thermionic emission equation.



Supplementary Fig. 5 Current-voltage (*I-V*) curves of **a-b** Pt film without CeO_x, **c-d** Pristine-CeO_x, **e-f** O_2 -CeO_x, **g-h** Ar-CeO_x, **i-j** Vac.-CeO_x on Pt/TiO_2 Schottky nanodiodes. The red lines exhibited the curve fitted to the thermionic emission equation. All the nanodiodes showed the Schottky barrier height of 0.80-0.90 eV, confirming that the difference in Schottky barrier height is negligible on the methanol oxidation reaction. All the ideal factors of the catalyt nanodiodes were closed to 1, indicating that the nanodiodes were well-fabricated.

Reviewer comments #1-6:

minor issues regarding English:

Abstract: is crucial to achieve (line 5, page 2);

page 3, line 56: which gives well-formed...

page 3, line 30: a trade-off between ... (no relation)

page 5, line 98: that provide...

Author reply #1-6:

Considering the helpful comments, we fixed the issues regarding English beyond the comments mentioned by reviewer in the revised manuscript. The fixed sentences are given below:

[Modifications in the manuscript]

(Abstract, page 2) "Modulating the physicochemical properties of oxides is crucial to achieve efficient and desirable reactions in heterogeneous catalysis."

(Main, page 3) "In multi-path chemical reactions, it is difficult to achieve high selectivity for a specific product simultaneously with a high reaction rate, because there is a trade-off between activity and selectivity[1,2]."

(Main, page 4) "In addition to the metal-oxide interface, modulating inherent characteristics of metal oxides such as crystallinity, which gives well-formed and evenly distributed active sites compared to the amorphous state,[26] is also a key strategy for augmenting selectivity."

(Results, page 6) "This ultrahigh-resolution patterning of nanowires enhances the density of the heterogeneous interfaces, which provides a remarkable improvement of catalytic selectivity, as demonstrated in our previous research[4]."

Response to Reviewer 2

Reviewer comments #2-0:

The manuscript from Jeong Young Park et al presents a CeOx/Pt heterogeneous catalysts as a model platform to identify the key factor in governing the selectivity. In this well-defined heterostructures, the reaction-induced hot electron can directly be detected by unique Schottky nanodiode, which may be act as a real-time indicator for give feedback on the catalysts properties. The controlled and comparative experiments demonstrate that the improvements in selectivity are associated with the reduction of the activation barrier driven by a high fraction of oxygen vacancy in the Vac-CeOx/Pt, which leads to efficient charge transfer to reaction intermediates.

The main claim of the article, namely oxygen vacancy-driven catalytic selectivity and hot electron generation on CeOx/Pt heterointerfaces, is well documented by the experimental evidences and theoretical calculation presented in the manuscript. In my opinion, the findings are practically interesting, they constitute a relevant technological understanding. However, some key issues concerning the reliable assess the contribution of reaction parameters for selectivity and hot electron generation as well as relaxation dynamics should be addressed.

Author reply #2-0:

We are very glad to hear the reviewer's comment that "*The findings are practically interesting, they constitute a relevant technological understanding.*". The authors thank the reviewer for the constructive comments. Detailed responses are given below.

Reviewer comments #2-1:

In Figure 2b, the nanowires treated in Ar show some remarked changes, such as fracture into shorter nanowires or random deformation. Could you give a more detailed discussion on the possible reasons? And this morphology variation may change the charge transport and/or injection efficiency, so complicate the resulting conclusion.

Author reply #2-1:

We appreciate the comment from the reviewer on the morphology variation after high-temperature annealing and its impacts on charge transport. First, not only the nanowires treated in Ar but also the nanowires treated in O_2 and vacuum atmospheres exhibited partial structural

defects such as fracture. Even if the annealing atmosphere affects the formation of fractures or cracks, these defects are primarily attributed to the inherent thermal stress induced during the annealing process, and this occurs regardless of the annealing atmosphere[1]. The apparent prominence of these deformations in the Ar-annealed nanowires in the initial scanning electron microscopy (SEM) images (Fig. 2b) is likely due to variations in image contrast. Therefore, in response to the reviewer's comment, we further conducted additional SEM characterizations to obtain higher-resolution images of CeO_x nanowires under various annealing conditions, as compared to **Fig 2b**. As shown in the high-resolution images (**Supplementary Fig. 1**), there are no significant structural differences in the nanowires based on the annealing conditions. Moreover, despite the breakings generated during the annealing process, the total interfacial area contacting with the Pt film remained unaffected. This is because the fractures occurred only along the vertical direction (normal to the substrate). From the perspective of charge transport to reactant molecules, the heterogeneous interface plays a crucial role, which is described in our DFT results. Therefore, we maintain our claim that the enhancement in catalytic performance (specifically, selectivity) is primarily driven by the modulated physicochemical properties of oxides rather than structural factors.

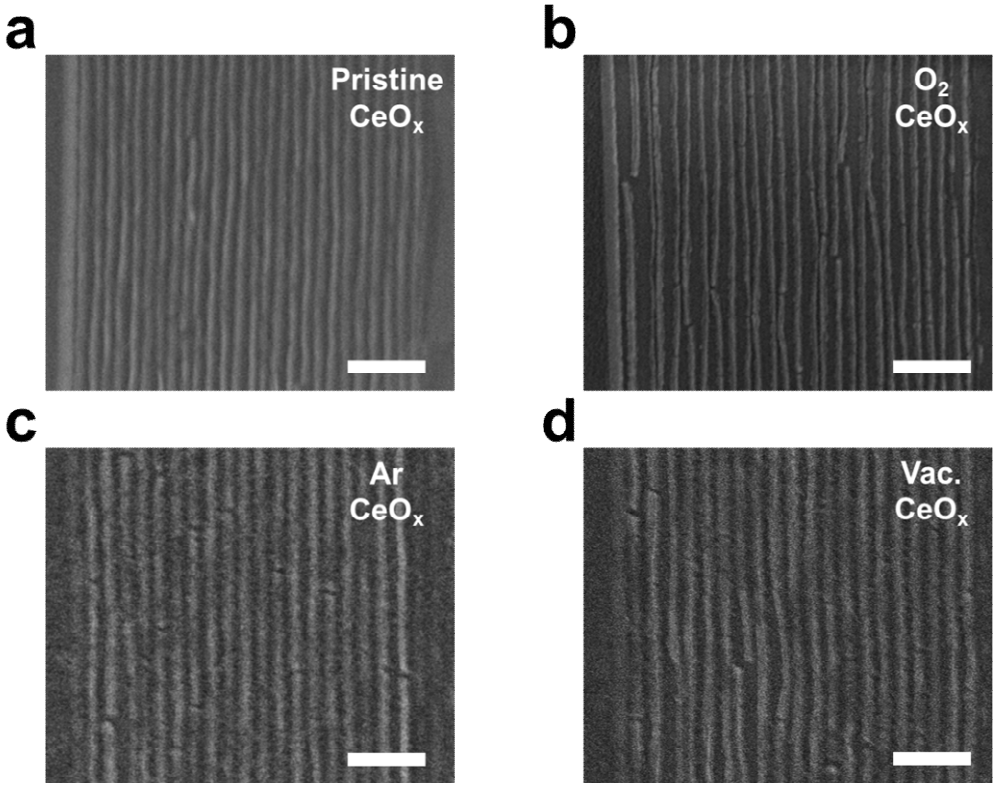
Reference

1 Solovyeva, A. E. Structural and Phase Transformation Defects Within Polycrystalline Cerium Dioxide on Heating in Vacuum and in Air. *Refract. Ind. Ceram.* **64**, 397-406 (2023)

[Modifications in the manuscript]

(Results, page 5) "As shown in **Fig. 2b** and **Supplementary Fig. 1**, the overall morphologies of the CeO_x nanowire arrays …""

(Supplementary information)



Supplementary Fig. 1. High-resolution SEM images of the pristine CeO_x nanowire array without annealing and CeO_x nanowire arrays annealed with various conditions as indicated (scale bar, 200 nm).

Reviewer comments #2-2:

In the process of Fabrication of CeOx nanowire arrays on Pt film/TiO2 Schottky nanodiodes, the nanocrystalline non-stoichiometric CeOx nanowire arrays were transferred onto Pt film/TiO2 Schottky nanodiodes to construct the heterogeneous catalysts for evaluating MOR performance. As shown in main text, although the design array structure, the single nanowire within the array may show some differences from one to one, such as orientation, surface defect distribution and inter-distance of nanowire, those parameters may influence the charge transport, reaction pathway and thus the reaction selectivity. So in order to precisely probe and distinguish the contribution of each variable to catalytic performance, can you transfer single nanowire to form a heterogeneous catalysts on single-particle level, and then test the corresponding performances for identify the limiting factor and contribution. In this way, the single-particle device can decouple other impacting factors and minimize the average effects from nanowire array to investigate the resulting influence of single variable.

Author reply #2-2:

The reviewer's suggestion to utilize a single nanowire for analysis is highly appreciated. While this approach could potentially offer a more controlled environment and minimize the influence of extraneous factors, it presents significant challenges in the context of this study. Specifically, the reduction in interfacial area associated with a single nanowire configuration would substantially suppress the catalytic reaction, leading to a significant decrease in product yield. This decrease would likely result in product concentrations falling below the detection limit of the TiO_2/Pt Schottky nanodiode used for hot electron flux measurements. Additionally, the reduced product yield would compromise the reliability of gas chromatography analysis.

The CeO_x nanowire arrays employed in this study were fabricated with a precisely controlled thickness and pitch of 25 nm. While minor variations in individual nanowires, such as orientation, surface defect distribution, and inter-nanowire distance, may exist, this array architecture provides a well-defined system that minimizes variability in these structural parameters. This level of control is particularly advantageous compared to conventional random structures, such as nanoparticle ensembles, where numerous uncontrolled structural factors can influence the observed behavior.

Although subtle differences in catalytic performance between individual nanowires within the macroscopic (cm-scale) measurement samples may arise due to minor structural variations, the measured outcomes represent the collective behavior of a large number of nanowires. Given that the degree of variation between individual nanowires is consistent across all samples, any effects arising from these minor structural differences are considered negligible at this scale.

Therefore, we conclude that the observed differences in catalytic performance between samples are primarily attributed to the modulated physicochemical properties of the CeO_x nanowires, rather than the minor structural variations highlighted by the reviewer.

Reviewer comments #2-3:

It is known to us that the strain (stress) play an important role in influencing and optimizing the catalytic performances. In the manuscript, the heterogeneous catalysts treated in vacuum, Ar, and O2 atmosphere may undergo different level of strain, which is most likely to impact the charge carrier dynamics and transport and the resulting catalytic performances. In other word, you should give relevant experiment evidence and associated discussion on the strain effect on the selectivity in the heterogeneous catalysts.

Author reply #2-3:

We are grateful for the reviewer's constructive advice related to the strain effect on the catalytic performance. Before proceeding, we would like to clarify that CeO_x nanowire arrays were treated with high-temperature annealing separately and then formed onto the Pt/TiO_2 nanodiode using the wet-transfer method. In our heterogeneous catalysts, there are two main regions where significant strain differences can occur: one is the interface between Pt film and the nanowires, and the other is within the nanowires themselves. Among these, the strain at the interface plays a more crucial role in catalytic performance, as most reactions in heterogeneous catalysts occur at the interfaces. However, as mentioned before, the interfaces with Pt film form later, regardless of the annealing conditions, so the different levels of strain that may arise here can be considered consistent across catalysts treated in vacuum, Ar, and O_2 atmospheres.

The strain within the nanowire can be inferred through XRD results. If there were differences in internal strain depending on the annealing conditions, changes in the position or full width at half maximum (FWHM) of the peaks can be observed[1]. However, as shown in **Fig. 2d**, no significant differences in the XPD spectra can be confirmed under different annealing atmospheres. This indicates that the influence of strain within the nanowire can also be ruled out, allowing us to conclude that the improvement in catalytic selectivity discussed in this study is driven by the modulated physicochemical properties rather than the strain effect. We cited the relevant references in the revised manuscript.

Reference

1 Bunaciu, A. A., UdriŞTioiu, E. G., & Aboul-Enein, H. Y. X-ray diffraction: instrumentation and applications. *Crit. Rev. Anal. Chem.* **45**, 289-299 (2015)

[Modifications in the manuscript]

(Results, page 7) "… (**Supplementary Fig. 4**). The interfaces with Pt film form later, regardless of the annealing conditions, so the possibility of strain effects[40], which can influence the catalytic performance, can be ruled out."

Reviewer comments #2-4:

In page 6, line 144, the exothermic reaction energy of MOR generates hot electrons through nonadiabatic electron excitation at metal-oxide interfaces. Could you give more information on the mechanism of how to generate hot electron, and they relax at the whole process, namely the hot electron relaxation dynamics.

Author reply #2-4:

We appreciate the reviewer's helpful comments on improving the manuscript. We agree with the reviewer's comments that we need more information on the hot electron relaxation dynamics. For more details of hot electron relaxation dynamics, we revised the original sentence: (Main, page 3 in the original manuscript) "This process, initiated by exothermic reactions on metallic catalysts, results in nonadiabatic energy dissipation that excites electrons, thereby generating a hot electron flux," and added the explanation of hot electron generation and relaxation dynamics with proper references[1,2,3,4,5] in the revised manuscript.

References

1 Nienhaus, H. Electronic excitations by chemical reactions on metal surfaces. *Surf. Sci. Rep.* **45**, 1-78 (2002)

2 Gumhalter, B. Single-and multiphonon atom–surface scattering in the quantum regime. *Phys. Rep.* **351**, 1-159 (2001)

3 Mantell, D. et al. The exciting oxidation of CO on Pt. *Chem. Phys. Lett.* **81**, 185-187 (1981)

4 Frischkorn, C. & Wolf, M. Femtochemistry at metal surfaces: nonadiabatic reaction dynamics. *Chem. Rev.* **106**, 4207-4233 (2006)

5 Park, J. Y., Kim, S. M., Lee, H. & Nedrygailov, I. I. Hot-Electron-Mediated Surface Chemistry: Toward Electronic Control of Catalytic Activity. *Accounts Chem. Res.* **48**, 2475-2483 (2015)

[Modifications in the manuscript]

(Main, page 3) "Recently, it was demonstrated that *in-situ* measurement of catalytic selectivity in MOR is feasible through the detection of the quantity of generated energetic electrons (i.e., hot electrons), manifesting as chemicurrent.[4,7]. As external energy accumulates on the metal

catalyst during MOR, which is an exothermic reaction, energy conversion occurs *via* non-adiabatic processes (e.g., electron-hole pair excitation, chemiluminescence, and exo-emission) and adiabatic vibration (e.g., phonon).[8,9,10,11] Among the energy dissipation processes, due to the significantly lower heat capacity of electrons than lattice[12], electronic excitation can generate hot electrons that are not in thermal equilibrium with metal atoms.[13,14,15] However, as hot electrons decay *via* scattering of electron-phonon and electron-electron in ultrafast time (~fs), detecting hot electrons has been proven challenging .[8,16]"

Reviewer comments #2-5:

The electron transfer rate is very sensitive to the energy barrier due to its exponential relationship with the barrier height. In page 7, line 160, you proposed that the flux of hot electrons is not governed by Schottky barrier height, could the Schottky barrier height has an effect on the hot electron injection?

Author reply #2-5:

We completely agree with the reviewer's point that "*The electron transfer rate is very sensitive to the energy barrier due to its exponential relationship with the barrier height.*" In our study, due to the sensitive relationship between the barrier height and hot carrier injection, we chose the Pt/TiO_2 nanodiode as a model system of the hot carrier detection and physically fabricated CeO_x nanowires on the Pt film/TiO_2 nanodiode to preserve the Schottky barrier height at the interface of Pt/TiO_2 as illustrated in **Fig. 3a**. We obtained that the Schottky barrier height of 0.8-0.9 eV for all CeO_x nanowires/Pt/TiO_2 nanodiodes as shown in **Fig. 3c** and **Supplementary Fig. 5**, corresponding to Schottky barrier height of Pt/TiO_2. From the result, we concluded that all the CeO_x/Pt/TiO_2 Schottky nanodiodes exhibited a negligible difference in Schottky barrier height compared to the bare Pt/TiO_2 nanodiode without CeO_x nanowire arrays, thereby confirming that the Schottky barrier height does not affect hot electron injection in this study.

To clearly explain our results, we revised the original sentence: (Results, page 7 in the original manuscript), "Consequently, all the CeO_x/Pt Schottky nanodiodes exhibited a negligible difference in Schottky barrier height compared to nanodiode without CeO_x nanowire arrays, confirming that the flux of hot electrons is not governed by Schottky barrier height (**Fig. 3c**, **Supplementary Fig. 5**)." To enhance the data accuracy, we revised the **Fig.3c** and **Supplementary Fig. 5** with additional sample data and error bars. Therefore, we updated all the values of the ideality factor and Schottky barrier height (e.g., Pt-TiO_2 as 1.35 and 0.835 eV, respectively) in the revised manuscript.

[Modifications in the manuscript]

(Results, page 8) "As shown in **Fig. 3c** and **Supplementary Fig. 5**, all the CeO_x/Pt/TiO_2 Schottky nanodiodes exhibited a negligible difference in Schottky barrier height compared to nanodiode without CeO_x nanowire arrays, indicating that the deposition of CeO_x nanowires on Pt/TiO_2 nanodiode does not affect the interface at Pt/TiO_2 because the CeO_x was physically deposited on the surface of Pt film. Consequently, the results confirmed that, due to the intact interfacial junction at Pt/TiO_2, the negligible difference in Schottky barrier height does not influence the flux of hot electrons in this study. Furthermore, through XPS ~"

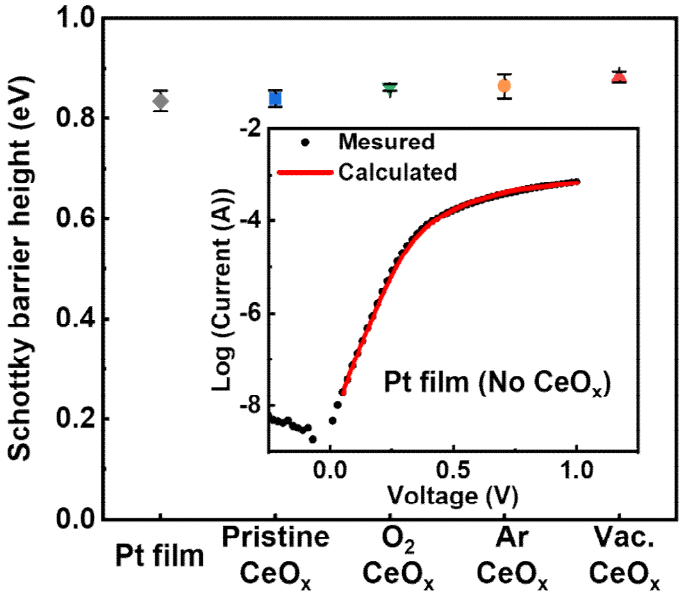
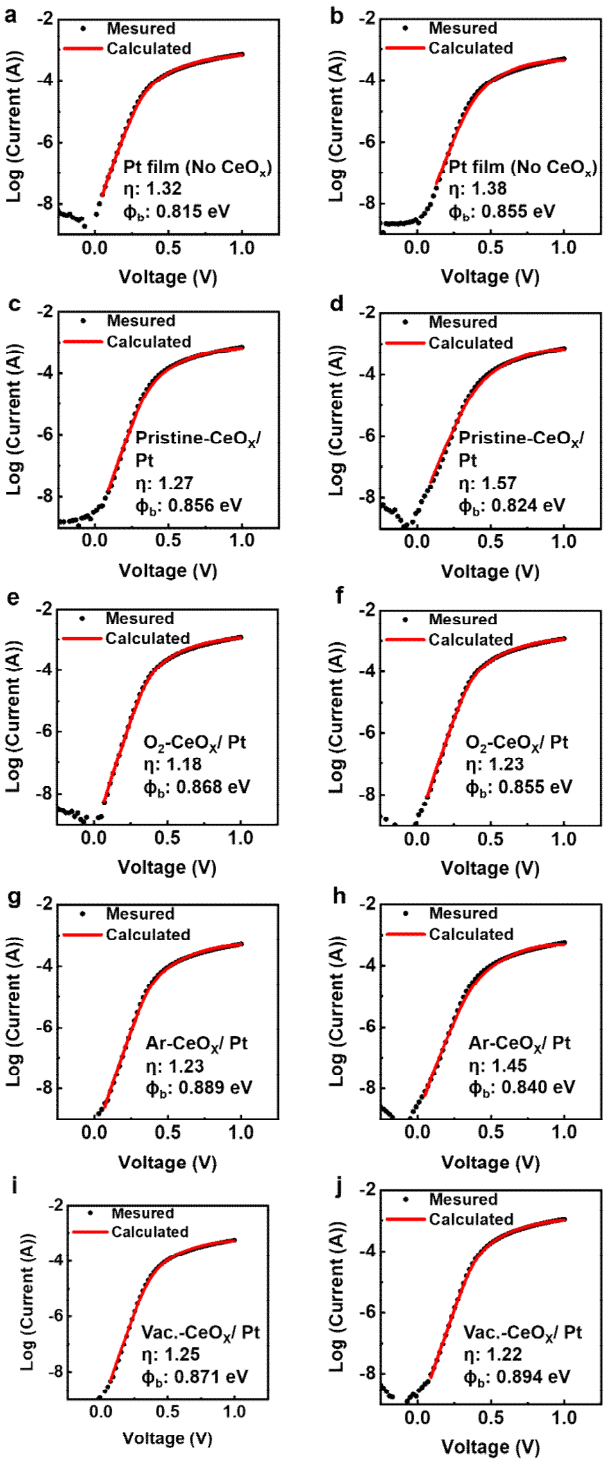


Fig. 3c Schottky barrier height of fabricated nanodiodes with independently modulated CeO_x nanowire arrays. The inset figure showed current-voltage curves of Pt-TiO_2. The red line means the curve that was calculated by the thermionic emission equation.



Supplementary Fig. 5 Current-voltage (*I-V*) curves of **a-b** Pt film without CeO_x, **c-d** Pristine-CeO_x, **e-f** O_2 -CeO_x, **g-h** Ar-CeO_x, **i-j** Vac.-CeO_x on Pt/TiO_2 Schottky nanodiodes. The red lines exhibited the curve fitted to the thermionic emission equation. All the nanodiodes showed the Schottky barrier height of 0.80-0.90 eV, confirming that the difference in Schottky barrier height is negligible on the methanol oxidation reaction. All the ideal factors of the catalyt nanodiodes were closed to 1, indicating that the nanodiodes were well-fabricated.

Reviewer comments #2-6:

In general, the hot carrier has a characteristic lifetime, beyond the timescale, the hot carriers become relaxed cold carriers. The evidence of hot electron generation based on the fact that the current density under the MOR condition exhibits an apparent enhancement compared to the non-reaction condition may not reliable, because the relaxed electron can also generate the current. Could you provide more evidences to show the hot electron generation.

Author reply #2-6:

We appreciate the reviewer's valuable comment. We agree with the point that "*the relaxed electron can also generate the current.*" To prevent the current from the relaxed electrons, we used the Schottky nanodiode, which has the Schottky barrier at the metal/semiconductor interface. Due to this barrier, only electrons with an energy above the barrier height can transfer to the semiconductor, while the relaxed electrons are unable to flow to the semiconductor.

To clarify the process of the hot electron detection, we revised the original sentence: (Main, page 3) "Schottky nanodiodes, which have metal-semiconductor junctions, enable the prompt collection of hot electrons that possess sufficient energy (1 – 3 eV) to exceed the potential barrier," and added the sentences for the explanation of hot electron detection process in the revised manuscript.

[Modifications in the manuscript]

(Main, page 3) "Especially, Schottky nanodiodes, which have the potential barrier (i.e., Schottky barrier) at the interface between metal and semiconductor, enable the prompt collection of hot electrons[9,17]. As only hot electrons with sufficient energy (1-3 eV) can overcome the Schottky barrier, the electrons promptly flow from the metal to the semiconductor enabling the selective detection of these electrons before recombination. In this regard, Schottky nanodiodes ~"

Reviewer comments #2-7:

The enhanced crystallinity and low oxidation state of Vac-CeOx/Pt plays a crucial role in enhancing selectivity and reaction-induced hot electron generation. Could you give a quantitative analysis in the threshold of vacancy contraction in influencing the selectivity and reaction-induced hot electron generation.

Author reply #2-7:

We appreciate the comment from the reviewer regarding the threshold of vacancy contraction and its influence on selectivity and reaction-induced hot electron generation. In metal oxide materials, the oxygen vacancy concentration formed during annealing is typically determined by the oxygen partial pressure in the annealing environment. For this study, we employed O_2, Ar, and vacuum atmospheres in order of decreasing oxygen partial pressure. In response to the reviewer's comment, we conducted an additional quantitative analysis by using a sample annealed in the air (20% of O_2, called Air-CeO_x/Pt), which has an intermediate oxygen partial pressure between the O_2 and Ar conditions, to confirm the threshold of vacancy contraction.

As shown in **Fig. R1a**, the Ce (III) to Ce (IV) ratio for the Air-CeO_x/Pt was 27.10%, slightly higher than the 25.22% observed for the O_2-CeO_x/Pt. Consistent with our findings, the measured total TOF of Air-CeO_x/Pt was comparable to that of O_2-CeO_x/Pt (**Fig. R1b**), indicating that the stoichiometry of CeO_x did not significantly affect the overall reaction activity of the methanol oxidation reaction. The selectivity of partial oxidation, as depicted in **Fig. R1c**, was marginally higher for Air-CeO_x/Pt, aligning with its slightly higher Ce (III) ratio. In addition, similar results were obtained in the reaction-induced hot electrons measurement (**Fig. R1d**).

These findings suggest that as the oxygen vacancy concentration decreases, both selectivity and reaction-induced hot electron generation also decrease. Moreover, the effects of oxygen vacancy concentration on catalytic performance appear to saturate once it drops below a certain threshold, because the catalytic performance of Air-CeO_x/Pt and O_2-CeO_x/Pt are almost identical. Annealing in the O_2 atmosphere provides the highest oxygen partial pressure achievable in our setup, indicating that the threshold of vacancy contraction in influencing selectivity and hot electron generation is reached at a Ce (III) ratio of 25.22%.

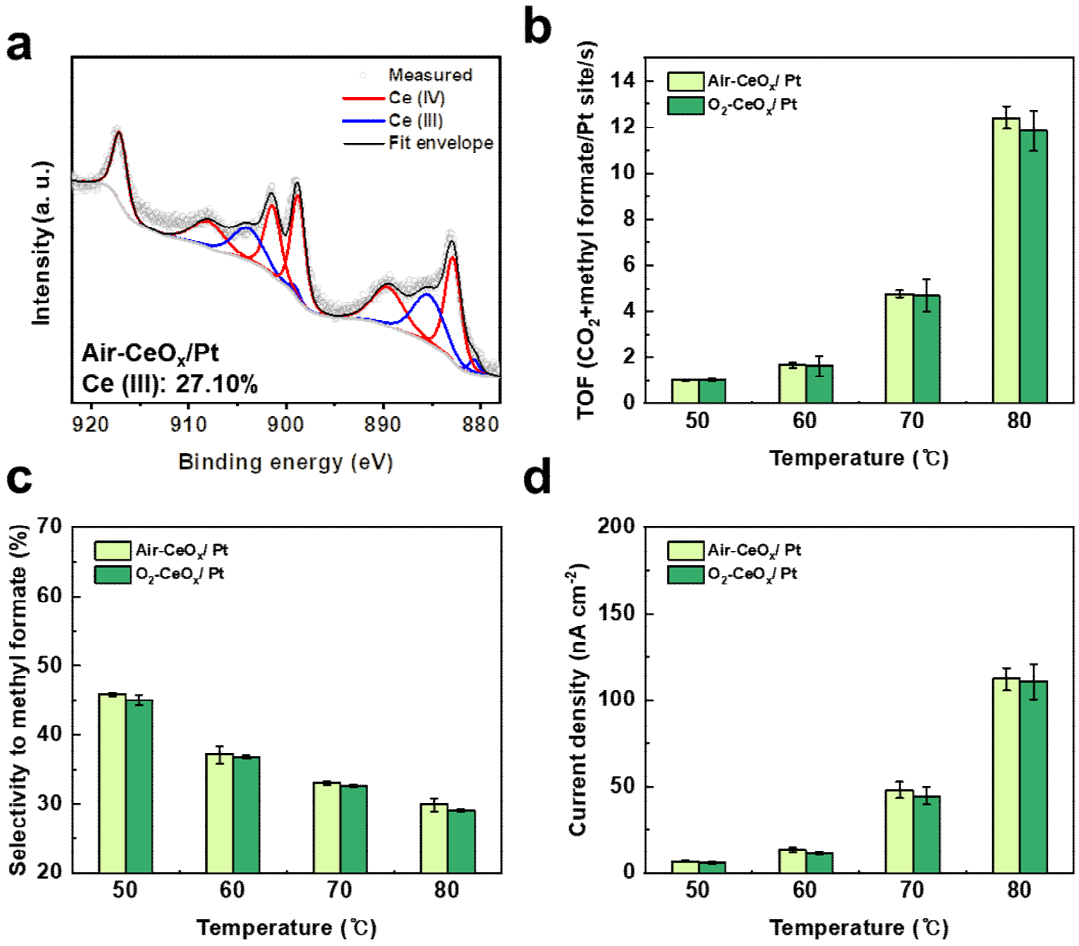


Fig. R1 a X-ray photoelectron spectroscopy (XPS) spectra of the Ce 3d peaks on Air-CeO_x. The deconvolution of the Ce 3d peaks into Ce $3d_{5/2}$ and Ce $3d_{3/2}$ was carried out to analyze the ratio between Ce (III) and Ce (IV) according to the annealing conditions. The red and blue lines indicate the Ce^{4+} and Ce^{3+}, respectively. Note that a. u. represents arbitrary units. **b** Total TOFs and **c** Selectivity of methyl formate formation during methanol oxidation of Air-CeO_x/Pt and O_2-CeO_x/Pt depending on temperature. **d** Current density difference between under methanol oxidation reaction (methanol 4 Torr and oxygen to 760 Torr) and under non-reactive condition (oxygen 760 Torr) of Air-CeO_x/Pt and O_2-CeO_x/Pt according to temperature.

Response to Reviewer 3

Response to Reviewer 3

Reviewer comments #3-0:

In the manuscript "Unraveling Oxygen Vacancy-Driven Catalytic Selectivity and Hot Electron Generation on Heterointerfaces using Nanostructured Platform", the authors present a combined experimental-theoretical study on the oxidation of methanol on CeO_x/Pt(111) with particular emphasis on the role of the substrate's crystallinity and its oxygen vacancy concentration.

Experimentally, the CeO_x nanowires, initially amorphous, were deposited on templates and subsequently post-processed employing different procedures to modulate the nanowires' crystallinity and oxygen vacancy concentration. Thence, those nanowires were transferred onto Pt films on a TiO2 Schottky diode and the overall devices were exposed to a methanol-oxygen mixture to study the methanol oxidation reaction. The reaction's performance and selectivity to methylformate was analysed with the help of both Gas Chromatography and hot electron flux, i.e., chemicurrents.

The experiments were supported by theory with the help of density functional calculations where the CeO_x-nanowire/Pt substrate was modelled as CeO2 cluster on a Pt(111) surface. Bader charge analysis and climbing image nudged elastic band calculations for the individual elementary reactions in the author's proposed reaction network have been carried out to study the role of the oxygen vacancies, i.e., the hot electrons in the methanol oxidation.

The experiments have been well designed and great care has been taken in their conduction and analysis and should definitely be published. As a consequence, the authors convinced me on a phenomenological level that the structural and electronic properties have a substantial impact on the reactivity and selectivity of CeO_x/Pt(111). However, many questions on the atomistic level remain and therefore I consider this work to be suitable for publication once the following concerns have been appropriately addressed:

Author reply #3-0:

We appreciate the reviewer's positive comments on the design and conduction of our experiments. The reviewer pointed out several valid concerns, especially in the atomistic

modeling parts. Therefore, we have made significant corrections in the revised manuscript and provide our point-by-point responses below.

Reviewer comments #3-1:

The authors write on p.10 line 267 "The reaction profiles of methanol oxidations to form MF are well documented in literature[4], which suggests four sequential reaction steps as governing steps including [...]" I would not call a reaction profile being well documented if only one paper is cited, in particular when the cited paper was published by the same group. Is there independent work which confirm the author's claim of the reaction profile? Otherwise, I would like to see the justification why the methanol oxidation has this reaction network as the authors presented it.

Author reply #3-1:

We appreciate the reviewer's insightful comment regarding the reaction profile. To address this point, we have additionally cited three independent studies that corroborate the reaction profile proposed in our work. These references consistently demonstrate that O, OH-assisted coupling of methanol on metal surfaces is essential for partial oxidations to occur[1,2,3]. Notably, the methanol oxidation reaction follows the same mechanism on both Au(111) and Pt(111) surfaces, regardless of the specific metal involved. The mechanistic consistency in these literatures substantiates the reaction profile proposed in our study.

References

1 Xu, B. et al. Theoretical Study of O-Assisted Selective Coupling of Methanol on Au(111), *J. Phys. Chem. C* **115**, 3703-3708 (2011)

2 Zhong, W. et al. The O, OH and OOH-assisted selective coupling of methanol on Au–Ag(111), *Phys. Chem. Chem. Phys.* **18**, 9969 (2016)

3 Lee, S. W. et al. Intrinsic Relation between Hot Electron Flux and Catalytic Selectivity during Methanol Oxidation, *ACS Catal.* **9**, 8424-8432 (2019)

[Modifications in the manuscript]

(Results, page 12) "The reaction profiles of methanol oxidations to form MF are well documented in literature[4,7,50,51], which suggests four sequential reaction steps as governing steps ~"

Reviewer comments #3-2:

In the section where the origin for the enhanced selectivity for methylformate is discussed, the authors fail to present DFT calculations for the barriers of CO_2. How much is the reaction barrier for CO_2 formation affected by the increased concentration of the oxygen vacancies? From an experimental point of view, the CeO_x/Pt(111) with the higher oxygen vacancy concentration, henceforth called vac-CeO_x/Pt, shows the highest chemicurrent yield indicating this sample to be the most reactive one for methanol oxidation but the chemicurrent yield is insensitive to the formation of CO_2 or methylformate. Therefore, support from theory is required but not provided. For instance, should it turn out that the reaction barrier for CO_2 is even further reduced than the one for methylformate, it would contradict the author's conclusions.

Author reply #3-2:

We thank the reviewer for the insightful comment emphasizing the need for theoretical support in comparing the partial oxidation barrier with the full oxidation barrier, particularly concerning CO_2 formation. To address this, we focused on the mechanism by which CO_2 formation occurs through the additional dehydrogenation of CH_2O, bypassing alkoxy hemiacetal formation (**Fig. R2**). Using DFT calculations, we systematically compared the reaction energy barriers for the following processes:

(1) $*CH_3O + *CH_2O \rightarrow *CH_3OCOH_2$ (*aka* alkoxy hemiacetal formation)

(2) $*CH_2O + *OH \rightarrow *CHO + H_2O(g)$ (additional dehydrogenation)

If reaction (1) is more favorable, methyl formate formation is expected to dominate. Conversely, CO_2 formation would be preferred if the additional dehydrogenation of CH_2O (reaction 2) proceeds more readily than the alkoxy hemiacetal formation pathway.

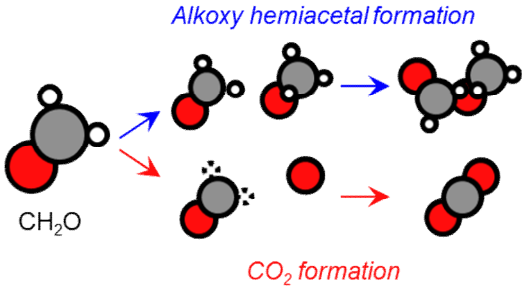


Fig. R2 A schematic illustrating partial oxidation (alkoxy hemiacetal formation) and full oxidation (CO_2 formation) of a methanol molecule.

The reaction energy barriers for these two processes were compared across Pt, CeO_2/Pt, and Vac.-CeO_x/Pt surfaces, with the results are summarized in **Table R1**. On Pt and CeO_2/Pt, the barrier for additional dehydrogenation is lower than for alkoxy hemiacetal formation, favoring CO_2 formation. In contrast, on Vac.-CeO_x/Pt, alkoxy hemiacetal formation becomes more favorable pathway. These findings provide strong theoretical evidence supporting the conclusion that increasing oxygen vacancies in ceria enhances the selectivity for methyl formate.

Barrier (eV)	Alkoxy hemiacetal formation	Additional dehydrogenation
Pt	0.634	0.431
CeO_2/Pt	0.398	0.281
Vac.-CeO_x/Pt	0.032	0.191

Table R1. DFT-computed reaction energy barriers (in eV) for the two reactions of alkoxy hemiacetal formation and additional dehydrogenation of CH_2O.

[Modifications in the manuscript]

(Results, page 12) Additional dehydrogenation calculations further confirmed that the formation of the alkoxy hemiacetal intermediate is favorable only on the Vac.-CeO_x/Pt(111) system (**Supplementary Table 3**).

(Supplementary information) We have added Table R1 to Supplementary information.

Barrier (eV)	Alkoxy hemiacetal formation	Additional dehydrogenation
Pt	0.634	0.431
CeO_2/Pt	0.398	0.281
Vac.-CeO_x/Pt	0.032	0.191

Supplementary Table 3. DFT-computed reaction energy barriers (in eV) for the two reactions of alkoxy hemiacetal formation and additional dehydrogenation of CH_2O.

Reviewer comments #3-3:

I am very uneasy about the quality of the DFT calculations of this study in general. As a matter of fact, I consider them to be the manuscript's Achilles heel. The DFT settings are most likely to be underconverged. Using only the Gamma point for instance for a (6×6) slab is definitely not enough. Furthermore, using only three layers is not suitable to model a surface which is supposed to have bulk properties as well. The author's stated that the bottom layer was fixed to mimic exactly that but by pure geometry arguments, one can show that one will never achieve that when only using three layers and fixing only the last one. The authors ought to model the

slab with at least six layers. Moreover, the force convergence criterion of 0.05 eV/Å is also a too loose criterion. I am severely questioning the barriers which the authors propose based on this criterion. Therefore, I want to see a thorough set of convergence tests for the systems from single point energies, over relaxations to NEB with respect to the parameters that are typically checked.

Author reply #3-3:

We thank the reviewer for raising concerns regarding the quality of the DFT calculations. First, we would like to clarify the reasoning behind our DFT computational settings. The unit cell sizes of our systems are approximately 17 Å×17 Å×35 Å, corresponding to a very small Brillouin zone in reciprocal space. Given the very large real-space supercell, the Brillouin zone becomes sufficiently small that Γ-point-only sampling is often adequate, as contributions from other k-points are negligible. Please note that previous studies investigating methanol oxidation reactions on Au(111) and Pt(111) surfaces utilized only 20~30 metal atoms with 3×3×1 k-point sampling[1,2]. In contrast, our system size involves over 110 metal atoms (>1,100 electrons) which is about 4~5 times larger in terms of both the unit cell size and the number of electrons, and this led us to choose the Γ-point-only sampling. In addition, these previous studies used a three-atomic-layer (3×3) surface unit cell, and one of these studies explicitly demonstrated that increasing the number of layers had negligible effects on the calculated reaction energies and energy barriers[1].

Nevertheless, we acknowledge the reviewer's concerns regarding the need for further justification of our computational settings. To address this, we performed additional calculations for methanol oxidation reactions on the Pt(111) systems under more stringent conditions: a (2×2×1) k-point grid and a force convergence criterion of 0.02 eV/Å. These calculations revealed only small differences of less than 0.06 eV in reaction energies and 0.05 eV in barriers, compared to the original setting. Importantly note that these variations did not alter the overall trends in reaction energies or barriers across different reaction steps, reaffirming the robustness and reliability of our conclusions.

References

1 Xu, B. et al. Theoretical Study of O-Assisted Selective Coupling of Methanol on Au(111), *J. Phys. Chem. C* **115**, 3703-3708 (2011)

2 Lee, S. W. et al. Intrinsic Relation between Hot Electron Flux and Catalytic Selectivity during Methanol Oxidation, *ACS Catal.* **9**, 8424-8432 (2019)

Reviewer comments #3-4:

The authors also did not discuss the possible role of the change of the local cerium oxide structure introduced by the higher oxygen vacancy concentration but completely assign it to the different electronic structure of the nanowires. This is again a point where DFT might be able to provide. Yet, first of all, I am not quite sure whether or not the author's relaxed the vac-CeO_x cluster on Pt(111) again. If the same convergence criteria, i.e., 10^{-5} eV and 0.05 eV/Å were used, again, they are most likely underconverged. Besides, why did the authors removed two oxygens close to the Pt(111) surface and no other sides. Is this justified? What would DFT predict if the oxygen vacancies were introduced somewhere else in the CeO_x cluster? Would the author's picture still hold. This is a point that also needs to be properly addressed in the manuscript.

Author reply #3-4:

We appreciate the reviewer's insightful comment on the potential effects of oxygen vacancies. However, we did not find any experimental evidence suggesting that Vac.-CeO_x undergoes significant structural changes. Additionally, we relaxed the Vac.-CeO_x cluster on Pt(111) using more strict criteria outlined in comment 3 ($2\times2\times1$ k-point sampling, the force convergence criterion of 0.02 eV/Å), and observed little structural changes induced by the oxygen vacancy. As a result, our focus shifted to examining how the altered electronic structure, arising from oxygen vacancies, influences the reaction barrier of methanol oxidation.

To further clarify, we have provided our rationale for removing two oxygen atoms near the interface, guided by defect formation energies. Specifically, the removal of an oxygen atom from the ceria cluster revealed that the lowest defect formation energy occurs at the interface. This observation motivated our decision to remove the interface oxygen atom from the ceria cluster.

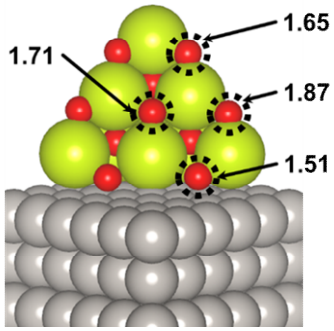
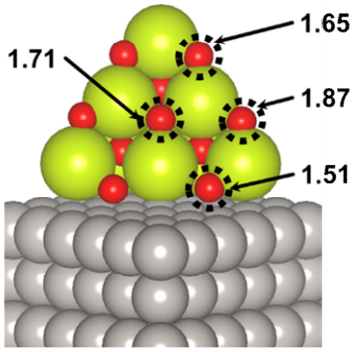


Fig. R3 DFT-computed oxygen defect formation energy (in eV) at different sites of ceria cluster on Pt(111). The sites near the interface are the most energetically favored.

[Modifications in the manuscript]

(Methods, page 18) Based on the DFT-computed oxygen defect formation energies, the two oxygen vacancies were modeled at the perimeter interface (**Supplementary Fig. 14**).

(Supplementary Information) We have added Fig. R3 to Supplementary information.



Supplementary Fig. 14 DFT-computed oxygen defect formation energy (in eV) at different sites of ceria cluster on Pt(111). The sites near the interface are the most energetically favored.

Reviewer comments #3-5:

How was the optimal U-parameter actually determined? The authors cited a paper for their choice but this is paper about the study is about NiO and ceria oxide is not mentioned in there a single time. Is this a mistake in the citation? Please either provide a convincing citation or a benchmark which justifies the use of 5 eV.

Author reply #3-5:

We thank the reviewer for this comment regarding the choice of the optimal U parameter. The reference cited in this part demonstrate that we employed the simplified (rotationally invariant)

approach to the DFT+U, reported by Dudarev et al. To justify our selection of U=5 eV, we have included the following references supporting this choice[1,2]:

1 Kim, H. Y. et al. CO Oxidation Mechanism on CeO_2-Supported Au Nanoparticles. J. Am. Chem. Soc. **134**, 1560-1570 (2012)

2 Andersson, D. A. et al. Modeling of CeO_2, Ce_2O_3, and CeO_{2-x} in the LDA+U formalism, Phys. Rev. B **75**, 035109 (2007)

In the literature, U values ranging from 4.5 to 5.5 eV are commonly used for GGA calculations[3]. Additionally, Yong Li *et al.* demonstrated that reaction energies and barriers in ceria-metal inverse oxide/metal systems are largely insensitive to the precise value of the Hubbard U parameter[4]. Nonetheless, we selected a U value of 5 eV, based on studies that suggested the need for $U \geq 5$ eV when employing GGA to accurately describe partially reduced ceria[2].

References

1 Kim, H. Y. et al. CO Oxidation Mechanism on CeO_2-Supported Au Nanoparticles. *J. Am. Chem. Soc.* **134**, 1560-1570 (2012)

2 Andersson, D. A. et al. Modeling of CeO_2, Ce_2O_3, and CeO_{2-x} in the LDA+U formalism. *Phys. Rev. B* **75**, 035109 (2007)

3 Yang, F. et al. CO Oxidation on Inverse CeO_x/Cu(111) Catalysts: High Catalytic Activity and Ceria-Promoted Dissociation of O_2. *J. Am. Chem. Soc.* **133**, 3444-3451 (2011)

4 Li, Y. et al. What Changes on the Inverse Catalyst? Insights from CO Oxidation on Au-Supported Ceria Nanoparticles Using Ab Initio Molecular Dynamics. *ACS Catal.* **10**, 3164-3174 (2020)

[Modifications in the manuscript]

(Methods, page 18) **"**We adopted the Hubbard U-J value of 5 eV to describe the electronic properties of the ceria[56,57,58]."

Reviewer comments #3-6:

Another concern which I have regarding the ciNEB calculation is that the system was modelled with a single methanol molecule and a single OH molecule but given the large pressures under which the reactions are carried out, I am pretty sure the surface concentration in the DFT calculations does not reflect the experimental conditions. Additionally, it is very well-known that the barriers in ciNEB are sensitive to the size of the simulation cell. Yet, I have not seen any checks on the size of the simulation cell, i.e., increasing the lateral size of the Pt(111) slab.

Author reply #3-6:

We thank the reviewer for the insightful comment regarding the potential variability of results based on reactant concentration and simulation cell size. As noted, in a real experiment setting, a large number of methanol and OH molecules would be present on the heterointerface of our nanoplatform. Reaction energies and barriers between (3 × 3) and (6 × 6) unit cells were compared to understand the effect of reactant concentrations. Considering the periodic boundary conditions employed in DFT simulations, these unit cells reflect sufficiently high-concentration scenarios. In our previous study[1], methanol oxidation was modeled on a (3 × 3) unit cell of the Pt(111) surface. In the present study, we have used a larger (6 × 6) unit cell and compared the reaction energies and barriers to assess the effect of simulation cell size. The results are summarized in **Table R2** below.

	Reaction pathway	Reaction energy (eV)		Barrier (eV)	
		Pt (3 × 3)[1]	Pt (6 × 6)	Pt (3 × 3)[1]	Pt (6 × 6)
1	$^*CH_3OH + {}^*O \rightarrow {}^*CH_3O + {}^*OH$	0.26	0.303	0.28	0.321
2	$^*CH_3O + {}^*OH \rightarrow {}^*CH_2O + {}^*H_2O$	-1.25	-0.870	0.42	0.113
3	$^*CH_3O + {}^*CH_2O \rightarrow {}^*CH_3OCOH_2$	-0.06	-0.062	0.64	0.634
4	$^*CH_3OCOH_2 + {}^*OH \rightarrow CH_3OCOH + H_2O$	-2.56	-1.246	0.00	0.287

Table R2. Comparison of reaction energies and barriers between (3 × 3) and (6 × 6) unit cells.

Except for reaction 2, the reaction energies and barriers are quite similar, suggesting that the chosen simulation cell size yields reasonably accurate results. Although reaction 2 exhibits a notable difference, potentially indicating a cell size effect, the primary factor governing the selectivity toward methyl formate remains unchanged as alkoxy hemiacetal formation (O-C bonding formation). Since the difference in reaction 2 does not alter the rate-determining step in either both (3 × 3) or (6 × 6) unit cell, we believe that our chosen simulation cell size is adequate for capturing essential physics and chemistry of the system.

References

1 Lee, S. W. et al. Intrinsic Relation between Hot Electron Flux and Catalytic Selectivity during Methanol Oxidation. *ACS Catal.* **9**, 8424-8432 (2019)

Reviewer comments #3-7:

These are now minor issues which I would recommend the authors to refine to enhance the paper's quality but I leave it to their discretion.

I) Please unify the notation in SI Note 1 and SI Table 1 (please adhere to the notation in Note 1 as that's the appropriate one in terms of scientific notation).

II) Figure 5b) could definitely benefit from some reworks: Insert the actual barriers into the figure and change the scale of the axis accordingly to work out the differences between the samples appropriately.

III) In Table 2 the authors should provide the units of those numbers (eV). If Figure 5b) is refined elegantly, maybe Table 2 would not be needed at all.

IV) A very very minor issue which doesn't address the scientific quality of the paper, but I noticed that the authors sometimes mix up modeled (American spelling) vs. modelled (British spelling). Whilst I don't have a preference for either one or the other, I think the authors want to be consistent throughout their manuscript.

Author reply #3-7:

We thank the reviewer for raising these comments, and have revised the manuscript as follows.

[Modifications in the manuscript]

I) We have unified the notation in SI Note 1 and SI Table 1 to ensure consistency throughout Supplementary information.

(Supplementary information)

Supplementary Note 1. Thermionic emission equation

We determined the Schottky barrier height and ideality factor as indicators of the formation of a catalytic nanodiode by fitting the I-V curve to the thermionic emission equation[1],

$$I = A^{*}T^{2}A\exp\left(-\frac{q\phi_b}{k_bT}\right)\left[\exp\left(\frac{q(V-IR_s)}{\eta k_bT}\right)-1\right]$$

where A^{*} is the effective Richardson constant of TiO_2, T is the temperature when the measurement is implemented, A is the active area of Schottky contact, q is an elementary electric charge, k_b is the Boltzmann constant, ϕ_b is the Schottky barrier height, η is an ideality factor, and R_s, is a series resistance of CeO_x nanowires/Pt/TiO_2.

Supplementary Table 1. Parameters in the thermionic emission equation.

Term	Value	Units
A^{*} (TiO_2)	72	A/cm^2K^2
T	298	K
k_b	$8.60x10^{-5}$	eV/K
$\frac{k_bT}{q}$	0.026	V
A	0.08	cm^2

II) The actual reaction barriers have now been incorporated into the figure. The alkoxy hemiacetal formation reaction barrier is identified as the most critical factor in determining the selectivity for methyl formate. This is because the difference between this barrier and the barrier for additional dehydrogenation ($CH_2O \rightarrow CHO$) governs selectivity. To emphasize this, we highlighted that on Pt, CeO_2, and Vac.-CeO_x, the alkoxy hemiacetal formation barrier exhibits the most significant variations across materials compared to other reactions. Accordingly, we retained the original scale in **Fig. 5b** to visually represent this variation clearly.

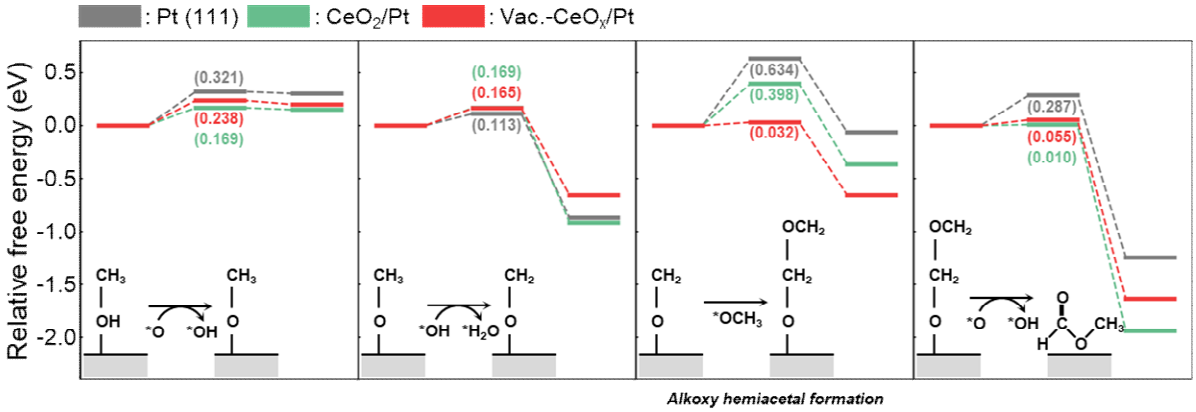


Fig. 5b The free energy profiles of methyl formate production from methanol oxidation on three modeling systems. Numbers in parentheses represent the reaction barrier (in eV).

III) Units have been added to the values in Table 2.

(Supplementary information)

Supplementary Table 2. Calculated reaction energies and barriers for methanol oxidation on Pt(111), CeO_2/Pt, Vac.-CeO_x/Pt.

	Reaction pathway	Reaction energy (eV)			Barrier (eV)		
		Pt	CeO_2/Pt	Vac.-CeO_x/Pt	Pt	CeO_2/Pt	Vac.-CeO_x/Pt
1	$^*CH_3OH + {}^*O \rightarrow {}^*CH_3O + {}^*OH$	0.303	0.151	0.200	0.321	0.169	0.238
2	$^*CH_3O + {}^*OH \rightarrow {}^*CH_2O + {}^*H_2O$	-0.870	-0.916	-0.997	0.113	0.169	0.165
3	$^*CH_3O + {}^*CH_2O \rightarrow {}^*CH_3OCOH_2$	-0.062	-0.365	-0.657	0.634	0.398	0.032
4	$^*CH_3OCOH_2 + {}^*OH \rightarrow CH_3OCOH + H_2O$	-1.246	-1.939	-1.635	0.287	0.010	0.055

IV) The terminology has been standardized to ‘modeled’ throughout the manuscript for consistency.

(Results, page 11) “As depicted in **Fig. 5a**, three systems are modeled, which include Pt(111), CeO_2/Pt(111), and Vac.-CeO_x/Pt(111).”

(Methods, page 16) “To construct the CeO_2/Pt and Vac.-CeO_x/Pt systems, we combined tetrahedral $Ce_{10}O_{20}$ and $Ce_{10}O_{18}$ clusters with the modeled Pt film, as mentioned above.”

(Discussion, page 14) “Our model platform combined with Schottky nanodiode is an effective and powerful technique to analyze the effects of ~”

Response to Reviewer 3

Reviewer comments #3-1:

The authors have addressed my scientific concerns in a satisfactory manner. I have only a slight request: I would like to see the figure R2, showcasing the two competing reaction pathways, with Supplementary Table 3. The authors correct may correct me if I am wrong (and I apologise in advance in case I missed it) but the additional dehydrogenation reaction is never properly written down in the manuscript in contrast to the elementary reaction in the other pathway towards methylformate. So far this table comes out of nowhere which is a consequence of me asking for that but one way to put it into the context of the paper would be the following: Giving more details in Figure R2, i.e., just showing the abstraction of one H atom and then two arrows to CO2, which indicates a series of more elementary steps towards CO2 would, clarify the reaction that is investigated.

That is everything from my end. In my opinion, the paper can be subject to publication, and from my end, I do not need another round of review.

Author reply #3-1:

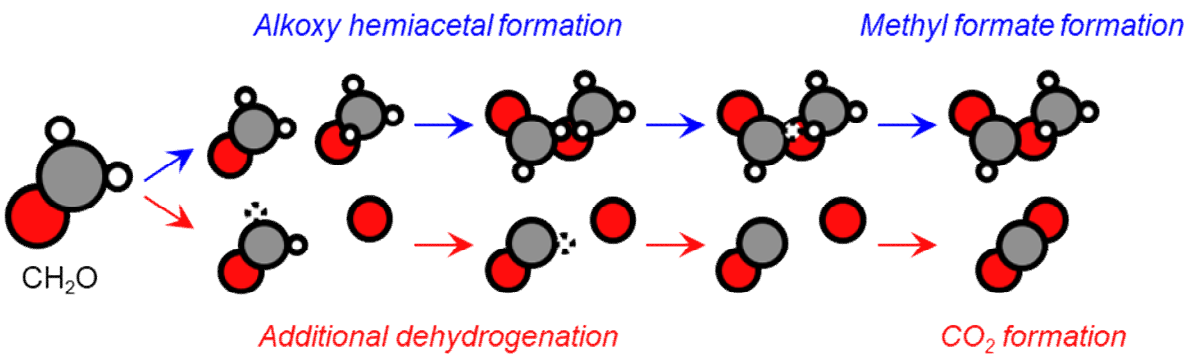
We thank the reviewer for this comment, and agree that the additional dehydrogenation reaction is not properly written down in the manuscript in contrast to the elementary reaction in the other pathway towards methyl formate. To address this, we have revised the manuscript and updated **Supplementary Table 3** as below.

[Modifications in the manuscript]

(Results, page 12) It is important to note that CH_2O, an intermediate in the oxidation of methanol, can follow two competitive pathways: alkoxy hemiacetal formation leading to partial oxidation into methyl formate) and additional dehydrogenation resulting in full oxidation to CO_2. The latter pathway, which can be described by the reaction $*CH_2O + *OH \rightarrow *CHO + H_2O_{(g)}$ is detailed in **Supplementary Table 3**. Our studies have shown that in the Vac.-CeO_x/Pt(111) system, the alkoxy hemiacetal formation is energetically more favorable than the competing pathway. Conversely, in the CeO_x/Pt(111) and pure Pt(111) systems, the opposite trend is observed. These findings support the critical role of the vacancy formation within ceria in selectively promoting the formation of methyl formate rather than CO_2.

(Supplementary information) We have added the modified Figure R2 to Supplementary Table

3 in response to your comment.



Barrier (eV)	Alkoxy hemiacetal formation	Additional dehydrogenation
Pt	0.634	0.431
CeO_2/Pt	0.398	0.281
Vac.-CeO_x/Pt	0.032	0.191

Supplementary Table 3. DFT-computed reaction energy barriers (in eV) for the two reactions of alkoxy hemiacetal formation and additional dehydrogenation of CH_2O.

Review of the manuscript
"Unraveling Oxygen Vacancy-Driven Catalytic Selectivity and Hot Electron Generation on Heterointerfaces using Nanostructured Platform"

In the manuscript "Unraveling Oxygen Vacancy-Driven Catalytic Selectivity and Hot Electron Generation on Heterointerfaces using Nanostructured Platform", the authors present a combined experimental-theoretical study on the oxidation of methanol on CeO_x/Pt(111) with particular emphasis on the role of the substrate's crystallinity and its oxygen vacancy concentration.

Experimentally, the CeO_x nanowires, initially amorphous, were deposited on templates and subsequently post-processed employing different procedures to modulate the nanowires' crystallinity and oxygen vacancy concentration. Thence, those nanowires were transferred onto Pt films on a TiO_2 Schottky diode and the overall devices were exposed to a methanol-oxygen mixture to study the methanol oxidation reaction. The reaction's performance and selectivity to methylformate was analysed with the help of both Gas Chromatography and hot electron flux, i.e., chemicurrents.
The experiments were supported by theory with the help of density functional calculations where the CeO_x-nanowire/Pt substrate was modelled as CeO_2 cluster on a Pt(111) surface. Bader charge analysis and climbing image nudged elastic band calculations for the individual elementary reactions in the author's proposed reaction network have been carried out to study the role of the oxygen vacancies, i.e., the hot electrons in the methanol oxidation.

The experiments have been well designed and great care has been taken in their conduction and analysis and should definitely be published. As a consequence, the authors convinced me on a phenomenological level that the structural and electronic properties have a substantial impact on the reactivity and selectivity of CeO_x/Pt(111). However, many questions on the atomistic level remain and therefore I consider this work to be suitable for publication once the following concerns have been appropriately addressed:

I) The authors write on p.10 line 267 "The reaction profiles of methanol oxidations to form MF are well documented in literature[4], which suggests four sequential reaction steps as governing steps including [...]"
I would not call a reaction profile being well documented if only one paper is cited, in particular when the cited paper was published by the same group. Is there independent work which confirm the author's claim of the reaction profile? Otherwise, I would like to see the justification why the methanol oxidation has this reaction network as the authors presented it.

II) In the section where the origin for the enhanced selectivity for methlyformate is discussed, the authors fail to present DFT calculations for the barriers of CO_2. How much is the reaction barrier for CO_2 formation affected by the increased concentration of the oxygen vacancies? From an experimental point of view, the CeO_x/Pt(111) with the higher oxygen vacancy concentration, henceforth called vac-CeO_x/Pt, shows the highest chemicurrent yield indicating this sample to be the most reactive one for methanol oxidation but the chemicurrent yield is insensitive to the formation of CO_2 or methylformate. Therefore, support from theory is required but not provided. For instance, should it turn out that the reaction barrier for CO_2 is even further reduced than the one for methylformate, it would contradict the author's conclusions.

III) I am very uneasy about the quality of the DFT calculations of this study in general. As a matter of fact, I consider them to be the manuscript's Achilles heel. The DFT settings are most likely to be underconverged. Using only the Gamma point for instance for a (6×6) slab is definitely not enough. Furthermore, using only three layers is not suitable to model a surface which is supposed to

have bulk properties as well. The author's stated that the bottom layer was fixed to mimic exactly that but by pure geometry arguments, one can show that one will never achieve that when only using three layers and fixing only the last one. The authors ought to model the slab with at least six layers. Moreover, the force convergence criterion of 0.05 eV/Å is also a too loose criterion. I am severely questioning the barriers which the authors propose based on this criterion. Therefore, I want to see a thorough set of convergence tests for the systems from single point energies, over relaxations to NEB with respect to the parameters that are typically checked.

IV) The authors also did not discuss the possible role of the change of the local cerium oxide structure introduced by the higher oxgyen vacancy concentration but completely assign it to the different electronic structure of the nanowires. This is again a point where DFT might be able to provide. Yet, first of all, I am not quite sure whether or not the author's relaxed the vac-CeO_x cluster on Pt(111) again. If the same convergence criteria, i.e., 10^{-5} eV and 0.05 eV/Å were used, again, they are most likely underconverged. Besides, why did the authors removed two oxygens close to the Pt(111) surface and no other sides. Is this justified? What would DFT predict if the oxygen vacancies were introduced somewhere else in the CeO_x cluster? Would the author's picture still hold. This is a point that also needs to be properly addressed in the manuscript.

V) How was the optimal U-parameter actually determined? The authors cited a paper for their choice but this is paper about the study is about NiO and ceria oxide is not mentioned in there a single time. Is this a mistake in the citation? Please either provide a convincing citation or a benchmark which justifies the use of 5 eV.

VI) Another concern which I have regarding the ciNEB calculation is that the system was modelled with a single methanol molecule and a single OH molecule but given the large pressures under which the reactions are carried out, I am pretty sure the surface concentration in the DFT calculations does not reflect the experimental conditions. Additionally, it is very well-known that the barriers in ciNEB are sensitive to the size of the simulation cell. Yet, I have not seen any checks on the size of the simulation cell, i.e., increasing the lateral size of the Pt(111) slab.

These are now minor issues which I would recommend the authors to refine to enhance the paper's quality but I leave it to their discretion.
I) Please unify the notation in SI Note 1 and SI Table 1 (please adhere to the notation in Note 1 as that's the appropriate one in terms of scientific notation).
II) Figure 5b) could definitely benefit from some reworks: Insert the actual barriers into the figure and change the scale of the axis accordingly to work out the differences between the samples appropriately.
III) In Table 2 the authors should provide the units of those numbers (eV). If Figure 5b) is refined elegantly, maybe Table 2 would not be needed at all.
IV) A very very minor issue which doesn't address the scientific quality of the paper, but I noticed that the authors sometimes mix up modeled (American spelling) vs. modelled (British spelling). Whilst I don't have a preference for either one or the other, I think the authors want to be consistent throughout their manuscript.

In summary, the article is well-structured, the figures are informative and convey support the author's arguments. The experimental procedures are well-described and the experiments in general are, from what I can tell, carefully conducted and analysed. Yet, the supporting DFT calculations are on a shaky ground which hinders the work to provide a mechanism on the atomic scale. Hence, before my concerns are not appropriately addressed I cannot recommend this manuscript for being published in Nature communications.