Faraday Discussions

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Nanoalloy magnetic and optical properties, applications and structures: general discussion

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Magnetic and optical properties of nanoalloys, part 1

Ewald Janssens opened discussion of the paper by Rolf Schäfer: From the deflection profiles of the superatomically behaving MSn_{12} clusters, you find using eqn (6) in the paper (https://doi.org/10.1039/d2fd00091a) a *g*-factor of 2.6–2.7 for M = Al, Ga, In. This is more than the free electron value and also not the *g*-factor of the isolated dopant atoms. You write that these *g*-factors provide information about the orbital moment of the clusters. Can you comment on this? Is it possible to extract a value for the orbital moment from this result?

Rolf Schäfer answered: Following the perturbation theory approach outlined in the manuscript (https://doi.org/10.1039/d2fd00091a), deviations in the *g*-factor from the free electron value can mainly be traced back to a term that arises between the orbital-Zeeman interaction and the spin–orbit coupling (*cf.* eqn (4) in the manuscript). From this follows that pure spin magnetism in clusters will always yield a *g*-factor of (very close to) 2, since the orbital-Zeeman term vanishes. If, however, there are contributions from excited states involved that contribute with a nonzero orbital angular momentum (here referring to molecular orbitals with Sn 5p character), significant *g*-shifts can arise. The orbital part of the mean magnetic dipole moment can therefore be estimated from the shift in the *g*-factor with respect to the free electron value.

Ewald Janssens asked: To be able to see an atomic-like magnetic deflection behavior of clusters, the number of avoided crossings during the passage through the magnet should be small. This is a stringent condition and requires a low temperature and a high symmetric cluster (low density of rovibrational states). The spin 1/2 MSn_{12} clusters studied in this paper fulfill these conditions. Are there more clusters where you expect similar atomic-like behavior?

Rolf Schäfer responded: Critical to the observation of super-atomic behavior is the spin dynamics at avoided crossings. If the coupling between spin and rotation is low, *i.e.* the vast majority of avoided crossings would be traversed diabatically, the number of traversed avoided crossings can also be higher in order to still observe super-atomic behavior. This is the case, for example, with $MnSn_{12}$, which is an $S = 5/2$ spin system. However, there are limits to this, because the spin–rotation coupling never completely disappears and thus the spin dynamics will never be completely diabatic. Since the rotational density of states is inversely proportional to the rotational constant, studying clusters with lighter elements would automatically lead to fewer avoided crossings. Thus it would be conceivable that possibly doped carbon clusters show super-atomic behavior even if they are not spherical tops.

Joost M. Bakker enquired: If I understand it correctly, the lower density of rotational states for spherical tops leads to a lower number of avoided crossings and a higher chance to observe atomic-like deflection patterns rather than Brillouin-type ones. I wonder up to what limit this will hold, as for optimal separation one would want to ever increase the magnetic field gradient, but in the end one would always hit the point where rotational Zeeman-multiplets start crossing each other.

Rolf Schäfer replied: The rotational density of states is independent of the magnetic flux density. However, the deflection of the clusters increases linearly with the gradient of the magnetic field and thus also with the magnitude of the magnetic field itself. Thus, the number of avoided crossings increases linearly with the magnetic flux density. In practice, this means that one has to compromise the value of the magnetic flux density in order to separate the super-atomic clusters from the rest on the one hand and to avoid too many forbidden crossings on the other.

Piero Ferrari said: In your paper (**https://doi.org/10.1039/d2fd00091a**) it is discussed that there are two isomers in the molecular beam, one polar and one nonpolar. Moreover, it is mentioned that so far the geometry of the polar isomer is unknown. Are you planning future experiments in order to elucidate the geometry of the polar isomer?

Rolf Schäfer responded: Yes, we would like to do isomer selective spectroscopy in the future. For example, the super-atomic clusters could be separated with a Stern–Gerlach magnet. Since the magnetic deflection of these clusters is very large, the remaining part can easily be masked out with a ridge in the middle of the molecular beam. The UV-Vis spectrum of the super-atomic clusters could then be measured using depletion spectroscopy. Of course, the vibrational spectroscopic investigation would also be interesting.

Ewald Janssens questioned: In the outlook of the manuscript (**https://doi.org/10.1039/d2fd00091a**) you propose to select one superatomic component after the Stern–Gerlach magnet and perform absorption spectroscopy on this component. That is a very interesting proposal to perform isomer selective investigations of clusters on the fly. But will this experiment not be very time consuming in view of the low amount of clusters in a magnetic deflection experiment? In a deflection experiment the molecular beam must be cut to a narrow slice to be able to detect the deflection, throwing away more than 90% of the produced clusters.

Rolf Schäfer replied: The Stern–Gerlach experiments show that about 40% of the clusters behave super-atomically. Since the magnetic deflection of these clusters is very large, the remaining part can easily be masked out using a ridge located in the middle of the molecular beam. This should make it possible to examine the super-atomic component optically. It is much more difficult to observe the polar isomer spectroscopically, since its proportion is only about 20% and the polar isomer does not differ magnetically from vibrationally excited non-polar clusters. Here, an electric field would have to be used for isomer separation. The polar component would then be enriched in the shoulder in the direction of increasing field gradient, so that in fact only about 10% of the molecular beam is available for the spectroscopic investigations.

Michael Bowker opened discussion of the paper by Joost M. Bakker: What is the source of the carbon. Does it come from the source material or reactions in the gas phase, and if the latter is it from residual pump oil in the vacuum system? Is the electron delocalised in the Cu_6 carbon cluster? What is ‘magic’ about the 6 cluster compared with the Cu_7 cluster, for instance.

Joost M. Bakker responded: We do not know the source of the carbon. We varied the purity of the helium carrier gas, and did intensive leak checking of the carrier gas inlet system, but to no avail. We suspect it could be from residual pump oil of the roughing pumps, but it may also come from a contamination of the copper target. Whether the contamination is a gas phase reaction is also difficult to say, but because the bond strength between Cu and C is significantly larger than between Cu and Cu, we suspect that the seed for cluster formation is a Cu–C dimer.

We do not know why the Cu_6C cluster is less efficient than Cu_7C. Such odd/even effects have been observed for reactions involving other clusters. We could speculate that the closed shell nature of Cu_7C versus the open shell nature of Cu_6C may play a role, but this is not more than that: speculation.

Yufei Zhang asked: Thank you for your presentation; my question is that you mentioned the carbon contamination on copper anion clusters, what about the contamination on cationic clusters? Also I want to know whether the charge state of the cluster will affect the reactivity against CO_2 because in your manuscript (**https://doi.org/10.1039/d2fd00128d**) you mentioned that the higher carbon-to-metal ratios can reduce the copper cluster's ability to donate electron density to CO_2.

Joost M. Bakker answered: For cationic copper clusters contamination is much lower, and dominated by CuO clusters, which we attribute to residual water in the vacuum chamber, or to trace oxygen in the helium carrier gas. We are able to reduce such contaminations by baking the gas lines going into the pulsed valve of the ablation source.

The charge state is a very important factor in CO_2 activation. It is well-known that donating electron density into the 2π LUMO leads to a bending of the CO_2 molecule, which gains anionic character (see *e.g.* ref. 1). The limited previous work on clusters and ions has shown that only the anionic species are able to activate or dissociate CO_2.[2–4]

1 H.-J. Freund and M. W. Roberts, *Surf. Sci. Rep.*, 1996, **25**, 225–273, DOI: **10.1016/S0167-5729(96)00007-6**.

2 J. M. Weber, *Int. Rev. Phys. Chem.*, 2014, **33**, 489–519, DOI: **10.1080/0144235X.2014.969554**.

3 A. Yanagimachi, K. Koyasu, D. Y. Valdivielso, S. Gewinner, W. Schöllkopf, A. Fielicke and T. Tsukuda, *J. Phys. Chem. C*, 2016, **120**, 14209–14215, DOI: **10.1021/acs.jpcc.6b04360**.

4 A. E. Green, J. Justen, W. Schöllkopf, A. S. Gentleman, A. Fielicke and S. R. Mackenzie, *Angew. Chem., Int. Ed.*, 2018, **57**, 14822–14826, DOI: **10.1002/anie.201809099**.

Alessandro Fortunelli enquired: Nice work. Many years ago we studied the catalytic transformation of CO_2 on Ni_3 and Ni_2Cu (supported on MgO, but also in the gas phase; partially published in ref. 1) finding that these bare clusters were able to dissociate CO_2. Did you consider doping Cu clusters with these more active metals?

Also, we observed interesting non-linear effects due to co-adsorption of H_2 and CO_2, as reducing and oxidizing agents, respectively; did you consider H_2 and CO_2 co-adsorption?

1 L. Sementa, F. R. Negreiros and A. Fortunelli, The use of hydrogen in ammonia synthesis, and in oxygen and carbon dioxide catalytic reduction – the reaction mechanisms, in *Utilization of Hydrogen for Sustainable Energy and Fuels*, ed. M. Van de Voorde, De Gruyter, Berlin, Boston, 2021, ch. 6, vol. 3, pp. 269–302, DOI: **10.1515/9783110596274-014**.

Joost M. Bakker responded: Yes, this is what we plan to do next. We have commissioned a new dual-target dual-laser cluster source based on the KU Leuven design,[1] and are planning to study the activation of cationic Cu clusters doped with 3d elements.

For cationic, pure copper clusters, we studied both the adsorption of H_2 (dominant H_2 dissociative adsorption)[2] and of CO_2 (physisorption) and co-adsorption of H_2 and CO_2 onto cationic copper clusters.[3] For the latter, we saw no synergistic effects, so only a “sum” of the spectra of the individual adsorptions. However, the accompanying DFT calculations suggested that the reduction of CO_2 to formate would have been thermodynamically feasible. We think that the reaction is kinetically hindered by thermalizing collisions with the helium bath, and that the final barrier (still below the energy of the reactants but on the order of 1 eV) could not be overcome.

We recently observed the direct influence of the helium bath in these experiments when we observed the double dehydrogenation of two methane molecules by Pt^+ forming $Pt^+C_2H_4$ in the much lower pressure environment of an ion trap,[4] whereas the reaction was throttled, leading to the formation of $Pt^+(CH_3)_2$,[5] in the experimental instrument with which we studied the co-adsorption of CO_2 and H_2 on cationic copper clusters.

1 W. Bouwen, P. Thoen, F. Vanhoutte, S. Bouckaert, F. Despa, H. Weidele, R. E. Silverans and P. Lievens, *Rev. Sci. Instrum.*, 2000, **71**, 54–58, DOI: 10.1063/1.1150159.
2 O. V. Lushchikova, H. Tahmasbi, S. Reijmer, R. Platte, J. Meyer and J. M. Bakker, *J. Phys. Chem. A*, 2021, **125**, 2836–2848, DOI: 10.1021/acs.jpca.0c11527.
3 O. V. Lushchikova, M. Szalay, H. Tahmasbi, L. B. F. Juurlink, J. Meyer, T. Höltzl and J. M. Bakker, *Phys. Chem. Chem. Phys.*, 2021, **23**, 26661–26673, DOI: 10.1039/d1cp03119h.
4 F. J. Wensink, N. Roos, J. M. Bakker and P. B. Armentrout, *Inorg. Chem.*, 2022, **61**, 11252–11260, DOI: 10.1021/acs.inorgchem.2c01328.
5 O. W. Wheeler, M. Salem, A. Gao, J. M. Bakker and P. B. Armentrout, *J. Phys. Chem. A*, 2016, **120**, 6216–6227, DOI: 10.1021/acs.jpca.6b05361.

John McGrady asked: You noted in your talk some significant discrepancies between experiment and theory, and that there were a number of factors that determined the intensity of the measured bands. For this technique, is there a direct correlation between the transition dipole intensities that we can compute using DFT and the measured intensity?

Joost M. Bakker answered: In the technique used, IR multiple-photon dissociation (IR-MPD) spectroscopy, we resonantly pump a vibrational mode. Absorption of one photon is not enough to induce dissociation, so for the mode to accept photons again, the energy of the photon absorbed needs to be dissipated by the bath of vibrational states through intramolecular vibrational redistribution. In general, the dissociation yield, or the depletion yield, used in this study tends to scale linearly with laser power once a certain threshold is overcome, for the excitation efficiency to be enough to induce dissociation. Unfortunately, this threshold is different per mode, as it depends on the mode's anharmonicity and absorption cross-section. The intensities in the IR-MPD spectrum therefore do not necessarily correspond one-on-one with those of the (calculated) linear absorption spectrum. However, a large body of work on IR-MPD spectroscopy shows that the comparison between an IR-MPD spectrum and a calculated linear absorption spectrum allows for unique identification of a molecule's structure.

Yufei Zhang enquired: My second question is about the argon attachment, you mentioned the argon attachment on the copper clusters, so in this experiment, did you use argon to obtain the IR-MPD spectra? And will the argon attachment affect the IR feature on the spectra or even the reaction between Cu clusters and CO_2.

Joost M. Bakker replied: I showed an example of argon atoms binding to cationic Cu clusters, but we did not use argon in this experiment. The example was taken to illustrate the principle of IR action spectroscopy, and originates from our earlier study trying to assess the structures of cationic Cu clusters.[1] We there use DFT to show how the spectrum of the bare copper cluster is modified by the presence of the argon atoms. I doubt that the presence of argon atoms would affect the current reactivity towards CO_2. For copper cations, where CO_2 only physisorbs, the binding energy of Ar atoms is comparable to that of CO_2, on the order of 0.5 eV,[2] but for anionic clusters the binding to Ar is much weaker, for instance calculated to be 0.05 eV for the Cu–Ar complex.[3]

1 O. V. Lushchikova, D. M. M. Huitema, P. López-Tarifa, L. Visscher, Z. Jamshidi and J. M. Bakker, *J. Phys. Chem. Lett.*, 2019, **10**, 2151–2155, DOI: **10.1021/acs.jpclett.9b00539**.
2 O. V. Lushchikova, M. Szalay, H. Tahmasbi, L. B. F. Juurlink, J. Meyer, T. Höltzl and J. M. Bakker, *Phys. Chem. Chem. Phys.*, 2021, **23**, 26661–26673, DOI: **10.1039/d1cp03119h**.
3 X.-F. Tong, C.-L. Yang, M.-S. Wang, X.-G. Ma and D.-H. Wang, *J. Chem. Phys.*, 2011, **134**, 024306, DOI: **10.1063/1.3526955**.

Fuyi Chen communicated: The $Cu_nC_m^-$ cluster studied in this paper has n values between 3–10 and m values between 1–2. Is this carbon-doped copper cluster stable in the experimental environment? If some parameters of the experiment in Fig. 1 in the paper (**https://doi.org/10.1039/d2fd00128d**) are changed, will the m value of the $Cu_nC_m^-$ clusters of the product be affected, such as the formation of complexes with $n > 10$, or are the m and n values of the clusters generated within a range of experimental parameters similar?

Joost M. Bakker communicated in reply: In the experiment, the carbon doped cluster is stable at least over the experimental time window of approximately 100 ms, but we do not doubt it is stable over longer times (in vacuum).The second question is a bit more difficult to answer, but in general terms the distributions formed in laser ablation cluster synthesis can be quite sensitive to the transient pressure in the clustering formation chamber, and thus to relative timings of the ablation laser and the opening of the valve, and the sampling of the formed distribution with the mass spectrometer.

Christine Mottet opened discussion of the paper by Piero Ferrari: My question concerns the theoretical part, in particular the DFT calculations: how is the microcanonical temperature of the cluster taken into account in the TD-DFT calculation, before the photon emission and electronic transition? What kind of thermodynamic equilibrium do you consider?

Piero Ferrari responded: The TD-DFT calculations are performed at 0 K. Only as an illustration of the effect doping has in the radiative cooling of the clusters, we selected the ground-state geometries of the clusters and performed calculations of the electronic transitions using TD-DFT. We believe that this limitation in the computational approach is one of the reasons why the computations are not in good agreement with the experimental results.

Alessandro Fortunelli asked: Nice work. It seems to me that you get the highest radiative rates for Au_{13}: do you have an explanation for this observation?

As a comment, the atomistic and electronic structure of small Au clusters is difficult to predict at the DFT level, and especially for the response, hybrid exchange–correlation functionals should be used, which may explain part of the inconsistencies between experimental and the theoretical simulations.

Piero Ferrari replied: The highest radiation rate of $Au_{13}{}^{+}$ can be partially explained by the subshell closed electronic configuration of the cluster. This means that $Au_{13}{}^{+}$ has a higher dissociation energy than its closer neighbors in size, with the consequence that the cluster is hotter in the molecular beam. Therefore, it is expected a higher radiation rate. Nevertheless, this is not the full story, since the electronic structure of the cluster also plays a role. As you correctly mention, calculations of excited electronic states are difficult, in particular for an element such as gold. Uncertainties in these calculations are certainly part of the disagreement between our experiments and the computational modelling.

Christian Kuttner questioned: Looking at experimental radiation rates (Fig. 5 in the paper; **https://doi.org/10.1039/d2fd00090c**), why does Ag doping almost always result in higher rates than Pd doping? Can this be explained?

Piero Ferrari responded: We are not certain about the explanation for this observation, partly because our calculations cannot grasp all features of the experimental results. One possibility is that Ag doping enhances the overall stability of the clusters. This means increasing the dissociation energy of the monometallic Au clusters, so that the doped species are hotter in the ensemble at the moment of photon emission. The opposite could occur by Pd doping: a decrease in dissociation energies. Another possibility is that Ag doping decreases the energy of the lowest electronic transitions, while Pd doping pushes them up in energy. Further investigation is needed to explain this interesting observation.

Fuyi Chen enquired: This work has investigated the effect of single Ag or Pd atom doping on the radiative cooling of $Au_{n}{}^{+}$ clusters, in the $n = 11–15$ size range. For $AgAu_{n-1}{}^{+}$ or $PdAu_{n-1}{}^{+}$ clusters, will the charge transfer between metal atoms affect the radiative cooling process in different alloy systems? Have you considered the correlation between electronic structure and radiative cooling channel?

Piero Ferrari answered: The main point of the work is the correlation between the electronic structure of the clusters and their radiative cooling. The rate of recurrent fluorescence, the process we believe is responsible for the observed radiation, depends drastically on the energy of the electronic transitions involved in the photon emission. Therefore, processes like charge transfers induced by adding dopant elements to the clusters will certainly affect their cooling *via* radiation. This is explicitly shown in Fig. 6 of our paper (**https://doi.org/10.1039/d2fd00090c**).

Robert M. Jones asked: Thank you for the talk. Is there any physical motivation behind applying a Gaussian broadening on your reported spectra? And have the parameters for this been selected in a way to ensure that no spectral features are smoothed over?

Piero Ferrari replied: The selection of Gaussians is just for visualization purposes. Regarding the second question; in the revised version of the manuscript, the width of the Gaussians will be reduced so that all features are clearly visible in the plot.

Christian Kuttner communicated: At the end, you stated that the relaxation process cannot yet be fully understood. Could you please elaborate on the mechanistic questions that are still open and indicate what is needed (experimentally) to answer them?

Piero Ferrari communicated in reply: The main point we believe is responsible for the disagreements between experiment and theory is the fact that at the moment of photon emission the clusters have a high temperature, even in the order of thousands of kelvin (depending on the species). Most computational studies, in contrast, calculate electronic excited states assuming the ground-state geometry, which is most probably different from the fluctional geometries of the real clusters when emitting photons. Therefore, from a computational point of view, it is important to consider the dynamics of the clusters due to temperature. Another possibility to explain the disagreements, however, is that time-dependent DFT cannot predict well the low-lying electronic transitions from which photons are being emitted. From an experimental point of view, is important to directly detect the photons emitted by the bimetallic clusters, and conduct precise spectroscopy on them. This will allow understanding much more in detail the nature of the photon emission process, and the role played by doping.

Wolfgang E. Ernst opened a general discussion : Exploring the magnetic properties of nanoparticles after deposition on a substrate and comparison with those in the cluster beam will be interesting. We have unfortunately not been successful with our attempts to measure magnetism of deposited particles in the SQUID facility in Graz. Have there been successful measurements of this kind with other means?

Rolf Schäfer responded: Some people are studying the magnetic properties of mass-selected clusters on surfaces using X-ray magnetic circular dichroism spectroscopy (see for example ref. 1).

1 M. Martins and W. Wurth, Magnetic properties of supported metal atoms and clusters, *J. Phys.: Condens. Matter*, 2016, **28**, 503002.

Francesca Baletto said: I have a general question on the experimental evidence of the so-called "super-atoms" and how such an idea/model couples with the structural and chemical fluxionality observed in nanoalloys.

Rolf Schäfer replied: Super-atomic behavior is observed in Stern–Gerlach experiments when the original cluster beam is split into several beamlets. For each of these beamlets the projection of the magnetic dipole moment on the direction of the magnetic field is a constant of motion. This behavior is only observed if either the coupling between spin and cluster rotation is vanishingly small or if no avoided crossings are traversed in the rotational Zeeman diagram. The latter is very unlikely for thermally excited nanoalloys, *i.e.* flexible non-rigid clusters, since the number of traversed avoided crossings, when passing through the magnetic deflector, increases sharply with vibrational excitation. In contrast, a very specific chemical composition of the nanoalloy cluster is usually necessary to observe super-atomic behavior, especially when highly symmetrical structures are associated with it, because then the density of avoided crossings is significantly reduced.

Miguel Jose Yacaman answered: This is a key point. Most of the experimental evidence for super-atoms is obtained by X-ray diffraction of cluster crystals. That represents a spatial and temporal average of the structure. One of the ways to proceed is to use nano-beam diffraction of individual clusters. This will allow detecting any structural changes. The other option will be to use a free electron laser to diffract individual clusters.

Joost M. Bakker enquired: I would be curious to know whether there exists experimental information comparing the structural and/or catalytic activity differences between on the one hand clusters synthesized with protective ligands that are deposited on a surface and subsequently stripped of the ligands, and on the other hand clusters generated using physical methods such as laser ablation or sputtering followed by aggregation in an inert gas.

Noelia Barrabés responded: As far as I know, I am not aware of such a study, although I think it will be very interesting.

Miguel Jose Yacaman replied: There are few reports of the catalytic activity of ligand protected clusters as this would be a serious challenge. In addition most catalytic reactions occur at temperatures in which the ligand is not stable. Therefore I think we should not expect catalytic activity of ligand protected clusters.

Wolfgang E. Ernst responded: Unfortunately I have not found any such comparative measurements. It seems to me that up to now, there have been almost two separate communities that either produce the particles naked and are closer to physics or come from a chemistry route involving different cluster generation. It is important to have such comparisons!

Applications of nanoalloys

Riccardo Ferrando opened discussion of the paper by Vincenzo Amendola: Can you comment on the ability of laser ablation in liquids to synthesise different sizes of nanoparticles and to control size dispersion?

Vincenzo Amendola replied: Laser ablation in liquids (LAL) does not allow the control of nanoparticle size, which can be performed only by post-synthesis procedures. When the nanoparticles are stably dispersed in the liquid solution, one can use a sedimentation-based separation protocol to select some specific size ranges through their different sedimentation speed.[1–3] Alternatively, the whole mass of nanoparticles obtained by LAL can be reduced in size, with a consequent decrease in polydispersity, by laser fragmentation in liquid (LFL), where a laser pulse is directed into the colloid to photofragment the pristine nanoparticles.[1,2] A procedure to increase the size of the nanoparticles, after their controlled aggregation into larger agglomerates, has been also developed, which is called laser melting in liquid (LML).[2,3] LML is performed with lower laser fluence than LFL and is best suited to achieve submicrometric particles.[3]

1 F. Bonaccorso, M. Zerbetto, A. C. Ferrari and V. Amendola, *J. Phys. Chem. C*, 2013, **117**, 13217–13229.
2 V. Amendola and M. Meneghetti, *J. Mater. Chem.*, 2007, **17**, 4705–4710.
3 V. Amendola, D. Amans, Y. Ishikawa, N. Koshizaki, S. Scirè, G. Compagnini, S. Reichenberger and S. Barcikowski, *Chem.–Eur. J.*, 2020, **26**, 9206.

Stephan Barcikowski added: There are variants of laser synthesis, which give access to different size ranges, namely LAL (5–10 nm), LFL (<5 nm) and LML (100–300 nm). Laser ablation of alloys in liquids does not provide a size-tunability equivalent to wet chemical synthesis, unless you want to employ ligands (then, SAW strategies can be used). At least, monomodal particles result if nanosecond laser pulses are used, and using micromolar anions, monodisperse quality is achievable (for noble metals). For accessible size ranges and dispersion, please see ref 1, which is a comprehensive review article. For LFL, sub-nanometer (!) size resolution has recently been shown, in combination with fractionation, still ligand-free.[2]

1 D. Zhang, B. Gökce and S. Barcikowski, *Chem. Rev.*, 2017, **117**, 3990–4103, DOI: 10.1021/acs.chemrev.6b00468.
2 A. R. Ziefuss, T. Steenbock, D. Benner, A. Plech, J. Göttlicher, M. Teubner, B. Grimm-Lebsanft, C. Rehbock, C. Comby-Zerbino, R. Antoine, D. Amans, I. Chakraborty, G. Bester, M. Nachev, B. Sures, M. Rübhausen, W. J. Parak and S. Barcikowski, *Adv. Mater.*, 2021, **33**, 2101549, DOI: 10.1002/adma.202101549.

Didier Grandjean asked: Do you have more information on the mechanism of nucleation and stabilisation of these clusters produced in liquid by laser ablation of a bulk Au–Fe target? Would you expect Au to oxidise Fe which could be a problem in solution? Do you have more insight on the charge transfer between Fe and Au in the nanoparticle and how it could lead to its degradation by a type of galvanic replacement?

Vincenzo Amendola responded: Thank you for your question. In our synthesis by laser ablation in liquid (LAL) we start from a metallic Au–Fe alloy target to generate Au–Fe alloy nanoparticles.[1] We have always observed that the fraction of Fe in the nanoparticles is lower than in the target, meaning that part of the iron is lost.[1,2] We hypothesized that, in our experimental conditions using nanosecond laser pulses, this is due to the immiscibility of iron with gold and to its strong tendency to react with trace oxygen or water molecules present in the liquid. Indeed, we also demonstrated how the increase in water fraction in organic solvents is associated with the decrease in iron fraction in the Au–Fe nanoalloys.[2,3] However, from X-ray photoelectron spectroscopy we have not found evidence of charge transfer from Fe to Au in the nanoparticles, and the optical properties comply with those expected for a metallic Au–Fe alloy.[2,4] At the level of nucleation and cluster formation, however, there is still little information and one cannot exclude that other complex chemical processes take place between Au and Fe in this early stage.

1 V. Torresan, D. Forrer, A. Guadagnini, D. Badocco, P. Pastore, M. Casarin, A. Selloni, D. Coral, M. Ceolin, M. B. Fernández van Raap, A. Busato, P. Marzola, A. E. Spinelli and V. Amendola, *ACS Nano*, 2020, **14**, 12840.

2 V. Amendola, S. Scaramuzza, S. Agnoli, S. Polizzi and M. Meneghetti, *Nanoscale*, 2014, **6**, 1423, DOI: 10.1039/c3nr04995g.
3 S. Scaramuzza, S. Agnoli and V. Amendola, *Phys. Chem. Chem. Phys.*, 2015, **17**, 28076–28087, DOI: 10.1039/c5cp00279f.
4 D. T. L. Alexander, D. Forrer, E. Rossi, E. Lidorikis, S. Agnoli, G. D. Bernasconi, J. Butet, O. J. F. Martin and V. Amendola, *Nano Lett.*, 2019, **19**, 5754.

Christian Kuttner enquired: Did I understand correctly that the composition is the main parameter to tune the so-called "softness" of AuFe clusters and to make them more biodegradable?

Vincenzo Amendola replied: Yes, composition is the key parameter. We have experimentally verified that Au–Fe alloy nanoparticles with *ca.* 20 at% Fe are not biodegradable, while for Fe > 30 at% the nanoparticles show biodegradability.[1] With density functional theory we calculated the diffusion barriers for Fe atoms in the Au lattice, showing that they are too large to allow dealloying. This means that when the Au content is high enough to form an Au-rich skin on the surface of the nanoparticles, the "core" will be stable. Conversely, for Fe close to 50 at%, there are percolative paths of pure iron through the nanoalloy, along which pitting and corrosion can take place without the passivation of an Au layer.

1 V. Torresan, D. Forrer, A. Guadagnini, D. Badocco, P. Pastore, M. Casarin, A. Selloni, D. Coral, M. Ceolin, M. B. Fernández van Raap, A. Busato, P. Marzola, A. E. Spinelli and V. Amendola, *ACS Nano*, 2020, **14**, 12840.

Jonathan Quinson addressed Vincenzo Amendola and Stephan Barcikowski: Since you state the importance of oxidation. I am wondering if you know what would happen in O_2 free solvent for the synthesis?

Vincenzo Amendola responded: Thank you for your question on an important aspect of the process. Synthesis of Au–Fe nanoalloys by laser ablation in deaerated liquids (under argon or nitrogen bubbling) has been associated with an increase in the fraction of transition metal in the alloy.[1] Nonetheless, laser ablation with nanosecond pulses has been also associated with the systematic decrease of the fraction of transition metal in the nanoalloy, compared to the bulk target.[1] This could be attributed to the immiscibility of Au and Fe, with element segregation, and to the high reactivity of Fe with trace amounts of oxygen (which cannot be eliminated in the liquid). When iron reacts with oxygen, it is no longer available for the formation of the metal alloy nanoparticles. Possible evidence for this process has been found experimentally by laser ablation of Fe/Au multilayers in ethanol, showing that the decrease in available oxygen in the plasma plume, by use of a sacrificial Fe layer, is associated with experimental indications of Au–Fe alloys with higher Fe content.[2]

1 S. Scaramuzza, S. Agnoli and V. Amendola, *Phys. Chem. Chem. Phys.*, 2015, **17**, 28076–28087, DOI: 10.1039/c5cp00279f.
2 V. Amendola, S. Scaramuzza, F. Carraro and E. Cattaruzza, *J. Colloid Interface Sci.*, 2017, **489**, 18.

Stephan Barcikowski answered: Both have to be avoided, molecular oxygen and also water. It is known that LAL causes water splitting and H_2O_2 formation, which strength depends on the redox activity of the ablated material.[1] Marzun used a Schlenk line to check the influence of oxygen free conditions on the oxidation of copper in water and acetone.[2] Degassing and solvent drying is required, see ref. 3.

1 M.-R. Kalus, R. Lanyumba, N. Lorenzo-Parodi, M. A. Jochmann, K. Kerpen, U. Hagemann, T. C. Schmidt, S. Barcikowski and B. Gökce, *Phys. Chem. Chem. Phys.*, 2019, **21**, 18636–18651, DOI: 10.1039/c9cp02663k.
2 G. Marzun, H. Bönnemann, C. Lehmann, B. Spliethoff, C. Weidenthaler and S. Barcikowski, Role of dissolved and molecular oxygen on Cu and PtCu alloy particle structure during laser ablation synthesis in liquids, *ChemPhysChem*, 2017, **18**, 1175, DOI: 10.1002/cphc.201601315.
3 R. Nadarajah, S. Tahir, J. Landers, D. Koch, A. S. Semisalova, J. Wiemeler, A. El-Zoka, S.-H. Kim, D. Utzat, R. Möller, B. Gault, H. Wende, M. Farle and B. Gökce, Controlling the oxidation of magnetic and electrically conductive solid-solution iron-rhodium nanoparticles synthesized by laser ablation in liquids, *Nanomaterials*, 2020, **10**, 2362, DOI: 10.3390/nano10122362.

Alessandro Fortunelli asked: Nice work. It seems to me that the residual presence of oxygen within the particle as iron oxide species, in particular along planes partitioning the particle may be beneficial for the degradation phenomenon that you observe and that is important for the “death” of the particle. Do you have or could you have evidence of oxygen distribution inside the particle?

Vincenzo Amendola replied: Thank you for this question on a key open point about the degradability of Au–Fe alloy nanoparticles. Unfortunately, we don’t have experimental evidence about the dependence of oxidised iron inside the Au–Fe nanoparticles and their ability to degrade in physiological or aqueous environment. However, the general theory about corrosion of nanoalloys suggests that any corrosion percolative path inside the mass of the nanoparticles is crucial to favour dealloying and leaching of the not-noble metal.[1–3] Besides, the release of iron and pitting in nanoparticles is required to open the way to further iron diffusion and release, which instead is not possible through the Au lattice.[3] In summary, the presence of oxidised iron, especially at the grain boundary of polycrystalline Au–Fe nanoparticles, is likely to act as a “highway” for corrosion and we are directing experimental efforts to elucidate this aspect.

1 D. M. Artymowicz, J. Erlebacher and R. C. Newman, Relationship between the parting limit for de-alloying and a particular geometric high-density site percolation threshold, *Philos. Mag.*, 2009, **89**, 1663–1693.
2 X. Li, Q. Chen, I. McCue, J. Snyder, P. Crozier, J. Erlebacher and K. Sieradzki, Dealloying of noble-metal alloy nanoparticles, *Nano Lett.*, 2014, **14**, 2569–2577.
3 V. Torresan, D. Forrer, A. Guadagnini, D. Badocco, P. Pastore, M. Casarin, A. Selloni, D. Coral, M. Ceolin, M. B. Fernández van Raap, A. Busato, P. Marzola, A. E. Spinelli and V. Amendola, *ACS Nano*, 2020, **14**, 12840.

Marcelo M. Mariscal enquired: Have you tried to change the viscosity of the liquid to determine if this parameter can control the nanoparticle sizes?

Vincenzo Amendola responded: Thank you for your stimulating question. Although laser ablation in liquid (LAL) is performed with a simple experimental procedure, which can be even controlled remotely,[1] the physical-chemistry of the LAL process is very complicated and still unclear in several aspects, despite the important advancements achieved in these years.[2–4] Although viscosity will surely influence the diffusion of ablated species, and it is known that the cavitation bubble size and lifetime are affected by viscosity, as well as productivity,[2] the switch from a low-viscosity solution to a high-viscosity solution will likely imply also relevant changes in the chemistry of the species present in the plasma plume and in the cavitation bubble. Therefore, the final result may be affected by viscosity but also by other chemical–physical parameters which changed when the new solution with higher viscosity is adopted.

Apart from this, it is reasonable hypothesizing that nanoparticles size tends to be smaller in highly viscous environments, and this will be associated with a reduction in nanoparticles' polydispersity.

1 S. Crivellaro, A. Guadagnini, D. M. Arboleda, D. Schinca and V. Amendola, *Rev. Sci. Instrum.*, 2019, **90**, 033902.
2 A. Kanitz, M.-R. Kalus, E. L. Gurevich, A. Ostendorf, S. Barcikowski and D. Amans, *Plasma Sources Sci. Technol.*, 2019, **28**, 103001.
3 V. Amendola, D. Amans, Y. Ishikawa, N. Koshizaki, S. Scirè, G. Compagnini, S. Reichenberger and S. Barcikowski, *Chem.–Eur. J.*, 2020, **26**, 9206.
4 C. Y. Shih, C. Chen, C. Rehbock, A. Tymoczko, U. Wiedwald, M. Kamp, U. Schuermann, L. Kienle, S. Barcikowski and L. V. Zhigilei, *J. Phys. Chem. C*, 2021, **125**, 2132.

Riccardo Ferrando asked: Au and Fe tend to phase separate in nanoparticles, so that, when starting from random chemical ordering, some degree of Fe agglomeration is expected. Have you any comment on how the percolation threshold of Fe in the Au nanoparticles is influenced by the agglomeration of Fe atoms?

Vincenzo Amendola answered: Thank you for your questions. We have quantified the tendency of Au and Fe to phase separate by calculating the mixing enthalpy in alloys with random chemical ordering. Then, we included this tendency to homoatomic clustering in a topological model to identify the parting limit for dealloying.[1–3] This was done by weighting the lattice site occupation with a function of the mixing enthalpy and using a thermal disorder parameter of 0.26 eV. The effect was that the threshold for the appearance of percolative Fe paths in the Au–Fe alloy was found at a lower iron fraction (in our calculation at 43 at% instead of 53 at%).[1]

1 V. Torresan, D. Forrer, A. Guadagnini, D. Badocco, P. Pastore, M. Casarin, A. Selloni, D. Coral, M. Ceolin, M. B. Fernández van Raap, A. Busato, P. Marzola, A. E. Spinelli and V. Amendola, *ACS Nano*, 2020, **14**, 12840.
2 I. McCue, J. Snyder, X. Li, Q. Chen, K. Sieradzki and J. Erlebacher, Apparent inverse Gibbs–Thomson effect in dealloyed nanoporous nanoparticles, *Phys. Rev. Lett.*, 2012, **108**, 225503.
3 D. M. Artymowicz, J. Erlebacher and R. C. Newman, Relationship between the parting limit for de-alloying and a particular geometric high-density site percolation threshold, *Philos. Mag.*, 2009, **89**, 1663–1693.

Isaac T. Daniel opened discussion of the paper by Stephan Barcikowski: By changing the composition of your AuAg alloy you show that you can change the activity of 5-(hydroxymethyl)furfural (HMF) oxidation towards either 2,5-furandicarboxylic acid (FDCA) or 5-hydroxymethyl-2-furan-carboxylic acid (HMFCA); we know that Au is more active for the full oxidation to FDCA and you note that when an element is in the minority, this will rise to the surface of the nanoparticle. However, you show that a Ag_3Au_7 composition is the most active towards FDCA – can you therefore elaborate on why certain alloy compositions favour either HMFCA or FDCA and what the other contributing factors are?

Stephan Barcikowski replied: This surface composition effect has been discussed in the original article.[1] In addition to the activities/selectivity, also the catalyst durability has been studied in there, which I think is worth considering as well when it comes to select the "optimal" AgAu catalyst.

1 O. R. Schade, F. Stein, S. Reichenberger, A. Gaur, E. Saraçi, S. Barcikowski and J.-D. Grunwaldt, *Adv. Synth. Catal.*, 2020, **362**, 5681–5696, DOI: 10.1002/adsc.202001003.

Jonathan Quinson said: I understand that one motivation for the work is to bypass the use of surfactants (*e.g.* citrate). We recently observed that citrate (for Au nanoparticles) might not be such an issue for electrochemistry (EC). I am wondering if you did any comparison of these catalysts with citrate-prepared ones and for the same reactions you studied.

Stephan Barcikowski responded: Academically, I would expect a reducing agent like citrate, which strongly adsorbs on AgAu surfaces, to affect catalysis. But of course, this will depend on reaction type and also EC parameters. No, we haven't tried yet to see what happens if we intentionally contaminate the ligand free surface and probed that in EC. But we compared the on release rate from alloy nanoparticles (NPs) with and without the presence of different agents, namely citrate and cysteine, where citrate had a strong effect.[1] But this was without applying potential and a different alloy system. For silver nanoparticles we showed that the addition of albumin significantly influenced bioactivity.[2] Hence, I believe that such ligands do affect ion leaching, even without electrochemical potential.

1 A. Hahn, J. Fuhlrott, A. Loos and S. Barcikowski, *J. Nanopart. Res.*, 2012, **14**, 686.
2 S. Grade, J. Eberhard, A. Neumeister, P. Wagener, A. Winkel, M. Stiesch and S. Barcikowski, *RSC Adv.*, 2012, **2**, 7190–7196, DOI: 10.1039/c2ra20546g.

Jonathan Quinson enquired: In your paper (**https://doi.org/10.1039/d2fd00092j**), you mention that it is not clear why $Ag_{80}Au_{20}$ does not show the alloy reduction peak. I am wondering if you constantly observed this trend, over say different batches of prepared nanoparticles.

Stephan Barcikowski answered: No, we do not constantly observe this trend in this study. That is why we have no robust explanation. In earlier studies on the bioresponse, the 80 : 20 composition also was prominent in toxicity. But in these older studies, we did not check its next gold molar fractions (GMF) neighbours 70 : 30 and 90 : 10. It would be good if we in future check this 80 : 20 composition along with 85 : 15 and 75 : 25 in more detail.

Jonathan Quinson asked: You mention the specific features of a 50 : 50 Ag : Au ratio. I am wondering if you screened closer to this value – *e.g.* have you tried 55 : 45 and 45 : 55? Is the composition control precise enough that you could get these?

Stephan Barcikowski replied: No, we haven't tried closer, yet. But yes, it would be doable to make 55 : 45.

Christian Kuttner requested: Could you elaborate on the definition of the surface composition? Is it exclusively the outermost atomic layer or a larger diffuse boundary layer?

Stephan Barcikowski responded: In our current *Faraday Discussions* contribution on AgAu (**https://doi.org/10.1039/d2fd00092j**), this is the surface-near volume, several atom layers (XPS penetration depth). I would expect the catalytic activity is being influenced as well by layers below the outermost one, in particular in defect-rich particles (it is assumed by the community that laser ablation in liquids creates very defect rich particles, in particular stable planar defects). We will extend the definition paragraph in the proofreading step of our article, thanks to your comment.

Graham J. Hutchings asked: I was fascinated by your observation that when you have a bimetallic nanoparticle with uneven amounts of the two metals that the minority component is enriched on the surface. If you add another metal/component, does it still hold? Can you use this effect to order a five component system so that the surface concentrations are ordered opposite to their bulk concentrations? Is this a way of thrifting rare elements in applications where surfaces are important.

Stephan Barcikowski answered: Great idea. So far, we have looked at the details of minority element enrichment at the surface only for AgAu (where we employed an extensive combination of characterization methods), would be good to check if this happens also in other systems. Let me summarise some observations we have so far, where we see that in LAL, both kinetic and nanothermodynamic contributions set the particle's structure:

AuFe, AuCo, AuFeCo: if we increase Fe and Co above 80%, Au will be on the shell, with phase segregation. Those shells are quite thin then. But that is a different phenomenon driving the minority element into the shell here, as that segregation is now clearly driven by surface energies, see the nanothermodynamic model in the paper, caused by immiscibility. CoAu with mechanism, see ref. 1; FeAu with atom probe, see ref. 2.

In Cantor-inspired high-entropy alloys (HEA) (5+ elements) we have seen an even distribution of the elements, and playing with one element enrichment, we have seen enrichment at the outer surface, but this can mainly be ascribed to oxidation. We would have to repeat that in a better oxygen exclusion environment. Note that depending on the solvent, we have indicators of amorphisation of the HEA. For CrCoFeNiMn and CrCoFeNiMn HEA metallic glass, see ref. 3; playing with Mn, see ref. 4; CrCoFeNiMn equimolar, see ref. 5.

Following your question/comment, it would be worth now substituting the Mn in the HEA with another minority, less oxygen affine, catalytically interesting element. Then, we would have to do in depth characterization, like done for the AuAg, in particular STEM-EDX and XPS and a catalytic model reaction. Anyone want to join, *e.g.* HR-STEM-EDX? We may also need atom probe tomography.

1 J. Johny, M. Kamp, O. Prymak, A. Tymoczko, U. Wiedwald, C. Rehbock, U. Schürmann, R. Popescu, D. Gerthsen, L. Kienle, S. Shaji and S. Barcikowski, *J. Phys. Chem. C*, 2021, **125**, 9534–9549, DOI: **10.1021/acs.jpcc.1c02138**.

2 J. Johny, O. Prymak, M. Kamp, F. Calvo, S.-H. Kim, A. Tymoczko, A. El-Zoka, C. Rehbock, U. Schürmann, B. Gault, L. Kienle and S. Barcikowski, *Nano Res.*, 2022, **15**, 581–592, DOI: 10.1007/s12274-021-3524-7.

3 J. Johny, Y. Li, M. Kamp, O. Prymak, S.-X. Liang, T. Krekeler, M. Ritter, L. Kienle, C. Rehbock, S. Barcikowski and S. Reichenberger, *Nano Res.*, 2022, **15**, 4807–4819, DOI: 10.1007/s12274-021-3804-2.

4 T. Löffler, F. Waag, B. Gökce, A. Ludwig, S. Barcikowski and W. Schuhmann, *ACS Catal.*, 2021, **11**, 1014–1023, DOI: 10.1021/acscatal.0c03313.

5 F. Waag, Y. Li, A. R. Ziefuß, E. Bertin, M. Kamp, V. Duppel, G. Marzun, L. Kienle, S. Barcikowski and B. Gökce, *RSC Adv.*, 2019, **9**, 18547–18558, DOI: 10.1039/c9ra03254a.

Fuyi Chen communicated: The surface segregation of Ag in AgAu alloy was confirmed in this work, but as far as I know, varying results with great discrepancies were obtained for AgAu alloy, from Ag rich on surface to Au rich on surface. What are the factors that affect the surface segregation tendency?

Stephan Barcikowski communicated in reply: Please read the article in the *Faraday Discussions* volume, it is discussed in there (https://doi.org/10.1039/d2fd00092j). First, its not varying, it is systematic, the minority element is enriched in the surface near volume. That also means that the 50 : 50 alloy has no segregation, indicating that entropy may play a role. Note that laser synthesis has a kinetic contribution (ultrafast solidification), so structural results are different from wet chemical co-reduction.

Didier Grandjean asked: We have found a reverse organisation (the minority element is always at the core of the particle) in a series of Au_xAg_{1-x} particles produced by laser ablation in the gas phase except for the $Au_{0.5}Ag_{0.5}$ composition which is an alloy as in your study.[1] Do you have a possible explanation for the occurrence of these different structures in the same system produced by the same technique? Can the liquid environment play a role in the final structural arrangement of the AuAg nanoparticles produced by laser ablation in liquid?

1 T. W. Liao, *et al.*, *Nanoscale*, 2018, **10**, 6684–6694, DOI: 10.1039/c8nr01481g.

Stephan Barcikowski answered: I would not consider it being the same method abating in air and liquid. As you mention, the liquid ambience makes a big difference, in particular regarding the unparalleled high cooling rates. Second, the resulting particles are in a colloidal state, which facilitates downstream processing such as supporting on a catalyst support by colloidal deposition. Thanks for the article, very interesting.

Robert M. Jones addressed Stephan Barcikowski and Vincenzo Amendola: Given that in this community we are concerned with sustainability and minimising damage to the environment, is there much scope for how to recycle functional nanoalloys once they have served their purpose as, for example from your talks, for drug delivery?

Stephan Barcikowski responded: I am not sure if I really caught your question. I don't see a point for recycling an alloy that has been administered medically, *e.g.* as we talk about ppm level doses that are applied (mg NP per kg body weight). But yes, sustainability is very important in general, including chemical technologies.

Here, I like to mention that laser ablation synthesis fulfills all (!) criteria of green chemistry.

Vincenzo Amendola replied: Thank you for your question. Fortunately, the mass of nanoparticles for biomedical use is of the order of a gram per patient for treatment. For other uses like bioassays, this quantity is orders of magnitude lower. Therefore, nanoparticles' cost and environmental impact are negligible compared to other applications such as catalysis or functional coatings. Besides, for *in vivo* use we are bound to the most biocompatible elements available, hence the environmental impact of nanoparticles cleared from the body is expected to be null, especially compared to standard drugs. On the other hand, the production of nanoparticles and nanoalloys often is problematic from the environmental point of view, because of energy-intensive procedures with the formation of pollutant wastes as byproducts. From this point of view, the synthesis by laser ablation in liquid (LAL) is one of the best techniques available because of the low energy consumption of lasers, which have reached excellent efficiencies so far, and the compatibility of LAL with the 12 principles of green chemistry.[1,2]

1 V. Amendola and M. Meneghetti, *Phys. Chem. Chem. Phys.*, 2009, **11**, 3805–3821, DOI: 10.1039/B900654K.
2 V. Amendola, D. Amans, Y. Ishikawa, N. Koshizaki, S. Scirè, G. Compagnini, S. Reichenberger and S. Barcikowski, *Chem.–Eur. J.*, 2020, **26**, 9206.

Damien Alloyeau asked: Some year ago we did a similar *in vivo* TEM study in which we followed Au–Fe_2O_3 nanodimers (Janus) into mice. In line with your findings, we saw that iron oxide is biodegraded much faster than gold, but more surprisingly the two metals end up in different organs. Do you observe the same results with Au–Fe nanoalloys?

Vincenzo Amendola answered: Thank you for this interesting question. We tracked *in vivo* the Au–Fe alloy nanoparticles with magnetic resonance imaging (MRI) and X-ray computed tomography (CT). We found that the two signals have a roughly similar time evolution over the first 30 days.[1] Some differences are observed, but may be ascribed to the decrease in the transversal relativity with time due to nanoparticle degradation (https://doi.org/10.1039/d2fd00087c). After organ explant (day 60 from injection), iron oxide was almost absent in liver, spleen and kidneys, whereas we could still find some residual traces of gold in liver and spleen.[1] A different result was found in the case of Ag–Fe (ref. 2) and Fe–B (ref. 3) alloy nanoparticles. In the case of Ag–Fe, no traces of silver were found after 30 days in explanted organs, while some traces of iron were present and attributed to possible remineralization into iron oxide as described in ref. 4. In the case of Fe–B nanoparticles, iron after 30 days was found primarily in kidneys, while the standard iron oxide nanoparticles (Endorem) resided in liver.[3]

1 V. Torresan, D. Forrer, A. Guadagnini, D. Badocco, P. Pastore, M. Casarin, A. Selloni, D. Coral, M. Ceolin, M. B. Fernández van Raap, A. Busato, P. Marzola, A. E. Spinelli and V. Amendola, *ACS Nano*, 2020, **14**, 12840.
2 V. Amendola, A. Guadagnini, S. Agnoli, D. Badocco, P. Pastore, G. Fracasso, M. Gerosa, F. Vurro, A. Busato and P. Marzola, *J. Colloid Interface Sci.*, 2021, **596**, 332.
3 V. Torresan, A. Guadagnini, D. Badocco, P. Pastore, G. A. Muñoz Medina, M. B. Fernàndez van Raap, I. Postuma, S. Bortolussi, M. Bekić, M. Čolić, M. Gerosa, A. Busato, P. Marzola and V. Amendola, *Adv. Healthcare Mater.*, 2021, **10**, 2001632.

[4] A. Curcio, A. Van De Walle, A. Serrano, S. Preveral, C. Péchoux, D. Pignol, N. Menguy, C. T. Lefevre, A. Espinosa and C. Wilhelm, *ACS Nano*, 2020, **14**, 1406–1417.

Nanoalloy structures, part 3

Cesare Roncaglia opened discussion of the paper by Robert M. Jones: Among all features offered by the Sapphire library, clustering of atoms of a single nanoparticle is mentioned. This approach is intended to distinguish between surface atoms, inner atoms and so on, for a total of six classes. However, unsupervised learning algorithms need the user to fix *a priori* this number of classes (clusters) or at least to provide a score or cost for this number in order to compare it with other possible numbers. Then, is there any particular reason to choose six clusters *a priori* or is it the result of some minimization/maximization of some cost/score?

Robert M. Jones answered: Thank you for the question. This matter is discussed in the referenced paper.[1] The six chosen classes are given as: solid inner (SI), liquid inner (LI), solid high-coordination surface (SHS), liquid high-coordination surface (LHS), solid low-coordination surface (SLS), and liquid low-coordination surface (LLS). These classes are better justified in the reference paper, although you raise a good question with respect to the motivation for the number of classes; this follows the physical argument of partitioning with respect to surface/inner, followed by low/high coordinated surface, with a final partition into liquid/solid like environments. Hence, the motivation for six classes is a physical one as opposed to statistical optimisation.

[1] C. Zeni, K. Rossi, T. Pavloudis, J. Kioseoglou, S. de Gironcoli, R. E. Palmer and F. Baletto, *Nature Commun.*, 2021, **12**, 6056.

Cameron J. Owen asked: Do you have any performance benchmarks for different parts of the package? Have you parallelized Sapphire for use on modern computational architectures?

Robert M. Jones replied: Thank you for the questions. We have performed benchmarking tests for monoatomic and bimetallic clusters up to the order of 5000 atoms on a typical desktop. It is at these sizes that we begin to observe performance issues with our methods. As for parallelisation schemes, we utilise natively parallelised mathematical operations from python libraries such as numpy and scipy to boost performance. We have not yet attempted to parallelise across nodes on HPC architectures, but we intend to do so.

Éric Marceau enquired: Is it possible to use Sapphire to model the influence of oxygen adsorption on the surface composition of the particles?

Robert M. Jones responded: Thank you for the question. Given that Sapphire requires an existing molecular dynamics (MD) trajectory, there is no reason why one could not use the library to describe the influence of adsorbates on nanoparticles. However, these trajectories will need to be created by an alternative package such as LAMMPS for example.

Fuyi Chen asked: The Sapphire library provides a new way to classify the structural characteristics of a given nanoparticle through several structural analysis techniques and order parameters. Will these descriptors accurately describe the relationship between "composition–electronic structure–electrocatalytic performance" in dynamic processes?

Robert M. Jones answered: Thank you for the question. There is no explicit way to map the structural/compositional information of a cluster to electronic structure explicitly in Sapphire as this requires electronic structure calculations to be performed which are not a feature of Sapphire. However, the ASE infrastructure Sapphire utilises does support the use of such methods, should the user require it. As for electrocatalytic performance, this is a small parametric model within the library which requires parameters obtained from DFT or experiment to set.

Vincenzo Amendola said: Thank you for your talk. Concerning the simulation of optical properties with your Sapphire library *via* Green's Dyadic Method (GDM), in your paper (**https://doi.org/10.1039/d2fd00097k**) it is stated that it works within the quasi-static coupled dipole approximation. This is surely accurate for the size range considered in your study. However, I was interested to know if this method is accurate also for larger plasmonic nanoparticles, which are subjected to retardation effects leading to multipolar excitations.

Robert M. Jones responded: Thank you for your question. It is true that in the paper (**https://doi.org/10.1039/d2fd00097k**) we state that the proposed method works well within the quasi-static approximation as we have only earnestly tested it within this regime.

However, according to the authors of the method, there is nothing preventing the GDM from being able to capture behaviour from objects saturating or above the quasi-static limit. We refer to ref. 1 for a deeper discussion on the properties of the method.

1 P. R. Wiecha, pyGDM—A python toolkit for full-field electro-dynamical simulations and evolutionary optimization of nanostructures, *Comput. Phys. Commun.*, 2018, **233**, 167–192 (ref. 64 in the paper).

Vincenzo Amendola questioned: Thank you for this amazing talk. You showed you have predicted the optical properties of gold and platinum nanoparticles. However, it is known that Au and Pt have full d-shells and this is a relatively simple case for predicting optical and plasmonic properties, compared to alloys with partially filled d-shells such as other transition metals.[1,2] In this case, the electronic structure of the alloy undergoes a more extended change.[1,3] Have you tried to test the reliability of your method with other alloys of this type?

1 V. Coviello, D. Forrer and V. Amendola, *ChemPhysChem*, 2022, **23**, e202200136, DOI: **10.1002/cphc.202200136**.
2 J. M. Rahm, C. Tiburski, T. P. Rossi, F. A. A. Nugroho, S. Nilsson, C. Langhammer and P. Erhart, *Adv. Funct. Mater.*, 2020, **30**, 2002122.
3 D. T. L. Alexander, D. Forrer, E. Rossi, E. Lidorikis, S. Agnoli, G. D. Bernasconi, J. Butet, O. J. F. Martin and V. Amendola, *Nano Lett.*, 2019, **19**, 5754.

Robert M. Jones answered: Thank you for the insightful question. We have not yet compared optical properties of partially filled d-band metallic alloys with experimental data – principally Au and Pt as acknowledged. Given the method we use requires experimental data for the mono-metallics from well-cited studies, such as Johnson and Christy,[1] and not explicitly for such alloys, it cannot be guaranteed that extensive changes in electronic structure from alloying partially filled d-band metals will be accurately captured by this method. To do so, it is likely that refractive data would need to be obtained from either experiment or *ab initio* calculations to make accurate predictions with Sapphire.

1 P. B. Johnson and R. W. Christy, Optical constants of the noble metals, *Phys. Rev. B: Solid State*, 1972, **6**, 4370–4379.

Pascal Andreazza addressed Robert M. Jones and Francesca Baletto: You suggest to use atom coordinates reconstruction from experiments. However, it is difficult to obtain the 3D coordinates experimentally even in atomic resolved techniques (such as HRTEM). With average experimental techniques like wide angle X-ray scattering, the typical procedure is to explore a library of simulated structures to fit with the experimental data (in the real space from PDDF analysis or in the reciprocal space from X-ray scattering function analysis). Have you suggestions or an idea to use Sapphire in this objective to help the interpretation of experimental data.

Francesca Baletto replied: We do realise that 3D atomic reconstruction is not a common tool yet, but different groups work on that. The idea is to estimate properties of real nanoalloys and not ideally geometrical morphology.

In the meantime, the numerical community on nanoalloys should collaborate more closely to create a database of possible morphologies correlated with the analysis that Sapphire can offer. Such a common, open and fair database is still missing, and eventually the community is underestimate the challenge we have. The challenge needs dedicated funding to be initiated and maintained. The following step will be to find the best match between experimental data and database images.

Robert M. Jones responded: Thank you for the very interesting question. In general, our view is to adopt a method previously explored within the community whereby transmission electron tomography may be used to create a reconstructed 3D map of a nanoparticle.[1,2] From here, the view would be to create a map of 3D coordinates which may be then analysed in the fashion outlined in our contribution (**https://doi.org/10.1039/d2fd00097k**). However, we welcome comments and further ideas on how we may better understand experimental data with computational techniques.

1 X. Y. Wang, R. Lockwood, M. Malac, H. Furukawa, P. Li and A. Meldrum, *Ultramicroscopy*, 2012, **113**, 96–105, DOI: **10.1016/j.ultramic.2011.11.001**.

2 Z. W. Wang and R. E. Palmer, Atomic-Scale Structure Analysis by Advanced Transmission Electron Microscopy, in *Protected Metal Clusters: From Fundamentals to Applications*, ed. T. Tsukuda and H. Häkkinen, Frontiers of Nanoscience, Elsevier, 2015, ch. 6, vol. 9, pp. 127–159, DOI: **10.1016/B978-0-08-100086-1.00006-3**.

Christian Kuttner asked: This library you have presented seems to be very useful. What are the upper limits for the size of clusters that Sapphire can handle?

Robert M. Jones answered: Generally speaking, for a standard desktop computer, on the order of 4000–5000 atoms can be managed. More are possible, but computational overheads of processing power become significant at this margin as some quantities scale as order $N!$.

Mona Treguer-Delapierre opened discussion of the paper by Catherine Amiens: What is the role of the ligands in the evolution of the redox processes of the nanocatalysts?

Catherine Amiens replied: Indeed, the ligands decompose when the temperature is increased and can participate in the reduction or oxidation of the nanomaterial. In some cases we detected the formation of metal carbides which may indicate a reaction between the ligands and the NiFe nanoparticles at elevated temperatures. However, the carbon could also come from the cell used for the *in situ* XAS measurements as the windows of this cell are carbon graphite. So we couldn't draw any clear conclusion on this point.

Didier Grandjean asked: What is the final loading of the NiFe nanoparticles on the silica surface after their deposition? Do you observe any aggregation of the nanoparticles after both processes of deposition and reduction compared to the original size of your as-synthesized nanoparticles? Do you foresee any possible applications of this NiFe system as an (electro)catalyst?

Catherine Amiens responded: The metal loading on the silica support is close to 7% (the exact values can be found in the experimental part of the paper; **https://doi.org/10.1039/d2fd00095d**). Some aggregates can be observed in the TEM images both before (Fig. SI 1–3 in the supplementary information of the paper) and after the reduction/re-oxidation process (Fig. SI 18 in the supplementary information of the paper). TEM images after re-oxidation do not show a larger extent of aggregation. Still, only a very limited part of the samples could be observed by TEM, so it is difficult to draw any firm conclusion on that point.

Concerning the use of these NiFe nanoparticles in catalysis, so far we have considered two applications: the electro-oxidation of water and the hydrogenation of a sugar, xylose.

For the electro-oxidation of water, unsupported NiFe nanoparticles of different compositions (Ni2Fe1, Ni1Fe1, Ni1Fe9) were used after exposure to air. Characterization results indicate that the structure and chemical state of these air-exposed NiFe NPs are very close to those of the silica-supported NiFe nanoparticles prepared in air, as described in the *Faraday Discussions* paper. For the electrocatalysis study, these NiFe NPs were dispersed into water, then deposited onto fluorine doped tin oxide electrodes. The results evidenced a higher electrocatalytic activity for the Ni2Fe1 composition.[1]

The study of the catalytic hydrogenation of D-xylose was performed with the silica-supported NiFe nanomaterials described in this paper. To compare with previous results obtained with NiFe nanocatalysts prepared on silica by deposition–precipitation with urea (DPU),[2] the catalytic tests were carried out in the same catalytic set-up, in water, at 80 °C and under 20 bar of H_2, with a molar ratio of 10.6 between xylose and the total metal content in the catalysts. The silica-supported catalysts were not exposed to H_2 prior to reaction.

Ni2Fe1-S, Ni1Fe1-S, Ni1Fe9-S and Ni2Fe1-S-Ox nanomaterials were evaluated as catalysts in comparison to a pure metallic nickel nanomaterial also supported onto silica (Ni-S).[3] The conversion of xylose and yield/selectivity towards xylitol were monitored by HPLC over a period of 7 h.

A freshly prepared Ni2Fe1-S nanomaterial was first compared to its oxidized counterpart Ni2Fe1-S-Ox. The former was extremely active (xylose conversion of 95% after 7 h). The latter displayed a good activity despite a long-term exposure to air (75% conversion after 7 h), as evidenced in Fig. 1 here. This interesting result is attributed to the persistence of a reduced Ni fraction that facilitates the reduction of the surface oxide under H_2 pressure, as observed during temperature-programmed experiments monitored by XAS. It is assumed that the higher hydrogen pressure (20 bar of pure H_2 in catalytic experiments, *versus* 5% H_2 in helium flow – 50 mL min^{-1} – at atmospheric pressure for XAS measurements) compensates for the lower temperature (80 °C in catalytic experiments, while the onset of reduction was observed at 272 °C in XAS measurements). In addition and remarkably, these nanomaterials displayed an excellent selectivity towards xylitol which was even exclusive with the Ni2Fe1-S-Ox nanomaterial.

A handling restricted to freshly prepared catalysts was not possible, and the effect of composition was assayed on a series of 7-months-old Ni2Fe1-S, Ni1Fe1-S and Ni1Fe9-S nanomaterials in comparison to a pure metallic nickel nanomaterial also supported onto silica (Ni-S). The conversion of xylose after 7 h was measured as 73, 44 and 29% for Ni2Fe1-S, Ni1Fe1-S and Ni1Fe9-S, respectively (Fig. 2a here). These values are higher than the conversion measured for the silica-supported Ni catalyst (Ni-S, 18% of xylose conversion only), thus confirming the synergistic effect between Ni and Fe in the NiFe-S catalysts, previously observed for DPU prepared nanomaterials,[2] with a higher performance for the composition Ni2Fe1 as in the electro-oxidation of water (see above). The target polyol, xylitol, was the only hydrogenation product formed on Ni2Fe1-S and Ni1Fe1-S, thus evidencing a selectivity of 100% for the two catalysts (Fig. 2b and c here). The iron-rich nanomaterial Ni1Fe9-S displayed a poor selectivity towards xylitol (10%),

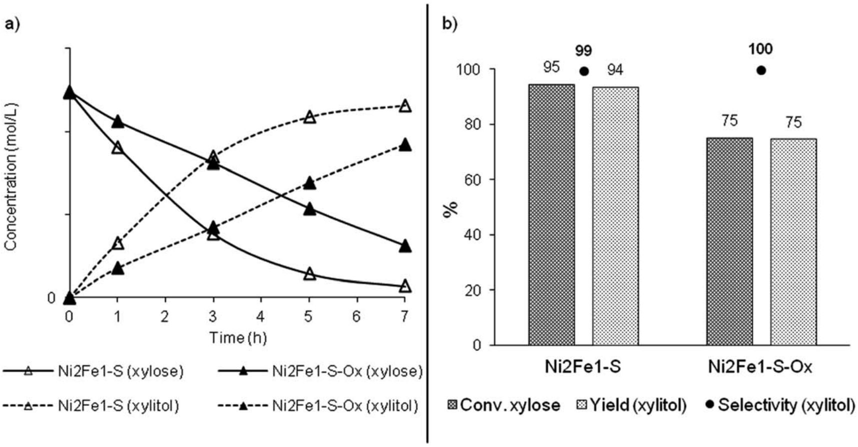


Fig. 1 (a) Concentration of xylose and xylitol as a function of time for freshly prepared Ni2Fe1-S and Ni2Fe1-S-Ox; (b) conversion (conv.) of xylose, and yield of and selectivity towards xylitol.

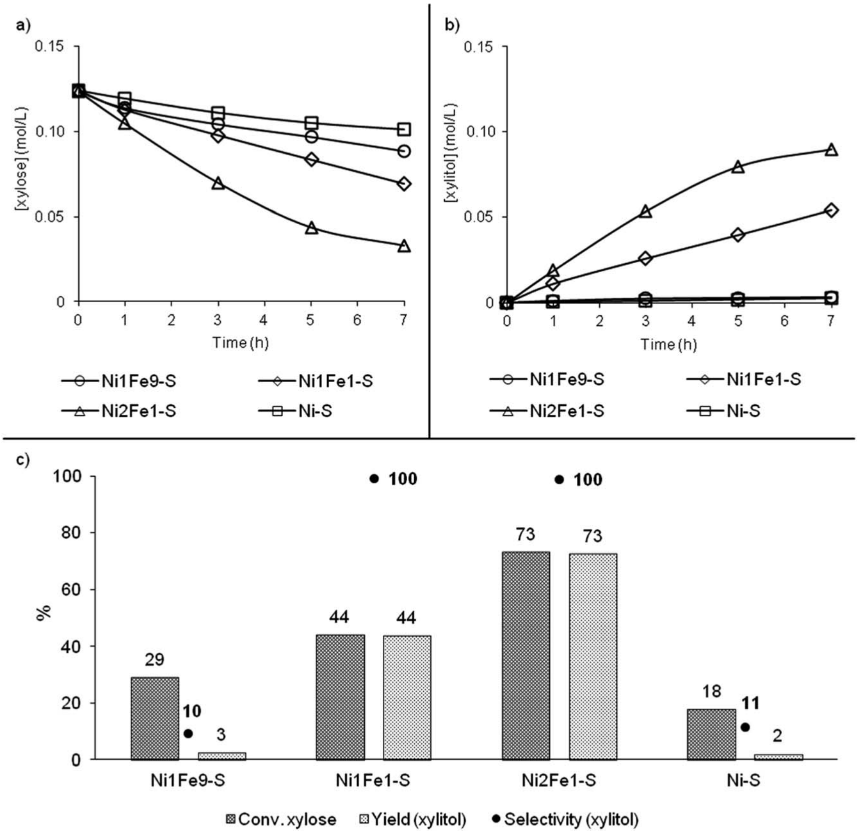


Fig. 2 (a) Concentration of xylose as a function of reaction time for Ni1Fe9-S, Ni1Fe1-S and Ni2Fe1-S (after 7 months of storage of the nanomaterials in a glove-box) in comparison with a 100% Ni nanomaterial Ni-S; (b) concentration of xylitol against time; (c) conversion (conv.) of xylose, and yield of and selectivity towards xylitol.

because the ketose isomer of xylose, xylulose, and a polyol isomer, arabitol, were also formed with this catalyst. Metal ions on partially oxidized/incompletely reduced Ni1Fe9-S may have acted as Lewis acidic sites for the isomerization of xylose. In terms of yield (Fig. 2c here), in the applied reaction conditions the Ni2Fe1-S nanomaterial was thus the most promising catalyst for the hydrogenation of xylose, which confirms the observations made by Sadier and colleagues[2] (when working in the same conditions with NiFe nanocatalysts prepared by DPU on the same silica support). Metal leaching after 7 h of reaction was low. Measurements in solution by ICP gave 1.5 ppm Ni for the monometallic Ni catalyst, and 4.7 ppm Ni and 4.1 ppm Fe for Ni2Fe1-S.

Altogether, these results emphasize the interest of NiFe nanomaterials prepared by the organometallic route for the catalytic hydrogenation of sugars: the very small size and the chemical composition of the nanoparticles are well controlled, the deposition onto silica can be made easily by a simple impregnation method, and even after purification and storage in air, these nanoscale catalysts display high activity and excellent selectivity in the hydrogenation of xylose.

1 Q. T. Nguyen, F. Robert, V. Colliere, P. Lecante, K. Philippot, J. Esvan, P. T. Tran and C. Amiens, Synthesis of NiFeOx nanocatalysts from metal–organic precursors for the oxygen evolution reaction, *Dalton Trans.*, 2022, **51**, 11457–11466, DOI: 10.1039/d2dt01370c.
2 A. Sadier, D. Shi, A.-S. Mamede, S. Paul, E. Marceau and R. Wojcieszak, Selective aqueous phase hydrogenation of xylose to xylitol over SiO_2-supported Ni and Ni-Fe catalysts: benefits of promotion by Fe, *Appl. Catal. B*, 2021, **298**, 120564, DOI: 10.1016/j.apcatb.2021.120564.
3 F. Robert, PhD dissertation, University Paul-Sabatier, 2022.

Fuyi Chen enquired: You performed an interesting study on the reconstruction of NiFe nanoalloys in reductive and oxidative environments. Using XAS and WAXS, the evolution of the chemical order and oxidation state for the elements was investigated. Especially, the change in structure and chemical ordering after heat-treatment in a reductive atmosphere has been observed. Have you considered the effect of concentration and flow of H_2 on the evolution of the NiFe nanoalloy?

Catherine Amiens answered: In our experiments, the hydrogen flow (5% H_2 in He) was first set at 50 mL per min in comparison with already published results on closely related systems (see for example ref. 1). Given the limited beamtime granted, we didn't get the chance to try different flow values.

For security reasons, in our experimental set up we could only use this diluted hydrogen flow at atmospheric pressure, but indeed it would be interesting to investigate the evolution of the nanoparticles in less diluted flows of hydrogen and even under hydrogen pressures closer to those actually used in catalysis (namely up to 20 bar).

1 D. Shi, *et al.*, *Catal. Today*, 2019, **334**, 162–172.

Christine Mottet asked: Did you control the size and size distribution of your samples and what is the effect of oxido-reduction on it?

Catherine Amiens replied: The size is controlled by the ligands present in the first step of the synthesis, namely hexadecylamine and hexamethyldisilazane. After deposition of the nanoparticles on the silica support, it is difficult to image a large enough number of nanoparticles to draw a significant size histogram, but the size of the nanoparticles observed falls well in the size distribution determined after the first step. So we consider that deposition on silica doesn't modify the size of the nanoparticles. Observation was even more complicated after the reduction and reoxidation process, as the material had been dispersed in boron nitride for the XAS monitoring of these two steps. Still, TEM images didn't show any significant change in size (one can refer to Fig. SI 18 in the supplementary information of the paper; https://doi.org/10.1039/d2fd00095d).

Christine M. Aikens opened discussion of the paper by Hazar Guesmi: The crown-like –H–Au–H–Au–H– structure that you have found is very interesting. Have you compared this with similar thiolate-based motifs (–SR–Au–SR–Au–SR–)? If so, what are the similarities and differences?

Hazar Guesmi answered: No, we did not compared our crown-like H–Au–H–Au–H structure with thiolate-based motifs. This is an interesting question which requires investigation.

Ewald Janssens asked: This work is a good example of obtaining deeper insight by combining experiments with theoretical modelling. The simulations carefully mimic the experimentally studied particles in term of size, composition, and temperature. How representative is a layer of adsorbed atomic hydrogen (122 H atoms) for the 1 bar molecular hydrogen in the experiment?

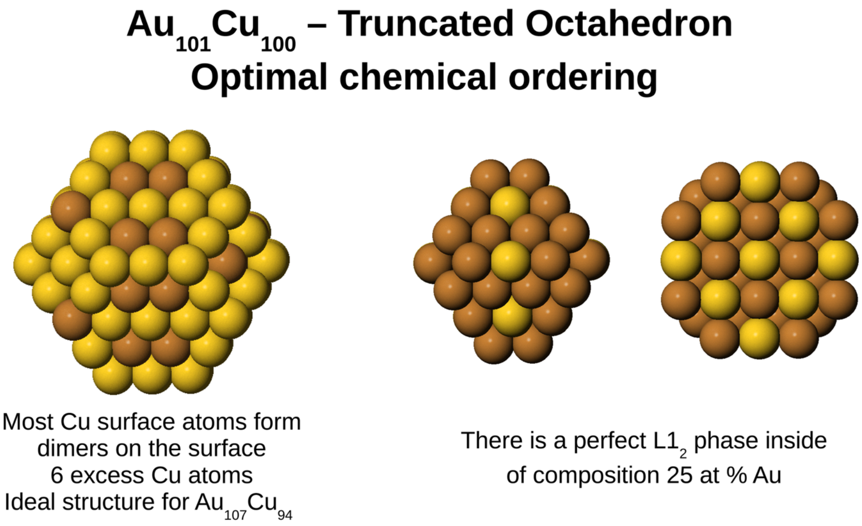
Hazar Guesmi replied: From our recent DFT calculations and AIMD simulations on Au_{201} nanoparticle saturated by coadsorbed hydrogen atoms, we have registered that a global coverage of 1 ML (122 adsorbed hydrogen per 122 Au surface atoms) corresponds to a nanoparticle oversaturated by the adsorbates. In our DFT models, the initial pressure in the 3D box is zero (strict vacuum). However, all along the trajectories of AIMD simulations and during the thermalization step, a significant number of adsorbed hydrogen atoms recombine into H_2 molecules which desorb rapidly from the Au_{201} nanoparticle. The number of desorbed molecules ranges from 3 to 10 H_2, thus leading to a progressive increase in pressure, in the 3D box, depending on the considered temperature. At 300 K, the pressure in the 3D box ranges from 0.9 to 3.3 bar, while at 500 K, the pressure is in the range 1.7–5.5 bar. Thus, the simulated temperature and pressure order are in agreement with the experimental conditions.

For AuCu nanoparticles, the analysis is similar. In addition, in these theoretical predictions, during the equilibration step along the AIMD trajectories (when statistics become meaningful), the remaining surface coverage of adsorbed hydrogen is in the range 0.84–0.94 ML (corresponding to 102–116 coadsorbed atoms). This theoretical result thus gives a good approximation of the unknown experimental surface coverage.

Riccardo Ferrando commented: For comparison with the cluster structures reported in the paper (**https://doi.org/10.1039/d2fd00130f**), we performed a few global optimization runs by our Basin-Hopping code.[1] The clusters were modelled by the second-moment tight-binding potential developed in ref. 2. Two types of optimization were made.

In the first type, chemical ordering of truncated octahedral $Au_{101}Cu_{100}$ was optimized at fixed shape by swaps of pairs of unlike atoms. In this case, the surface of the lowest-energy structure (see Fig. 3 here) contains 32 Cu atoms arranged in dimers inside (111) terraces, plus 6 Cu in edges or at the center of (100) facets. The remaining 84 surface atoms were of Au. In the inner part of $Au_{101}Cu_{100}$, a perfect $L1_2$ ordered phase was formed, with 17 Au and 62 Cu atoms, respectively. The formation of the $L1_2$ phase reinforces the results of the paper (**https://doi.org/10.1039/d2fd00130f**) about the tendency towards maximizing the number of mixed AuCu bonds inside the nanoparticle.

The second type of global optimization runs were made in order to optimize both shape and chemical ordering at the same time starting from completely random configurations. These runs found the icosahedral clusters (see Fig. 4 here) are the lowest in energy. These structures are proposed for investigation at the DFT level in order to check their stability. Moreover, it would be interesting to



$Au_{101}Cu_{100}$ – Truncated Octahedron
Optimal chemical ordering

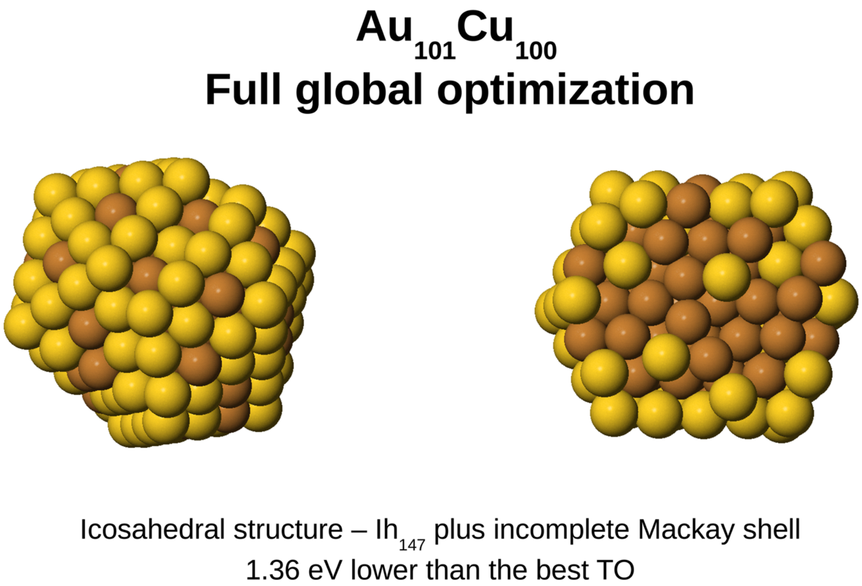
Most Cu surface atoms form dimers on the surface
6 excess Cu atoms
Ideal structure for $Au_{107}Cu_{94}$

There is a perfect $L1_2$ phase inside of composition 25 at % Au

Fig. 3 Optimal chemical ordering of truncated octahedral $Au_{101}Cu_{100}$.

know whether icosahedral structures can be experimentally observed for sizes around 200 atoms.

1 G. Rossi and R. Ferrando, *J. Phys.: Condens. Matter*, 2009, **21**, 084208.
2 J.-Q. Goh, J. Akola and R. Ferrando, *J. Phys. Chem. C*, 2017, **121**, 10809–10816.



$Au_{101}Cu_{100}$
Full global optimization

Icosahedral structure – Ih_{147} plus incomplete Mackay shell
1.36 eV lower than the best TO

Fig. 4 Full global optimization of $Au_{101}Cu_{100}$.

Hazar Guesmi responded: We will consider the ICO and TOh structures predicted under vacuum from the global optimization method and run DFT calculations and then AIMD simulations under fixed temperature and hydrogen pressure. This will allow investigation of the stability of the two structure symmetries and to identify the effect of hydrogen as a function of the gold structure. It would also be interesting to investigate the effect of the support on the structural stability of Au–Cu NPs under vacuum.

Rasmus Svensson enquired: In the simulations, 1 ML of dissociated hydrogen was used over the pure Au NP. How can the coverage be that high with a hydrogen pressure of 1 bar? Dissociated hydrogen on the gold NP is higher in electronic energy (and much higher in Gibbs free energy) compared to the pure gold NP and hydrogen in gas phase. Endothermic reactions like this should yield very low coverages on the surface. It seems like the system has been forced to start at a local minimum (due to the dissociation barrier of hydrogen), that would never occur if one started with a pure gold NP and hydrogen in gas phase. How can this simulation be compared with the experiment?

Hazar Guesmi replied: In our simulation, we assumed that under atmospheric hydrogen pressure, the surface of small gold NPs is fully covered by hydrogen. During the AIMD simulation, desorption and recombination of hydrogen atoms to H_2 were observed.

The experimental observations show changes in the structure and morphology of Au NPs and in the morphology of Au–Cu NPs, this means that hydrogen is inducing such changes. Prior to hydrogen exposure, we have followed the stability of the Au and Au–Cu NPs under vacuum and we saw no effect of the temperature nor of the beam. This indicates that the changes are induced by the adsorption of hydrogen.

The dissociation of hydrogen is endothermic over a flat gold surface but it is favorable over under coordinated sites in clusters and NPs. In the Au_{201} nanoparticle the computed adsorption energy is found to be exothermic for H coverage of 0.8 ML.

Marcelo M. Mariscal asked: I have a fundamental question: why you are attempting to adsorb hydrogen on gold nanoparticles? I believe you are not thinking to use gold as an energy storage material.

Hazar Guesmi answered: Gold nanoparticles have been shown to be effective for many catalytic reactions involving hydrogen, such as the selective hydrogenation of dienes and alkynes. The knowledge of the surface structure of gold nanoparticles under reactive media (hydrogen pressure and temperature) is a very important first step to accurately investigate their reactivity and to improve their performances.

Christine Mottet addressed Jaysen Nelayah and Riccardo Ferrando: related to Riccardo's point concerning the structure of Au–Cu nanoparticles of about 400–500 atoms (2 nm). Looking at Fig. 2 of the paper (**https://doi.org/10.1039/d2fd00130f**) it seems that the number of atomic planes suggests a larger size than 2 nm. For this size the nanoalloys should adopt the FCC structure with possible $L1_2$ chemical ordering if annealed a sufficiently long time at not too high temperature. However the icosahedral structure shown in the calculations by Riccardo (Fig. 4 here) should be excluded.

Jaysen Nelayah responded: The presence of an icosahedral structure can indeed be excluded from the STEM contrast shown in Fig. 2 of the paper (**https://doi.org/10.1039/d2fd00130f**). The nanoparticle maintains a FCC structure during the observation period. Moreover, regarding the possible presence of chemical ordering, the sample has been extensively studied using both *ex situ* and *in situ* TEM during the hydrogenation of 1,3-butadiene in a hydrogen-rich environment. In none of these observations, has chemical order been observed.

Riccardo Ferrando replied: The icosahedral structure shown in Fig. 4 here was of size 200 atoms. With increasing size, icosahedra should become less favourable. This point is still to be investigated for AuCu.

Micha Polak addressed Hazar Guesmi and Michael Bowker: (i) In general, can adsorption (not absorption!) be endothermic? (Hint: the role of entropy change.) What about the adsorption of hydrogen on Au–Cu? Does the entropy increase (*e.g.*, Fig. 4 in the paper; **https://doi.org/10.1039/d2fd00130f**)?

(ii) Are the results (under vacuum) similar to those presented by Diana Nelli *et al.* (**https://doi.org/10.1039/d2fd00113f**) (*e.g.*, they obtained a TO → Ih transition)?

Hazar Guesmi answered: (i) The adsorption of molecular hydrogen was reported to be endothermic on flat Au surfaces (as for example the (111) surface) but adsorption and dissociation could occur over under coordinated sites as present in clusters and NPs. Over Au–Cu NPs, the adsorption energies of H_2 are predicted to be more exothermic than on pure gold NPs because of the high affinity of hydrogen to Cu.

(ii) From experimental observations the TOh structure is found to be highly stable in the presence of inert gas. No transition from TOh to Ih structure was found in the absence of hydrogen.

Michael Bowker added: In response to point (i). Yes, adsorption can be endothermic, and long-lived in the right circumstances, those circumstances being a high net barrier to dissociation from the gas phase, into a potential well with bonding to the surface, which is higher in energy than the gas phase. A good way to get such adsorption is hot gas, cold surface, thus gas phase molecules can get over the barrier, but then the dissociated molecules are thermalised to the cold surface and then have difficulty getting over the desorption barrier. Another way is to pre-dissociate the molecules in the gas phase. It is likely that hydrogen and oxygen dissociation on gold are examples of such adsorption, and Madix and colleagues have obtained stable states in just this way on pure single crystal gold.[1] Note that the concept of endothermic adsorption has already been discussed (albeit briefly) in an earlier *Faraday Discussions* (see, for instance ref. 2) and in the textbook by Thomas and Thomas.[3]

1 N. D. S. Canning, D. A. Outka and R. J. Madix, The adsorption of oxygen on gold, *Surf. Sci.*, 1984, **141**, 240.
2 V. Ponec, Z. Knor and S. Černý, *Disc. Faraday Soc.*, 1966, **41**, 149, DOI: 10.1039/DF9664100149.
3 J. M. Thomas and W. J. Thomas, *The Principles and Practice of Heterogeneous Catalysis*, VCH, Weinheim, 1997, p. 84.

Maria J. Lopez enquired: Au–Cu nanoparticles are investigated under hydrogen atmospheric pressure. Have you performed dynamical simulations of the adsorption of molecular hydrogen on the surface of the Au–Cu NPs and its subsequent dissociation into two hydrogen atoms? What are the preferred sites for hydrogen dissociation? In this paper 1 ML of atomic hydrogen is considered for all configurations but, except for one configuration, the coverage of the NP with 1 ML H is endothermic. Therefore, I think it would be interesting to know for the different configurations of the Au–Cu NPs what is the maximum amount of hydrogen that can be adsorbed (exothermally) by the nanoparticle and if such a load of hydrogen is able to induce Cu segregation in the Cu–Au NPs. Did you investigate these points? A related question is if atomic hydrogen diffuses from the surface towards the interior of the nanoparticle, did you observe the inward diffusion of H in the simulations?

Hazar Guesmi replied: We did perform *Ab initio* Molecular Dynamics (AIMD) simulations of the adsorption of molecular hydrogen on the surface of a pure gold NP (Au_{201}). No adsorption process was observed after tens of picoseconds. However, by considering 1 ML of atomic hydrogen adsorbed on Au and Au–Cu NPs, the molecular dynamic simulations show desorption and recombination processes during the time simulation span. And the sites where the desorption occurs are under coordinated sites. These events will be carefully analyzed and activation energies will be calculated by DFT. The study of the stability of Au and Au–Cu NPs in the presence of different hydrogen coverage (saturation/over-saturation/under-saturation regimes) is the subject of an ongoing work. During the AIMD simulation time, no inward diffusion of atomic hydrogen toward the subsurface sites was observed.

Christine Mottet asked: Did you perform the same calculations for hydrogen adsorption on palladium clusters, especially in the sub-surface?

Hazar Guesmi responded: In order to check the accuracy of our *Ab initio* Molecular Dynamics simulation method to predict the adsorption and diffusion of hydrogen atoms over Au nanoparticle TOh_Au_{201}, we performed similar simulations for hydrogen interacting with Pd nanoparticle TOh_Pd_{201} at 300 K. As expected, the results show that atomic hydrogen absorbs in the subsurface of Pd. This absorption process is absent in the case of gold or gold–copper nanoparticles.

Conflicts of interest

There are no conflicts to declare.