Application of new nanoparticle structures as catalysts: general discussion

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Carlo Lamberti opened discussion of the paper by Chris-Kriton Skylaris: Do you think that your approach can be used also to investigate molecular absorption on the surface e.g. using CO as a probe? The coverage-dependent vibrational spectra of CO adsorbed on Pt and Pd nanoparticles (NP) are extremely rich in information and concern the progressive formation of three-fold bridged, two-fold bridged and linear CO adducts on different (h, k, l) faces, usually (111) and (100).[1–5] The complexity of such spectra contains coverage/size/shape-dependent information that has not been fully extracted so far. The creation, with your computational approach, of a huge library of coverage/size/shape dependent IR spectra, supported by a machine learning approach can potentially represent a breakthrough in the NP morphology determination.

1 T. Visser, T. A. Nijhuis, A. M. J. van der Eerden, K. Jenken, Y. Ji, W. Bras, S. Nikitenko, Y. Ikeda, M. Lepage and B. M. Weckhuysen, J. Phys. Chem. B, 2005, 109, 3822.
2 C. Lamberti, A. Zecchina, E. Groppo and S. Bordiga, Chem. Soc. Rev., 2010, 39, 4951–5001.
3 E. Groppo, S. Bertarione, F. Rotunno, G. Agostini, D. Scarano, R. Pellegrini, G. Leofanti, A. Zecchina and C. Lamberti, J. Phys. Chem. C, 2007, 111, 7021–7028.
4 G. Agostini, R. Pellegrini, G. Leofanti, L. Bertinetti, S. Bertarione, E. Groppo, A. Zecchina and C. Lamberti, J. Phys. Chem. C, 2009, 113, 10485–10492.
5 E. Groppo, G. Agostini, A. Piovano, N. B. Muddada, G. Leofanti, R. Pellegrini, G. Portale, A. Longo and C. Lamberti, J. Catal., 2012, 287, 44–54.

Chris-Kriton Skylaris answered: We can compute adsorption energies and vibrational spectra and the method can be applied to CO adsorbed on Pt and Pd as you suggest, so it should be possible to computationally investigate these systems and compare with experimental data as a function of nanoparticle size

and coverage. One difficulty is that to make a library of many cases as you suggest will require a very large amount of computational resources and human effort. An additional difficulty is that CO is well known to prefer to bind to the wrong site in DFT calculations compared to experiments on (111) surfaces so one has to be careful to make sure to place it on the correct adsorption sites.

Richard Catlow said: It is very impressive that we can perform realistic calculations on these large nano-particles. Can you comment on strategies and procedures for validation of the approach?

Chris-Kriton Skylaris replied: We always perform validation against conven-tional (cubic-scaling) DFT codes on smaller systems before proceeding to perform the calculations of large systems such as the nanoparticles in this case. Typically, we validate our calculations against a plane wave code like CASTEP (which has the advantage of being able to use exactly the same pseudopotentials such as ONE-TEP) or against calculations with a Gaussian basis set code with a very large basis set, as ONETEP is designed to perform calculations at the near complete basis set limit. A er we con rm that we obtain numerical agreement with the conventional DFT code we proceed using the same calculation settings to perform calculations on the larger systems. Furthermore, to check that we get the "correct" result as we make the system larger we can make an arti cial system for which we know the answer such as, for example, a collection of several small nanoparticles that are well separated from each other and which we have veri ed in calculations with a conventional code. Another such example is doing calculations on a big gamma-point-only supercell of a bulk solid or slab, which can be compared against a much smaller simulation cell calculation with a conventional code using a sufficient number of k-points to make it equivalent to the ONETEP gamma point calculation. In all cases, we aim to obtain (and we do obtain) the same result as a conventional DFT code would produce if it could be run on the large system

Hans-Joachim Freund commented: I wanted to point out that calorimetric data on CO adsorption on Pd particles with varying size have been published,[1] which could serve as a benchmark for DFT calculations on molecular binding energies on supported clusters of varying size.

1 M. Peter, J. M. F. Camacho, S. Adamovoski, L. K. Ono, K.-H. Dostert, C. P. O Brien, B. Roldan Cuenya, S. Schauermann, H.-J. Freund, Angew. Chem. Int. Ed., 2013, 52, 5175–5179.

Chris-Kriton Skylaris responded: Thank you, this reference is valuable for our work.

Wilke Dononelli communicated: You showed very interesting results for O adsorption on different sizes of Pt nanoparticles (NPs). It is especially noteworthy that you used NPs with more than 55 atoms in your calculations and did not see any drastic changes in the adsorption energies compared to the NPs with 55 atoms. For smaller Pt_{13} NPs you saw a stronger binding strength of atomic oxygen. These results are in good agreement with our results about CO adsorption on coinage metal NPs, where we found an increase in adsorption strength of 1.5 for M_{13} NPs (M ¼ Au, Ag, Cu or bi-metallic combinations of those) compared to the

bigger M_{55} NPs (DOI: 10.1039/c7fd00225d). On the other hand on the CCSD(T) level of theory these differences in adsorption energies were smaller. We now additionally calculated the adsorption energy of atomic oxygen on Pt_{13} using PBE as shown in the computational setup of our paper using equation 18 from your underlying study (DOI: 10.1039/c7fd00218a). We found an adsorption energy of 1.55 eV, which is in perfect agreement with your results. Additionally, we calcu-lated an adsorption energy for the relaxed geometries at the DLPNO-CCSD(T) level of theory,[1] using a DEF2-TZVP basis set.[2] Here an adsorption energy of 1.15 eV was found. Thus, we nd a similar trend, but the magnitude is different. Would you please be so kind as to comment on the differences between the adsorption energies calculated using the two different approaches?

1 W. B. Schneider, G. Bistoni, M. Sparta, M. Saitow, C. Riplinger, A. A. Auer and F. Neese, J. Chem. Theory Comput., 2016, 12, 4778–4792.
2 F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., 2005, 7, 3297.

Chris-Kriton Skylaris answered: It is not clear how well suited a CC calculation is for metallic clusters and also how converged it can be with a Gaussian basis set. It is difficult to make any judgement here without a study speci cally comparing CC and different avours of DFT under the same conditions (e.g basis set, pseudopotentials, etc). In ONETEP we use a psinc basis set which is equivalent to a plane wave basis set.

Notker Roesch commented: Several times during the discussions, the CCSD(T) method has been referred to as the "gold standard" of computational chemistry. However, this claim is only justi ed for systems where a single-reference approach is adequate, i.e., when one does not have to face a system with notable static correlation. Diagnostic indicators have been developed to judge whether this is the case and, hence, the total energy is reliable. Gold clusters may have small energy gaps, thus may require a multi-reference treatment, but diag-nostic indicators have not been quoted to ensure the adequacy of the CCSD(T) calculations presented. A second important aspect for reliable CCSD(T) results is related to the fact that this computational method requires rather exible basis sets. Before CCSD(T) results can be used as a reference, evidence has to be pre-sented for a sufficient convergence of the results with respect to this requirement. In summary, the label "CCSD(T)" by itself does not ensure a reliable calculation.

Rene Nome asked: I was wondering if you could comment on the application of your method to assess the sharp transition in atomically precise Au clusters, from nonmetallic Au_{246} to metallic Au_{279} with nascent surface plasmon resonance, as reported recently.[1]

1 T. Higaki, M. Zhou, K. J. Lambright, K. Kirschbaum, M. Y. Sfeir and R. Jin, J. Am. Chem. Soc., 2018, 140, 5691–5695.

Chris-Kriton Skylaris indicated that he had nothing to add.

Cynthia Friend asked: You studied the coverage dependence of the oxygen binding. It is well known that attractive interactions occur on single-crystal Pt but

the attraction depends on the speci c O–O distance. Did you benchmark your results against single crystals and study the dependence of the O–O separation?

Chris-Kriton Skylaris replied: Not yet. This is something we intend to study next.

Alexander Genest enquired: Your oxygen decorations appear like the begin-ning of a Pt-oxide overlayer. How similar is the oxide layer to Pt-oxide? Why does the E_{ads} at Pt_{147} have a kink at 0.6 ML oxygen coverage, which seems not to appear for the other two cluster nuclearities (Fig. 8)?

Chris-Kriton Skylaris responded: We observe that the behaviour of forming a Pt-oxide overlayer is observed only when we allow all atoms (Pt and O) to relax as shown in Fig. 5 and 6. As we decided to follow the strategy of freezing the Pt atoms we could not examine the similarity with conventional Pt-oxide but it would be worth exploring this in future work. Both Pt_{147} and Pt_{309} have a kink at about 0.6 ML (a bit earlier for Pt_{309}) where the average adsorption energy decreases abruptly, although this kink is more intense in Pt_{147}. As we explain in the paper the onset of this behaviour is due to O migrating to different adsorption sites and also due to changes in the electronic structure of the nanoparticle when O coverage reaches these levels.

Roy Johnston asked: Is the linear scaling method applicable to excited states, for example within the TD-DFT framework?

Chris-Kriton Skylaris communicated in reply: Yes. ONETEP has quite advanced capabilties for calculations of excited states using TD-DFT, see for example previous work and references therein.[1] This method is implemented for GGA functionals. We are currently working with our collaborators in Warwick to extend it to hybrids and range-separated hybrid functionals.

1 T. J. Zuehlsdorff, N. D. M. Hine, M. C. Payne and P. D. Haynes, J. Chem. Phys., 2015, 143, 204107.

Francesca Baletto questioned: We have shown that a peculiar charge transfer between vertex and vertex, takes place for Pt-clusters larger than 55 atoms,[1] and it depends on the cluster morphology, e.g. it is more pronounced in Ih than Co. We do expect a priori that O-adsoprtion might alter this picture and will in uence the electronic properties of the nanoparticle, including its magnetic behaviour and in general the nanoparticle electronic structure. Could the methodology derived within ONETEP shed light on this matter? Furthermore, how did you calculate the distortion of the nanoparticle as a function of the O-coverage? In the affirmative, how does this affect the adsorption properties? It would be nice to compare cluster distortion and the average E_ADS in the same Fig. 8.

1 C. DiPaola, et al., Nano Lett., 2016, 16, 2885–2889.

Chris-Kriton Skylaris replied: We didn't calculate the distortion of the nano-particle as in most cases we had frozen the Pt atoms. However, to assess the methodology we calculated a few cases where we relaxed all of the Pt atoms and

these are summarised in Table 1. As the coverage grows the relaxation becomes a more important effect for the adsorption energies; this will need to be explored in more detail in the future. Our method is able to do spin-polarised and spin-relaxation calculations so the magnetic properties could also be explored as a function of coverage and distortion of the cluster.

Parasuraman Selvam said: It would been good if you have considered icosa-hedron, cuboctaheron and anti-cuboctahedon geometries for the calculation of oxygen atom adsorption. Indeed, the hollow sites are quite different if we consider CCP (FCC) and HCP structures. In fact, the cuboctahedron is a consequence of the CCP structure and the anticuboctahedron is a HCP structure. In particular, this is very clear if you check the side-views. Secondly, in general, up to 147 atoms the preferred geometry is icosahedron (13, 55) and beyond (309 onwards) it changes to cuboctahedron/anticuboctahedron. Please could you comment on this?

Chris-Kriton Skylaris responded: I agree we need to extend our calculations to explore all of these different geometries. It is a matter of time and resources but we intend to do it.

David Willock commented: You consider quite high surface coverages of oxygen in some of your calculations. At these levels there is also the alternative that Pt could segregate forming an oxide and a metallic component. The structure of the oxide is quite different from the metal as in the +2 oxidation state Pt will tend to be square planar and form a more open structure. The structure of the related PdO has been studied and co-ordinates are available.[1] Would it be possible to calculate the energy of a pure PtO phase and then calculate the energy of the separate oxide and metallic phases with the same O content as your higher surface coverage? You could then estimate the oxygen the concentration at which such a segregation should occur.[1]

1 H. H. Kan and J. F. Weaver, Surf. Sci., 2008, 602, L53–L57.

Chris-Kriton Skylaris communicated in reply: It should be possible to do the calculations you suggest and very interesting indeed to explore if and at which point is segregation favoured by our DFT calculations. This would need to be done by relaxing all atoms and not by relaxing only the O and keeping the Pt xed as we did in the majority of the calculations for our present paper. As a consequence the computational effort will be signi cantly higher. We could start with the structure of PdO rst and relax it with DFT and compare with the structure in the paper by Kan and Weaver that you suggested.

Roy Johnston asked: The ONETEP program has linear scaling but there is a fairly (computationally) expensive prefactor. We have performed local energy minimisations for nanoparticles with up to 309 metal atoms using conventional $O(N^3)$ DFT, though they take quite a long time for the larger sizes. Could you say at what particle size (in terms of the number of atoms) it would be quicker to perform local minimisation using ONETEP rather than conventional DFT programs?

Chris-Kriton Skylaris replied: This is strongly dependent on the material and its structure. For insulators with open structures it can be as low as 200 atoms but for metallic systems I expect it would be at more than 500 atoms. This is some-thing we have not yet explored for the new linear-scaling method for metals (AQUA-FOE) in ONETEP and we intend to do so once we have had a chance to further test and optimise this new code.

Caetano Rodrigues Miranda enquired: Have you explored the solvent effects on those systems? Currently, how good is our capability to include these effects?

Chris-Kriton Skylaris responded: We have not yet used any solvent in our calculations of metallic nanoparticles, though we wish to do this in the future. We have very advanced accurate solvent capabilities in ONETEP. These include our "minimal parameter" (in the sense that it only depends on two parameters rather than tens of parameters) implicit solvent model that is one of the most accurate in terms of free energies of solvation. More information about this solvent model can be found in previous work.[1,2] Of course, another option is to include fully explicit solvent molecules, which is very computationally demanding. Finally, we could do the best of both worlds by describing explicitly a small number of solvent molecules that chemically interact with the nanoparticle and its ligands and use the implicit solvent model for the rest of the solvent environment.

1 J. Dziedzic, H. H. Helal, C.-K. Skylaris, A. A. Mosto and M. C. Payne, Europhys. Lett., 2011, 95, 43001.
2 J. C. Womack, L. Anton, J. Dziedzic, P. Hasnip, M. Probert and C.-K. Skylaris, J. Chem. Theor. Comput., 2018, 14,1412–1432.

Carlo Lamberti opened the discussion of the paper by Katharina Brinkert asking: You get the best results with 260 nm sized Rh nanoparticles (NPs), did you try (or are you planning to try) the system with smaller NPs? What is the oxidation state of Rh under operation conditions?

Katharina Brinkert replied: Yes, we are currently investigating the effect of smaller nanoparticles. The Rh oxidation state is 0 under operating conditions.

Andrea Russell said: In thinking about the effects of the particle size of the latex spheres used in the nanosphere lithography in your study, I had a few questions/thoughts. Did you use a commercial suspension of the nanospheres? The reason I ask is that these contain a mixture of surfactants. My group uses them to produce the templates for the preparation of sphere segment void substrates which we use as SERS substrates[1,2] and we must be very careful about residues of these surfactants to ensure our surfaces are clean. In fact, the suspensions of the nanospheres age and approximately once per year we simply have to throw them out and start with a new batch as something happens with the surfactants. When it comes to your study, I wonder if as you reduce the particle size, you are also increasing the relative concentration of the surfactant on the surface you will then deposit the Rh and this may be why you see a smaller sphere diameter of the Rh particles, with a narrower distribution, and the real effect has very little to do with the nanosphere template itself.

1 M. E. Abdelsalam, P. N. Bartlett, J. Baumberg, T. Kelf, S. Cintra, A. E. Russell, Electrochem. Comm., 2005, 7, 740.
2 S. Mahajan, R. M. Cole, B. F. Soares, S. H. Pelfrey, A. E. Russell, J. J. Baumberg, P. N. Bartlett, J. Phys. Chem. C, 2009, 113, 9284.

Katharina Brinkert responded: There are several problems with the latex suspensions. Firstly, one of the most important aspects is that the mono-dispersity varies between 10–30% SD in particle diameter among the different manufacturers. For our purposes, in particular in the work on plasmonic active nanostructures, we used latex particles whose SD particle diameter was smaller than 10%.[1–3] Secondly, it is important to know the exact values of their surface charge. For this purpose a Z potential measurement is recommended. The distribution of charge carriers (e.g., sulfonate groups -SO_3) on the latex surface is not homogeneous, which does not cause a good 2-D arrangement of particles. This may additionally cause problems with reactive etching in the production of perforated metal lm.[6] The stability of latex particles when kept in refrigerators was on average between 2–3 years. For the electrochemical deposition of rhodium particles, the most active structure is the metallic network on the substrate. The activity (also electrical) of the nanostructure depends on its size (quantum size effect) as we have shown in some publications, so the observed effects depend on the size of the latex particle used.[5,6]

1 G. Ctistis, P. Patoka, X. Wang, et al., Nano Lett., 2007, 7, 2926–2930.
2 P. Patoka and M. Giersig, J. Mater. Chem., 2011, 21, 16783–16796.
3 Y. Peng, C. Marcoux, P. Patoka, et al., Appl. Phys. Lett., 2011, 96, 16783–16796.
4 E. M. Akinoglu, A. J. Morfa and M. Giersig, Langmuir, 2014, 30, 12354–12361.
5 T. Sun, E. M. Akinoglu, C. Guo, et al., Appl. Phys. Lett., 2013, 102, 101114.
6 E. M. Akinoglu, T. Sun, J. Gao, et al., Appl. Phys. Lett., 2013, 103, 171106.

Christopher Hardacre asked: Could you comment on the possibility to use your method of preparation of the nanoparticles to tune the absorption of the photoelectrocatalyst?

Katharina Brinkert replied: In general, in semiconductor-electrocatalyst systems, the electrocatalyst is designed in a way that it does not absorb light to allow full light absorption of the semiconductor material. In our system, this is realised by the photoelectrodeposition of Rh from a $RhCl_3$ solution on the p-InP, where a sufficiently small lm of Rh is created with Rh nanoparticles possessing a small diameter. Nevertheless, we have shown that depositing the Rh electrocatalyst through the polystyrene spheres and subsequently removing them allows the creation of "empty" spots on the InP surface which are not covered with Rh; this allows an even better light penetration to the photoabsorbing semiconductor. Variation of the PS particle size allows therefore the "tuning" of the photoabsorbing properties of the semiconductor and the in uence of potential remaining light re ection of the Rh electrocatalyst.

Christopher Hardacre enquired: How good are your systems compared to state-of-the-art for water splitting/sacri cial water splitting and what is the next step in the development of these materials?

Katharina Brinkert answered: The measurements are carried out in a three-electrode setup, therefore, overall solar-to-hydrogen conversion efficiencies can not be determined. Nevertheless, we can report on an photocathodic conversion efficiency, which is about 11% in the best investigated system (application of 260 nm PS particle size). Unassisted water-splitting currently occurs at conversion efficiencies of 19%.[1] The next steps involve the optimization and further inves-tigations of the nanostructured electrocatalyst surface with respect to the in u-ence of the J–V behaviour of the semiconductor-electrocatalyst system and also further the theoretical modelling to describe the system. Furthermore, we would like to apply the nanostructuring to systems for (photo-)electrochemical CO_2 reduction and N_2 xation.

1 W.-H. Cheng, M. H. Richter, M. M. May, J. Ohlmann, D. Lackner, F. Dimroth, T. Han-nappel, H. A. Atwater and H.-J. Lewerenz, 2017, arXiv:1706.01493.

Said Said asked: Does the Rh have any effect on the bandgap of the material?

Katharina Brinkert responded: The semiconductor-metal junction forms a Schottky contact and it is only the Fermi level of the semiconductor which adjusts to the Fermi level of the metal in the dark. The electrocatalyst does not have any in uence on the bandgap of the semiconductor.

Francesca Baletto enquired: What is the minimum size of Rh-nanoparticle that can be produced via SNL? What is their size distribution? Do you have any information on the nal shape adopted by the Rh-clusters? Could you comment on the affect of the InP substrate on the shape/size distribution of Rh-clusters?

Katharina Brinkert responded: We have only explored the deposition of poly-styrene (PS) particles on the p-InP in the size range of 260 nm to 1400 nm; with 260 nm particles, we obtain the lowest Rh sphere diameter of about 30 nm. The Rh spheres form cluster sizes of 0.002 mm^2 to 0.02 mm^2 with Rh possessing cubic structures. The deposition of Rh through the PS particles occurs via photo-electrodeposition, i.e. p-InP is irradiated in an aqueous solution of $RhCl^3$ with a light intensity of 100 W cm^2. The electrons for the Rh^{3+} reduction originate from the p-InP conduction band and, therefore, the size and shape of the Rh-clusters strongly depend on the prepared p-InP surface prior to photoelectrodeposition and the passed photocurrent.

Graham Hutchings addressed Katharina Brinkert and Chris-Kriton Skylaris: Chris, you are using Pt nanoparticles and Katherina, you are making Rh nanoparticles. A question to you both: Can your methodologies be adapted for alloys?

Chris-Kriton Skylaris communicated in reply: There is nothing to stop us from doing these calculations on alloys as DFT is generally applicable to any material and atom combination (it does not depend on empirical parameters that are atom-speci c). However, the real difficulty is the huge number of combinations of atoms that one would have to study to obtain representative structures and

compositions of nanoalloys. So this would require combining DFT with experi-mental input and/or other types of simulation methods such as kinetic monte carlo (KMC) which could lead to the correct thermodynamic ensemble of alloy structures.

Katharina Brinkert responded: Yes, this is possible.

Christopher Hardacre opened discussion of Paul Sermon's paper: You have shown that these new materials are pretty active, what role is the support playing in the catalysis and, in particular, what is the role of the surface hydroxyls?

Paul Sermon replied: We chose AlOOH as a support because it could be synthesised through colloidal routes, was rich in surface OH groups[1] and allowed cation insertion.[2] Hydrogen bonding between the surface OH groups on AlOOH and the perovskite precursors is likely to be critical. Cation insertion may result in perovskite domain (e.g. LaAlO$_3$[3]) formation, which would enhance the catalyst stability and we expected support-active site interactions to be very important. Fig. 8 suggests that this is the case. However, the precise nature of the 'chemical glue'[4] linking the active site and the support remains to be de ned.

1 Z. Yan, Z. Xu, J. Yu and M. Jaroniec, J. Colloid Interface Sci., 2017, 501, 164–174.
2 S. S. C. Pushparaj, et al., Inorg. Chem., 2016, 55, 9306–9315.
3 Z. Q. Tian, W. J. Huang and Y. J. Liang, Ceramics International, 2009, 35, 661–664.
4 G. C. Bond, Surf. Sci., 1985, 156, 966–981.

Justin Hargreaves said: In your presentation you referred to some materials derived using biological sources. Please can you expand some more upon the interest in these and also please can you describe the preparation routes employed?

Paul Sermon responded: We have known for 10 years[1] that biotemplates could be overcoated with TiO$_2$ using surface treatment with titanium isopropoxide in solution or in the gas phase. We knew that these were effective biomimetic TiO$_2$-based photocatalysts a er calcination removed the biotemplate. We thought that the structure and microstructure of the TiO$_2$ replica was important,[2] but also recognized that CaTiO$_3$ perovskite might be formed if the Ca^{2+} content of the biotemplate was high or intentionally raised and the temperature of biotemplate removal was high, leaving a nanotextured TiO$_2$-replica. In addition, the assembly of perovskites on so templates is known.[3]

1 Y. Cheng, L. Courtney and P. A. Sermon, in Developments in Porous, Biological and Geo-polymer Ceramics, ed. M. Brito et al., Wiley, 2008, vol. 28, pp. 209–218.
2 I. A. J. Al-Timimi, U. K. Onwukwe, M. P. Worsley and P. A. Sermon, Proc. SPIE, 2016, 9928, 99280E.
3 A. J. Baca, M. J. Roberts, J. Stenger-Smith and L. Baldwin, Nanotechnol., 2018, 29, 255301.

Christopher Hardacre enquired: What are the challenges in developing the bio-derived catalysts into a scaled up system?

Paul Sermon replied: Biotemplated perovskites are known.[1] Biomimetic perovskites (e.g. grown on viruses[2]) are rare. Our biotemplated preparation is relatively slow if the biotemplate is a spore that has to be harvested, but easier and faster if the biotemplate is a leaf of e.g. Rotala rotundifolia. In addition we are nanoengineering biomimicking hydrophilic/hydrophobic templates for perov-skites and their preparation/production is very fast. So there are ways of scaling up and accelerating the routes to biomimetic perovskites.

1 D. H. Kim, B. Dudem, J. W. Jung and J. S. Yu, ACS Appl. Mater. Interf., 2018, 10, 13113–13123.
2 N. Nuraje, et al., Adv. Mater., 2012, 24, 2885–2889.

Julien Marbaix opened discussion of the paper by Andrea Russell by asking: You tried several characterization methods for the same sample and you got slightly different results. Did you try to understand why, and then to identify one characterization method as being the best one?

Andrea Russell communicated in reply: Each of the techniques provides a different view of the samples, weighting by atom, crystalline fraction, or having a different surface sensitivity, so no one method is really 'better' than the rest. However, if I could only use one, I'd probably select XAS, as this provides me the average oxidation state and local coordination, and I can calculate a lattice parameter from the results.

Carlo Lamberti commented: I really appreciated the comparison that you have reported among the different characterization techniques, showing that, although the trend is con rmed by all techniques, there is a quite large relative disagreement among the quantitative response of each single technique. This comparison is very instructive and tells us that care must be taken when we try to extract quantitative numbers using a single technique only. In my opinion, it would be of interest to try to report for all those values an estimated error bar; in such a way we can realize that the data are consistent within the relative errors, or that they are not, meaning that there is some relative bias among the different techniques.

Andrea Russell responded: Thank you for this question. The point behind our paper was to illustrate that the various characterisation techniques all have their own bias and that this skews the result when you are trying to determine the extent of alloying (or even the mean particle size), with the greatest differences being between a surface sensitive measurement such as XPS and a per atom weighted method such as the XANES. The errors are approximately 20% of the calculated value for the $J_{Pt–Sn}$ from EXAFS as the coordination numbers are coupled to the Debye–Waller term in the EXAFS analysis and are thus less precisely known. When using the lattice parameters from EXAFS and XRD, the calculated error is approximately 10% of the value, but in this case the assumption that Vegard's law is appropriate for nanoparticles must be kept in mind and we argue that it may not be correct. When using the XPS data, the peak areas for the Sn(IV) and Sn(0) species are considered and a lineshape assumed during the tting. An error estimate here would also be approximately 10% of

the value. Thus, even when the inherent error of each method is considered, the values for the extent of alloying shown in table 3 do not agree within the errors for any of the samples. The different values obtained are more a reflection of the bias of each characterisation technique and direct comparison of the absolute values of extent of alloying is less appropriate than a comparison of the trend across the set of samples.

Bruce Gates said: If you look at the old literature of supported bimetallics in which one metal is noble and the other is oxophilic you find models showing the oxophilic metal concentrated at the metal-support interface and present as positively charged species. Thus, one might expect particle size effects with smaller particles to be stabilized more by cationic tin at the metal-support interface. Is this simple model in accord with your data?

Andrea Russell replied: Yes, this model is in agreement with our results. The sample treated in air has the smallest average particle diameter, 3 nm, and the greatest fraction of Sn(IV), whilst that treated in hydrogen has the largest average particle diameter, 6 nm, and the smallest fraction of Sn(IV).

Jennifer Peron asked: Did you look at the XPS spectra of Pt and were there any differences between the particles calcined under different atmospheres? Did you perform stability studies and compare the degradation rate of the catalysts when calcinated under air, Ar or hydrogen?

Andrea Russell responded: Yes, we have also examined the Pt 4f spectra, which are shown in Fig. 1. These show similar Pt oxidation states for all three samples. The Pt 4f spectra were deconvoluted into Pt0 and Pt oxides. Apart from the air sample, which has a little more oxide than the others, the Ar and the H_2 sample show no significant difference in the Pt chemical environment. We have not examined the stability or degradation of this particular set of electrocatalysts, but have published another study of PtSn electrocatalysts where this was a feature of the work.[1]

1 L. Calvillo, L. Mendez De Leo, S. J. Thompson, S. W. T. Price, E. J. Calvo and A. E. Russell, J. Electroanal. Chem., 2018, 819, 136–144.

James Walker said: My question refers to the XPS peak component assignment in Fig. 4. In terms of nomenclature, could you please clarify reference to 'Sn 0' as well as 'Sn metal?' Could you also please comment on the origin of the 3/2 loss feature, and its peak position and magnitude.

Andrea Russell responded: I will pass this question on to one of my co-authors, Haoliang Huang.

Haoliang Huang communicated in reply: Thank you for your question. In Fig. 4, Sn 3d spectra were deconvoluted by oxidation state into Sn(0), Sn(4+) and the loss feature of Sn(0). The Sn(0) in this case is referred to the metallic Sn alloyed with Pt. The loss feature, also called Plasmon loss, originates from the interaction of photoelectrons with the oscillations of conduction electrons. This interaction
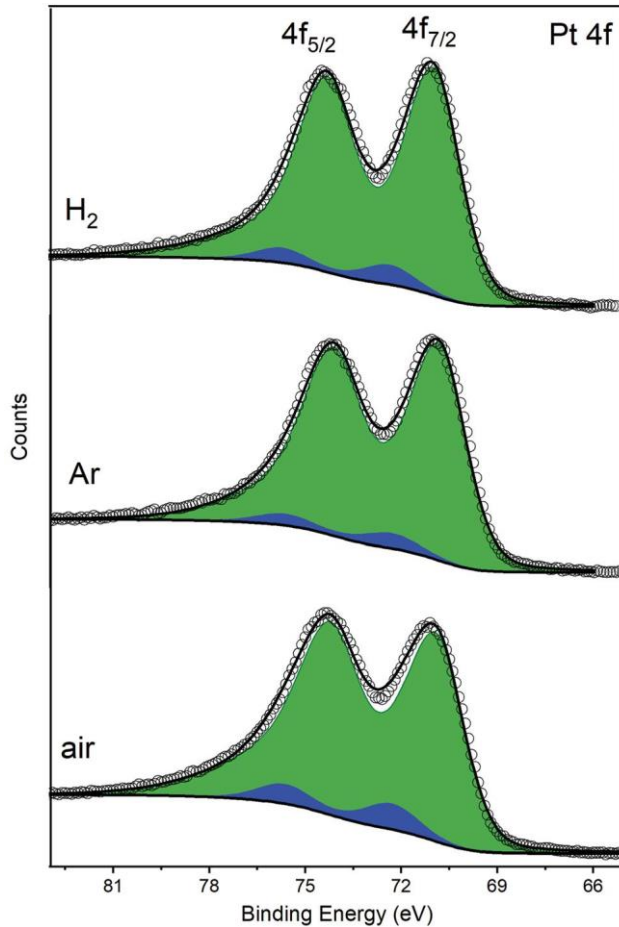
Fig. 1 Pt 4f spectra of samples synthesized under H_2/N_2, Ar or air. Peak convolution shown corresponding to Pt0 (green) and Pt oxides (blues).

may lower the kinetic energy of the photoelectrons, which concomitantly increases the apparent binding energy. In this study, the peak position of the loss feature was consistent for all samples, and the peak areas were kept proportional to those of Sn(0).

Maurits Boeije enquired: It was mentioned that the crystal structure of Pt and Pt_3Sn cannot be compared because the crystal structure is different. While this is formally the case, the crystal structure of Pt_3Sn is an ordered substitution of Pt, breaking the symmetry only because of the presence of two atomic species. Now that we can take this as a starting point, the relevant question becomes: is Sn homogeneously distributed in the nanoparticle or is it segregated (to the surface or the core), something that is expected in bulk (because Pt_3Sn is a line compound)? The PXRD patterns clearly show a change in the unit cell, something that is reected in the other measurements. It could be a sign of off-stoichometry, but it could also be a result of another effect.

Andrea Russell replied: We have not analysed these data in terms of a core-shell structure, as we had no other evidence from EELS or EDX mapping that suggested a core-shell structure. In the presence of air or at electrode potentials where the Sn is oxidised Sn will be drawn out of the nanoparticle. Thus, it is very likely that the surfaces of the particles are enriched in Sn.

Stanley Lai addressed Andrea Russell: As you mention, Pt_3Sn systems have been studied extensively in the electrocatalytic literature, with a wide spread of ndings. This spread does not only pertain to the activity, but also to the selec-tivity of such electrocatalysts. In the present study, have you also looked at vari-ations in selectivity for different pre-treated catalysts, for example in aldehyde vs. carboxylic acid formation, as well as the ability of the catalysts to break the carbon-carbon bond in ethanol and butanol?

Andrea Russell responded: You are indeed correct that the Pt_3Sn system is very well studied in the electrocatalysis literature. In designing this study we had intended to be able to look at the product distribution of the partial oxidation products, but unfortunately we have been unsuccessful in getting the DEMS (differential electrochemical mass spectrometry) system to work for alcohols beyond methanol at this stage. This is certainly a study worth doing and this set of sample treatments looks to provide an interesting set of electrocatalysts.

Christopher Hardacre commented in response: We have not looked at the effect of pre-treatment on the selectivity but have looked at a range of catalyst compositions. Bimetallic and trimetallic Pt-based systems have the ability to break the C–C bond but they also form the acid. We have not seen much evidence for aldehyde formation.

Roy Johnston said: I am confused by the statement at the top of page 8, to the effect that the Sn^0/Sn^{IV} ratio (11 : 1) is likely to be an overestimate. If the binding energy of Sn(II) is very similar to that of Sn(IV) (as stated in the next sentence), this implies that the Sn(IV) concentration may be overestimated, so the reported Sn^0/Sn^{IV} ratio is likely to be an underestimate, rather than an overestimate. Is there a typographical error somewhere, or have I misinterpreted the argument?

Andrea Russell responded: I will pass this question on to one of my co-authors, Haoliang Huang.

Haoliang Huang replied: The Sn(II) peak energy is actually very similar to that of both Sn(0) and (IV), which we agree is not as clearly stated in the manuscript as it could have been. According to a database provided by Thermo Scienti c, the gap in the binding energy between Sn(II) and Sn(0) is 0.8 eV and that between Sn(II) and Sn(IV) is 1.0 eV. Even though Sn(II) cannot be resolved from the other two oxidation states, the existence of Sn(II) overlaps more closely with the Sn(0) feature than that of Sn(IV), causing an overestimate of the former. This differential overestimate is exaggerated in the H_2 sample, due to the actual high proportion of Sn(0) and the asymmetric line shape of Sn(0).

Shaoliang Guan asked: The metal reference used for XANES measurements is very important. What's the difference between using metal foil and metal nano-particles as references? Is it always correct to use metal foil to compare with the presence of metal zero state in the nanoparticle system?

Andrea Russell responded: For the zero oxidation a metal foil is normally used as the fraction of atoms on the surface of the foil is small, so we're sure that any oxidation of the surface of the foil is not making a contribution. This works well if you are only comparing the position of the absorption edge, with the position shi ing linearly with oxidation state. However, in the analysis presented in Fig. 4, we were tting the edge shape as a linear combination of the two references. In this case the increase in the whiteline observed for a nanoparticle sample compared to the foil comes into play. Thus, we have shown two ts, one using the foil and a second using the Pt_3Sn/C catalyst with the data collected under H_2 to ensure complete reduction of the residual surface oxide. We'd argue that in the case where there is a signi cant whiteline, it may be more appropriate to use a nanoparticle reference for the zero oxidation state.

Graham Hutchings enquired: The SnPt alloys are unstable on cycling at high potential. Is there a component that would improve stability? Would trimetallic nanoparticles be useful?

Andrea Russell replied: As discussed in the answer to surface segregation, Sn is easily oxidised and it will not be stable at high (positive) potentials and this is the reason PtSn catalysts are not used widely in commercial cells. Adding a third element may provide further stabilisation and adding Ru or Ir does seem to provide some bene t.

Alexis Bordet asked: Could you please comment on the in uence of the size of the nanoparticles on their ability to form alloys? For a given heat treatment and atmosphere, would you expect different alloying extents depending on the size of the nanoparticles considered?

Andrea Russell communicated in reply: Yes, you'd certainly expect a particle size effect on the alloy formation, with smaller particles being less likely to form the alloys. However, we did not explore this in any detail in this particular study.

Bruce Gates enquired: In the chemistry you described involving redox processes of the tin, do the nanoparticle morphologies change? Does the struc-ture of the metal-support interface change? Have you done microscopy to inves-tigate these issues?

Andrea Russell responded: We have not yet done any operando microscopic studies. However, the particles in this particular study are all rather large, 3–6 nm average diameter depending on annealing conditions, and it is less likely that they will undergo signi cant morphological change that would be observed for smaller nanoparticles.

Federico Spolaore asked: I would like to ask you whether you have tried to vary the size of the nanoparticles while keeping the ratio of Pt/Sn constant? Do you believe it's possible with the polyol method you used?

Andrea Russell replied: We haven't succeeded in signi cantly varying the particle size in the direction of smaller particles, <3 nm average particle diameter, whilst keeping the Pt : Sn ratio constant. As mentioned above, it is harder to keep the Sn in the particle as the diameter is decreased. As for the polyol method, I don't think it is particularly useful in terms of preparing very small PtSn particles.

Josh Davies asked: How reproducible are your catalysts and have you tested multiple batches with your characterisation methods? In your paper you use multiple characterisation methods which result in diﬀering percentages of alloys. In other questions it was stated that your catalysts are not hugely air stable. So, is it possible that the diﬀerences in the values found from the characterisation techniques are in part due to changes in your catalyst due to a lack of stability over time? Have you repeated any XPS or other techniques to see if there has now been a change in those percentage alloy values?

Andrea Russell responded: We have not repeated the XPS or other character-isation methods on the same set of samples over extended periods of time. However, the electrochemistry is reproducible for electrodes prepared from a batch of catalysts that have been sitting on the shelf for up to a year. So, I don't think the origins of the diﬀerences we've seen are due to lack of air stability for the samples at ambient temperature. The stability issues that I was highlighting earlier are really a lack of stability under operating conditions in the electro-chemical environment if the catalyst is subjected to high potentials, above 0.8 V, as the Sn is gradually stripped from the sample and winds up in solution.

Christopher Hardacre opened a general discussion of Paul Sermon's and Andrea Russell's papers: Carbon has been used as an electrocatalyst support extensively, what are the possibilities of using other more stable supports?

Paul Sermon communicated in reply: Our own work with Pt-Au nanoalloys used graphitic carbon supports,[1] where the particles were found predominantly at atomic steps, but we were worried about stability. We ought to be able to design mixed ionic-electronic conductivity (MIEC) perovskites[2] with graded function-ality[3] in core-shell structures.[4,5] Here the core could be the support, with the shell as the active site. Designing both together in one step would be elegant, especially if the two could communicate electronically-ionically.

1 K. A. Grant, K. M. Keryou and P. A. Sermon, Faraday Discuss., 2008, 138, 257–271.
2 C. Su, et al., ACS Catal., 2017, 7, 388–397.
3 V. Sadykov, et al., in Solid Oxide Fuel Cells 11 (SOFC-X1), ed. S. C. Singhal and H. Yokokawa, The Electrochemical Society, 2009, vol. 25, pp. 2403–2412.
4 W. Z. Li, et al., Energy Environ. Sci., 2018, 11, 286–293.
5 J. Li, et al., J. Power Sources, 2018, 379, 206–211.

Andrea Russell responded: This is certainly an area of considerable current interest with people looking into alternate carbides such as boron carbide,

tungsten carbide and silicon carbide, as well as particulate boron doped diamond as supports and even oxide supports such as reduced TiO_2. The idea is to main-tain electrical conductivity, whilst increasing the corrosion resistance of the support.

Nia Richards addressed Andrea Russell: In the introduction you state an average particle size of 3 nm but the image shown in Fig. 1c has a scale bar of 50 nm and what looks like larger particles, please could you explain how you came to this average particle size?

Andrea Russell replied: There is some agglomeration of individual nano-particles on the support. So, if you look at other images forming the clusters you'd see the individual particles and those images were used to determine the average particle diameter.

Graham Hutchings addressed Paul Sermon: There is a lot of interest in perovskites for catalysis at present, in particular in photocatalysis. Can you make high area perovskites (e.g. >100 m^2 g^{1}) and is it possible to put the small perovskite nanoparticles on a conducting support so they will be useful for electrocatalysis or photocatalysis.

Paul Sermon communicated in reply: Libby was working with $LaCoO_3$ of 1.4 m^2 g^{1}. Here in a TX100 mE we have produced 10–21 nm $LaCoO_3$ (LCO; density 7.29 g cm^{3}). As the average particle size of the LCO decreases from 1 mm to 100 nm to 10 nm to 5 nm its surface area increases from 0.8 to 8.2 to 82 and to 412 m^2 g^{1}. We probably have reached 100 m^2 g^{1}, but of course the stability of that active area is still of concern and production on a realistic scale/cost has to be worked on.[1] The design of mixed ionic-electronic conductivity perovskites is known[2] and nanoengineering graded perovskite functionality is now on the horizon. We have not yet put the perovskite nanoparticles on a conducting support, but we plan to.

1 Y. Pu, et al., Ind. Eng. Chem. Res., 2018, 57, 1790–1802.
2 C. Su, et al., ACS Catal., 2017, 7, 388–397.

Maurits Boeije commented: More information can be extracted from the PXRD pattern, separating the in uence of the alloying element and the lattice expan-sion. The substitution of Sn for Pt leads to a lowering of symmetry, giving rise to additional peaks in the diffractogram. The shi of the peaks from the original Pt positions will yield the change in unit cell. This can be caused by strain due to the particle–substrate interaction, the heat treatment (particularly the cooling phase) and the amount of alloying. To decouple these contributions, the shi in the peak positions can be compared to the increase in intensity of the extra peaks. The former is due to strain, the latter due to alloying.

Andrea Russell responded: You are most certainly correct that more could be done with the PXRD. However, in doing so the heterogeneity of this system needs to be kept in mind.

Mzamo Shozi addressed Andrea Russell: Would these Pt_3Sn catalysts be applicable for the electro-oxidation of larger compounds such as glycerol?

Andrea Russell answered: Yes.

Keith Whiston asked Andrea Russell: Much of your talk focused on the diffi-culty of consistently determining catalyst composition using different analytical techniques and the problem of catalyst stability in use during oxidation reactions for the Pt_3Sn system. Do you have any suggestions based on formulation or composition that might improve catalyst stability?

Andrea Russell responded: Sadly no. The PtSn system is inherently unstable at the higher electrode potentials. The source of that instability is intimately linked to the enhanced activity of the catalysts, as you need to activate water at lower potentials to prevent accumulation of the partial oxidation products on the surface of the nanoparticles. I really don't think that there is a magic solution to this problem. As in most studies of catalysts, activity and instability go hand in hand.

Shaoliang Guan addressed Andrea Russell: What do you think of the role of electrochemistry in catalysis? Can electrochemistry play a wider part other than in fuel cells?

Andrea Russell replied: Of course I think electrochemistry brings a lot to the table. Combining the approaches of heterogeneous (thermal) catalysis and elec-trocatalysis can bring great bene ts and electrosynthesis is a growing eld both for CO_2 reduction and for ammonia synthesis to name but two areas.

Julien Marbaix opened discussion of the concluding remarks by Cynthia Friend: You exposed very interesting complementary ways (experiment and simulation) to investigate catalysis. You mentioned as well support free catalysts, new tools etc. Don't you think sustainability should be a driving force for our research, especially a er the Paris agreements last year? Should we systematically add an environmental assessment (for example by implementing new technolo-gies in a Life Cycle Assessment) in the results of our research in order to highlight the potential of catalysis and make a bridge toward industry?

Cynthia Friend responded: This is an excellent point and should be considered as part of catalyst performance. This is an excellent topic for further discussion in the future.

Richard Catlow commented: I think you have made a most important point. Modelling and simulation has made huge progress but the eld now requires careful consideration to benchmarking of different computational methods, especially different types of DFT against agreed standards and against experi-ment. Such a development should be a high priority.

Jonathan Quinson added a comment: We agree that benchmarking is neces-sary and useful. Our group has developed over the years a 'toolbox' to perform systematic studies.[1] Within this research we realized that benchmarking is

indeed important but is a complex thing to do. It is not only the catalyst selection and the testing protocols that need to be taken into account for benchmarking. Intermediate steps also need to be 'standardized'. We found for instance that for home made catalysts the quality of thin lms required to be prepared before (electro)catalytic tests are key to ensure optimal measurements. The optimal results were obtained by adjusting the pH of the so called 'inks', but for a commercial catalyst this pH adjustment had no to little effect. Depending at which pH the ink preparation is made, the home made catalyst will perform better or worse than the benchmark.[2] Our research now focusses on developing an integrated toolbox in order to perform truly systematic studies and as reliable as possible benchmarking. This approach is time consuming but rewarding in terms of catalyst comparison and understanding.

1 J. Speder, L. Altmann, M. Roefzaad, M. Baumer, J. J. K. Kirkensgaard, K. Mortensen and M. Arenz, Phys. Chem. Chem. Phys., 2013, 15, 3602–3608.
2 M. Inaba, J. Quinson and M. Arenz, J. Power Sources, 2017, 353, 19–27.

Carlo Lamberti commented: The problem of understanding catalyst deacti-vation is relevant on both academic and industrial grounds. With a huge time effort it can be followed with laboratory techniques under operando conditions, but it is evident that this approach is not applicable at large scale facilities because a single group cannot obtain months of beamtime on a synchrotron or neutron source. Consequently, only work on spent catalysts[1] or the use of an accelerated deactivation process may be envisaged. These constrains may limit the information that can be extracted from such studies. In this regard I believe that the catalysis community (both academic and industrial) should make a joint effort to have somewhere, a catalysis dedicated beamline, where several catalysts can run in parallel out of the beam and every weak each of them will be measured for some hours. Obviously, a single group cannot afford such a huge investment, only an uni ed community perhaps can.

1 R. Pellegrini, G. Agostini, E. Groppo, A. Piovano, G. Leofanti and C. Lamberti, J. Catal., 2011, 280, 150–160.

Graham Hutchings responded: I agree that having access to a dedicated beamline for catalysis for the international community would be an ideal way to study catalyst deactivation amongst other key problems. It is something that we have been trying to advance in the UK through the UK Catalysis Hub.

Cynthia Friend commented: Having dedicated facilities for catalysis research is a good one; however, there are several different types of experiments required to advance the eld, including X-ray absorption (XANES, EXAFS), X-ray emission, photoelectron spectroscopy and X-ray imaging. It may be more bene cial to have access to several key facilities to take advantage of the breadth of tools needed.

Bruce Gates addressed Cynthia Friend: This question calls for speculation, but would you let us know what occurs to you as just emerging in a preliminary way from this Discussion that might provide ideas for topics for other Faraday Discussions, say, ve years from now?

Cynthia Friend responded: This is an excellent question and cause for thought. The nature of Faraday Discussions stimulates critical and open discussion that can guide a eld. There is currently considerable discussion about the use of "machine learning" methods in heterogeneous catalysis. This area needs de ni-tion and evaluation in the next few years to determine if data-driven research coupled with well-de ned experiments can yield new and improved catalytic processes, including new materials and de ned reaction conditions for speci c processes. Another emerging topic is the development of sophisticated and advanced experimental tools to de ne structure-reactivity relationships in catal-ysis. These new tools are also o en improved by combining with theory and new mathematical approaches for "on-the- y" analysis of data. I suggest that this could be combined with the topic of machine learning. Lastly, guiding new and advanced materials synthesis using machine learning and advanced character-ization would tie these topics together.

Conflicts of interest

Maurits Boeije declared that the presented data was obtained using a commercial product, produced by VSPARTICLE and the presenter is an employee of this company. There are no other con icts to declare.