Faraday Discussions

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DISCUSSIONS

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Nanoalloy catalysis and magnetic and optical properties: general discussion

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Nanoalloy catalysis, part 3

Ewald Janssens opened a discussion of the paper by Daojian Cheng: Can you comment on the stability of the trimetallic PdAgCu catalysts? Does the structure of the nanoalloys change during the hydrogenation reaction?

Daojian Cheng replied: In this work (https://doi.org/10.1039/d2fd00074a), we did not study the long-term stability of the trimetallic PdAgCu catalysts. According to our experience, the composition and chemical ordering of nanoalloys may change with the temperature upon reaction. Our future work will focus on this point.

Alexander I. Large commented: Regarding your Pd 3d XPS spectra shown in Fig. S6 in the ESI of the paper (https://doi.org/10.1039/d2fd00074a), there seem to be significant peak shape variations in the Pd^{2+} peaks. Were the peak shapes restrained during the fitting process? Related to this, do you have an estimate for the level of error in the fitting process, and how this could affect the Pd^0/Pd^{2+} ratios?

Daojian Cheng answered: The reduction temperature of Pd is very low, and Pd^{2+} can be easily reduced to zero-valent Pd during calcination. Adding metal auxiliaries to the Pd catalyst can significantly hinder the conversion of Pd^{2+} to Pd^0. Therefore, the peak value of Pd^{2+} changes significantly among diverse samples.

There are inescapably some errors in the fitting process, so we have taken the average value by fitting a single sample several times. Moreover, the fitting results are not so different for repeated experiments, and thus there is no change in the relative order of Pd^0/Pd^{2+}.

Jonathan Quinson remarked: In light of other papers in this *Faraday Discussion* (see **https://doi.org/10.1039/d2fd00118g**), I am wondering if you see a size dependent composition of the alloys? And if so, what are the trends and how does that relate to the catalysis?

Daojian Cheng responded: In this work (**https://doi.org/10.1039/d2fd00074a**), the particle size peaks at around 6.27 nm. And the shape of the nanoparticles is spherical polyhedral with no specific atomic ordering. We did not study the size-dependent composition. The issue of size-dependent composition of the nanoalloys is very interesting and important for the application of the catalysts. I think it can be studied not only by laboratory experiments but also by molecular dynamics simulation.

Yufei Zhang asked: Considering the instability of your nanoparticles, do you have any plans to stabilize your nanoparticles such as applying some ligands for more practical use? And will those methods affect the catalytic properties of your nanoparticles?

Daojian Cheng answered: We agree with you that some ligands are useful for the stability of the nanoparticles. However, the aim for our prepared PdAgCu nanoalloys is to use them as industrial catalysts. In general, the equal volume impregnation method without ligands is used to prepare industrial catalysts, since the activity and selectivity will be affected by adding some ligands to the nanoalloys.

Mzamo Shozi communicated: Have you looked at or considered alloys containing nickel or cobalt instead of copper?

Daojian Cheng communicated in reply: In this work (**https://doi.org/10.1039/d2fd00074a**), we did not consider nickel or cobalt instead of copper. This idea is very interesting and we may try to study it in our future work.

Hakim Amara opened a discussion of the paper by Lichang Wang: When you calculate the properties of the bulk material, what is the lattice parameter that you consider? To describe a random structure, why not take into account the SQS structures which are perfectly adapted?

Lichang Wang replied: The lattice parameters were obtained from DFT optimizations of the bulk alloy structures. Three random bulk structures were studied in this work as shown in Fig. S1 in the ESI of the paper (**https://doi.org/10.1039/d2fd00101b**). Their energy differences are negligible, which led us not to investigate more random structures that could be generated using the SQS method. It would be interesting to investigate this in detail including the size of the unit cell.

Didier Grandjean commented: I am wondering whether the electrolyte and its properties can be directly included in the simulation as they strongly influence the leaching and possible deposition process of Cu?

Lichang Wang responded: The effect of the electrolyte on the leaching and deposition process of Cu is certainly an interesting issue to consider in electrocatalysis of the ORR. The electrolyte molecules or dissociated ionic species can be included in the simulation, however, the current calculations did not include them due to the cost of computations.

Francesca Baletto asked: Have you calculated the adsorption map of all the non-equivalent adsorption sites depending on the Cu amount at the surface?

Lichang Wang answered: This is a very interesting question, as it can certainly influence the stability of the nanoparticles. However, we did not perform exhaustive calculations in this work to develop the adsorption map. The adsorption energy was taken from the calculations of the non-equivalent sites at only one Cu surface composition. While we do not expect big differences at different Cu surface compositions based on the many non-equivalent adsorption sites shown in Fig. S2 in the ESI of the paper (**https://doi.org/10.1039/d2fd00101b**), it would be interesting for future studies to fully explore the effect of the non-equivalent adsorption sites as a function of Cu surface composition at different bulk compositions for an accurate description.

Robert M. Jones said: Thank you for the excellent talk. Given that you stated that the surface composition with respect to the Cu is fairly consistent with experimental results and that your calculations in this work (**https://doi.org/10.1039/d2fd00101b**) were done in a vacuum, could you comment on the significance of a lack of environment in keeping Cu at the surface?

Lichang Wang responded: The model system studied in this work are in the gas phase. The effect of the environment was only partially simulated by the incorporation of the adsorbed O species (see Fig. S2–S5 in the ESI of the paper, **https://doi.org/10.1039/d2fd00101b**). The preliminary results indicate that the presence of O species stabilizes surface Cu. Therefore, I would speculate that more adsorbed species will enhance the stability of surface Cu.

Alessandro Fortunelli remarked: Nice work. If I understand correctly, you extract from DFT modelling the values of surface energies by imposing that the oxygen coverage gives a work function that equalizes the given bias. However in our experience, on a pure Pt(111) ORR catalyst, the system achieves the given work function not simply *via* oxygen coverage, but *via* a background of hydroxyls that only partly transform into oxygen species.

Lichang Wang replied: The statements are correct. Indeed, the catalytic surfaces are covered by a variety of adsorbed species, OH, H, reactant species, reaction intermediates, and electrolyte species. The population distribution of these species on the surface depends on the applied potential as well as the surface facet. In this work (**https://doi.org/10.1039/d2fd00101b**), we included only the most abundant species on the (100) surface at the applied potential of 0.9 V, *i.e.* the adsorbed O species, and neglected all the others, such as OH as you mentioned here, in the calculations. This is certainly an important issue to investigate for future studies.

Fuyi Chen commented: This work (**https://doi.org/10.1039/d2fd00101b**) provided an interesting thermodynamics method to examine the stability of a trimetallic PtPdCu catalyst during the ORR, have you considered AIMD simulations to classify the dynamic stability of trimetallic PtPdCu nanoalloys under real working ORR conditions?

Lichang Wang responded: We have not performed AIMD simulations to explore the dynamic stability of trimetallic PtPdCu nanoalloys under real working ORR conditions. However, the current kinetics analysis based on DFT results demonstrates how the dynamic balance among the four processes involved maintains the stability of the trimetallic PtPdCu nanoalloys.

Hans-Christian Weissker opened a discussion of the paper by Valérie Caps: I had not understood from the talk: you talk about the quenching of the SPR by Pt addition to Au clusters. On the other hand, later you say that Pt dominates the response. You are talking about sub-nanometric clusters, so there should be no SPR visible for pure gold clusters and maybe that's why Pt dominates. Is this the main effect, or is there something else going on?

Valérie Caps answered: Sub-nm clusters do indeed exhibit a very limited plasmonic response, as observed for $Au_{2.5}Pt_{2.5}/TiO_2$, which exclusively contains sub-nm clusters. The weak optical absorption observed over Au_5/TiO_2 is attributed to the fact that this sample contains, in addition to sub-nm clusters, large aggregates as identified by SEM (Fig. 3 of the paper, **https://doi.org/10.1039/d2fd00094f**). Quenching of the localized surface plasmon resonance (LSPR) of Au NPs by Pt is observed in all other samples, which contain Au–Pt nanoparticles (6–8 nm). It is characterized by an overall decrease in the absorption in the visible range and, at higher Pt/Au ratios, by the disappearance of the distinct absorption peak shape of Au NP LSPR (located at about 500–580 nm in our samples, depending on their size and aggregation state at high Au loading). In fact, the optical absorption profile of all Au–Pt NPs appears similar to that of Pt NPs (and other metal NPs absorbing in the UV range), hence “dominated by the Pt response”, that is a continuously decreasing absorbance over the whole visible range. This absorption profile for Au–Pt NPs is typical of the occurrence of chemical interface damping.[1]

[1] S. A. Lee and S. Link, *Acc. Chem. Res.*, 2021, **54**, 1950.

Graham J. Hutchings asked: For the Janus particles which show a clear interface between the Pt and Au, how stable are these Janus particles during the reaction; do they form alloys on extended use?

Valérie Caps responded: We did not study the stability of the Janus segregated alloy structure in the reaction because the methane production rates observed over these catalysts were uniquely stable over time, which could suggest stability of the catalyst structure. Besides, the temperature reached upon illumination did not exceed 50 °C, which is well below the temperature at which the catalysts were pre-treated (200 °C in air). We thus did not expect any significant changes to the nanoalloy structure under the reaction conditions. Nevertheless, we will definitely consider this aspect in future work.

Graham J. Hutchings commented: This is very elegant work. Do you observe any partial hydrogenation products *en route* to methane? You might want to consider passing the gas products into a water trap and using NMR spectroscopy as this method is much more sensitive compared with gas chromatography.

Valérie Caps replied: No partial hydrogenation products were detected by micro-GC. If such products are formed and released in the gas phase, the amount produced is thus below the GC detection limit, *i.e.* below 10 ppm, which is minor compared to the amount of methane formed (several hundreds of ppm). To quantify them (or definitely rule out their existence), we would indeed need to trap them and analyze them with much more sensitive techniques.

Robert M. Jones remarked: Thank you for the excellent talk. Could you comment on the size scales within this realm of work, seeing as we generally want large sizes for the photon absorber and a small size for the active component? With these structures, how do we suppress electron–hole recombination if the excited carriers are created far from the active site?

Valérie Caps responded: Limiting electron–hole recombination is the underlying challenge in photocatalysis, whether charge carriers are produced within a semi-conductor or within plasmonic NPs. If the charge carriers are created far from the active site, they will indeed need to diffuse over a longer distance before they can reach the active site and the probability of recombination increases. Decreasing the size of the photon absorber is one option to enhance the probability of the charge carriers reaching the surface. But the general strategy to avoid recombination, and thus enhance charge carrier lifetime and probability of reaction, is to spatially separate electrons and holes. For plasmon-induced catalysis, it is generally accepted that charge separation is provided by the semi-conductor support, as at least some of the hot electrons generated within the bulk of metallic NPs are transferred through the Schottky barrier to the conduction band,[1] while the holes remain on the M NP. The trapped electrons then also escape electron–electron and electron–phonon scattering and are effectively stabilized and available for chemical reaction. It is possible that the reaction then takes place close to the M NP, typically at the M/support perimeter interface, which is a favorable adsorption site for CO_2.

1 S. Mubeen, G. Hernandez-Sosa, D. Moses, J. Lee and M. Moskovits, *Nano Lett.*, 2011, **11**, 5548.

Isaac T. Daniel commented: You note that Pt affinity for titania is poor when Au is not present, have you tried any other changes to the preparation technique (*e.g.* pH) that improve the deposition rate of Pt?

Valérie Caps answered: Platinum deposition may be improved by increasing the temperature of deposition. The synthesis based on sodium borohydride reduction in dimethylformamide is normally performed at room temperature, *i.e.* a temperature of 20–22 °C, which allows the reduction of $NaAuCl_4$ to Au NPs and complete deposition of gold over TiO_2. At this temperature the deposition of platinum is negligible (deposition yield of less than 1%), which is attributed to the poor reduction of the platinum salt (K_2PtCl_4) under these conditions and the poor affinity between the Pt precursor and the titania surface. The Pt deposition yield can be increased to about 50% by performing the synthesis at 140 °C, yielding titania-supported 5 nm Pt NPs (Fig. 3f and 4e of the paper, **https://doi.org/10.1039/d2fd00094f**).

Éric Marceau asked: What is the nature of the active site used for the calculation of TOF: Au, Pt, both? Based on this, can TOF be easily compared between Janus and alloyed particles?

Valérie Caps responded: The turnover frequencies (TOFs) used for the discussion (not included in the paper) took into account the whole metallic surface (Au + Pt), because methane is produced over both Au/TiO_2 and Pt/TiO_2 monometallic catalysts (Fig. 6 and Table 1 of the paper, **https://doi.org/10.1039/d2fd00094f**) and hence both gold and platinum surface sites appear active towards methane production. The metallic surface was determined on the basis of geometric calculations,[1] taking into account the whole metal content determined by ICP and the average NP size determined by TEM (whole round-shaped NPs for core–shell structures and size of the individual Au and Pt components for the Janus NPs), and assuming a pseudo-cuboctahedron shape and using size-dispersion relationships from Van Hardeveld and Hartog (1969).[2] These apparent TOFs aimed to highlight an overall activity trend amongst the catalysts with such different NP loadings, sizes, compositions and nanoalloy structures. They were intended to reflect metal utilization/noble metal efficiency in both Janus and core–shell nanoalloy structures. They clearly show the higher efficiency of the core–shell structure in which the activity per surface site is higher than in Janus NPs.

[1] G. Bergeret and P. Gallezot, Particle size and dispersion measurements, *Handbook of Heterogeneous Catalysis*, Wiley-VCH, 2008, pp. 738–765.

[2] R. Van Hardeveld and F. Hartog, The statistics of surface atoms and surface sites on metal crystals, *Surf. Sci.*, 1969, **15**, 189–230.

Vincenzo Amendola commented: Thank you for your fascinating talk. Beyond energy band levels, it is known that the interface between different components (titania, Au, Pt) is a critical factor for the performance of this type of photocatalysis. Do you have any experimental evidence that the interface coupling between titania and Au differs from that between titania and Pt or titania and Pt–Au? Can you address the contribution of this specific aspect to the efficiency and performance of the photocatalytic process?

Valérie Caps replied: The metal/semi-conductor interface indeed seems key for plasmon-induced catalysis, especially regarding plasmon-induced charge carrier separation and stabilization *via* transfer of hot electrons in the semi-conductor conduction band. In this regard, Au/TiO_2 and Pt/TiO_2 interfaces are not expected to be markedly different; only a slightly higher Schottky barrier is expected for Pt/TiO_2, due to the higher work function of Pt as compared with Au. No major differences in the chemical composition and reactivity of the perimeter interface are expected, with formation of oxygen vacancies and Ti^{3+} sites in both cases. The main differences lie in the intrinsic properties of the metals themselves, regarding reactivity towards light (absorption, dissipation) and reactivity towards CO_2 (adsorption). The superior activity of the bimetallic systems (titania-supported Au–Pt NPs) clearly relies on the interface between Au and Pt, allowing a synergistic combination between the enhanced light absorption properties of Au NPs and the enhanced catalytic properties of Pt NPs, likely *via* absorption enhancement in lossy Pt NPs in contact with Au NPs.[1,2]

1 T. J. Antosiewicz, S. P. Apell, C. Wadell and C. Langhammer, *J. Phys. Chem. C*, 2012, **116**, 20522.

2 A. Joplin, S. A. Hosseini Jebeli, E. Sung, N. Diemler, P. J. Straney, M. Yorulmaz, W.-S. Chang, J. E. Millstone and S. Link, *ACS Nano*, 2017, **11**, 12346.

Mona Treguer-Delapierre asked: Do you have an idea of the quantum yield of e/h that cross the surface of Au NPs?

What is the number of charges which can escape the recombination processes and are involved in the redox reaction on the gold surface?

Valérie Caps responded: The number of electrons escaping the recombination process and involved in the reaction can be calculating using the stoichiometry of the CO_2 reduction reaction ($CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$) and the number of moles of methane produced as determined by gas chromatography (in addition to the number of moles of hydrogen and the stoichiometry of the H^+ reduction reaction ($2H^+ + 2e^- \rightarrow H_2$), when hydrogen is produced too). It is only a fraction of the number of photons emitted by the lamp in the 400–800 nm range (low external quantum efficiency) and generally a fraction of the electrons generated within the bulk of metal NPs upon illumination (absorbed photons). Quantum yields are indeed generally in the order of magnitude of 0.1% (1 in one thousand), which is in line with the order of magnitude of the fraction of hot charge carriers crossing an Au/TiO_2 interface.[1] Only in the case of the weakly absorbing bimetallic sub-nm clusters ($Au_{2.5}Pt_{2.5}/TiO_2$) are the quantum yields somewhat higher.

1 S. Mubeen, G. Hernandez-Sosa, D. Moses, J. Lee and M. Moskovits, *Nano Lett.*, 2011, **11**, 5548.

Swathi Swaminathan commented: It is shown that holes are oxidising water. How do you know that? Did you observe oxygen evolution?

Valérie Caps answered: For methane artificial photosynthesis, CO_2 is reacted with water in the continuous-flow gas phase. Hence water is the reductant and the only source of hydrogen in the system. In the absence of water (*i.e.* flowing CO_2 bypassing the water saturator), no methane is produced. In the absence of a photocatalyst with a suitable band structure, allowing in particular water oxidation, no methane is produced. This implies that water is somehow oxidized with holes, releasing active protons and producing oxygen in the process. However there is no clear detection of gaseous oxygen or oxygen-containing products by GC above the detection threshold. It is possible that these maybe trapped somewhere (at the photocatalyst surface?). We do not exclude the possibility that the reaction may lead to reactive oxygen products (*e.g.* from a reaction between oxygen and hydrogen) that are not detected by our GC.

Didier Grandjean remarked: It is generally accepted that plasmon induced catalysis relies on short lifetime hot carriers generated within the bulk of plasmonic NPs upon LSPR decay that need to be stabilized in the conduction band of an interfaced semiconductor.

I am wondering whether the reaction can take place directly on the surface of the plasmonic nanoparticles without direct intervention of the semiconductor as Au and Pt are also efficient catalysts?

Valérie Caps responded: Preliminary results suggest that the reaction does not directly take place at the surface of the metal nanoparticle. Gold particles (4 nm) deposited on γ-alumina (180 $m^2 g^{-1}$) and silica (Aerosil 200 hydrophilic fumed silica, 200 $m^2 g^{-1}$) for example were found to be inactive in the reaction, while the same particles deposited on titania were active. It is not clear whether the absence of reaction is due to the absence of stabilization of the charge carriers on these non-semi-conductor supports, the less favored CO_2 adsorption or both. Nevertheless, it shows that, in the gold-catalyzed reaction at least, the support does play a role in the reaction. Based on the knowledge acquired in the low temperature gold-catalyzed CO oxidation about the reactivity of the Au/TiO_2 perimeter interface towards CO_2, we can speculate that the support provides, as a minimum, adsorption sites for CO_2 at the periphery of the gold nanoparticles. We have started a more comprehensive study of the support effects for both Pt and Au–Pt plasmonic nanoparticles, which should allow us to answer this question more straightforwardly soon.

Jonathan Quinson said: You performed the synthesis in one pot (in the presence of the support). I am wondering why this choice was made considering that you could expect that the colloidal DMF synthesis (without support) should lead to stable nanoparticles in the solvent, and that the nanoparticles could then easily be immobilised by solvent evaporation. This might have (positively) impacted the final loading you observed.

Valérie Caps replied: Although the syntheses are performed in one pot, supported bimetallic NPs are likely formed in consecutive/sequential steps, due to the poor reducibility and deposition of the platinum salt under the reduction conditions used (DMF/140 °C and $NaBH_4$/DMF/20 °C) and the ability of gold seeds and supported NPs to act as nucleation sites for Pt. Hence, although the methods used do not provide strict control over NP size and composition (due to uncontrolled Pt loading), they do provide a unique way to generate, in one pot, titania-supported bimetallic Au–Pt NPs with segregated Au and Pt phases, *i.e.* interfaced Au/Pt NPs, with unique plasmon-induced catalytic properties for the artificial photosynthesis of methane.

Jonathan Quinson commented: You have a heat treatment in your sample preparation. Maybe I missed it but I am wondering if you assessed if the heat treatment is changing anything (size, composition, morphology) in your samples? (I understand that all characterization was performed after the heat treatment at 200 °C).

Valérie Caps answered: All characterization was indeed performed after the heat treatment at 200 °C. We did not study the influence of the calcination at 200 °C on the size, composition or morphology of the titania-supported nanoparticles. Nanoparticles are formed in the liquid phase by chemical reduction with either DMF or $NaBH_4$ and stabilized on the support upon drying. The post-synthesis heat treatment is designed mainly to clean the surface of any residual hydrocarbons without impacting the supported nanoparticles. It is inspired by works related to the synthesis of size-controlled, oxide-supported gold oxidation catalysts.

Vana Chinnappa Chinnabathini remarked: From XPS investigation, you have shown the charge transfer from Au to Pt. Do you also observe the effect of substrate (TiO_2) and charge transfer from Au to TiO_2 or TiO_2 to Au? What details of XPS will explain the effect of substrate?

Valérie Caps replied: We do observe the presence of electron-rich gold in Au/TiO_2 and in all TiO_2-supported, gold-containing nanoparticles, as evidenced by the lower binding energy of the 4f core electrons of gold found in these samples, as compared with unsupported bulk gold. We infer a charge transfer from TiO_2 to Au NPs which is explained by the higher work function of gold as compared with titania. Upon formation of the Au/TiO_2 junction, electrons indeed flow from the Fermi level of titania to the Fermi level of gold until the levels are aligned, inducing curvature of the semi-conductor conduction and valence bands. A local electric field pointing towards gold at the Au/TiO_2 interface is created, due to the local charge depletion on the titania side and electron enrichment on the gold side.

Jonathan Quinson commented: I understand that you used $HAuCl_4$ as a precursor for the thermal reduction but $NaAuCl_4$ for the $NaBH_4$ reduction. I am wondering if there is any rationale behind this choice and what would happen if the precursors were "switched".

Valérie Caps responded: Both syntheses were inspired by previous work[1] which determined the choice of the gold precursors, as the type of precursor will indeed affect the nucleation *vs.* growth kinetics and hence the resulting NP sizes and structures.

1 H. Kawasaki, H. Yamamoto, H. Fujimori, R. Arakawa, Y. Iwasaki and M. Inada, *Langmuir*, 2010, **26**, 5926, and unpublished results from the lab.

Pinkie Ntola communicated: Have you considered the use of black titania for this application?

Valérie Caps communicated in reply: We have not considered the use of black titania for this application yet.

Christian Kuttner communicated: In the UV-Vis data, the plasmon of the Au5 particles seems to be red-shifted compared to the Au NPs used as a reference. Is this due to the TiO_2 or a difference in size?

Valérie Caps communicated in response: The same TiO_2 is used throughout the study, including for the Au/TiO_2 and Pt/TiO_2 references used for analysis of the UV-vis data (Fig. 1 of the paper, **https://doi.org/10.1039/d2fd00094f**). Hence the red-shift observed in the plasmon position of $Au5/TiO_2$, as compared with that of the Au/TiO_2 reference, may be attributed to a difference in Au NP size, and more specifically to the population of larger metal aggregates evidenced by SEM (Fig. 3 of the paper), which is not present in the reference material.

Fuyi Chen communicated: What is the mechanism of Pt surface segregation? Why did the surface segregation trend change upon increasing the alloy loading?

Valérie Caps communicated in reply: Pt surface segregation is attributed to the preferential nucleation of Pt over supported gold seeds, rather than over the bare TiO_2 surface. The presence of supported gold seeds, when the platinum salt is introduced in the reaction mixture, is attributed to the fact that the gold salt is introduced shortly before the platinum salt and to the faster reduction of the gold salt as compared with the platinum salt. The more extensive/efficient coverage of gold in $Au7.5Pt7.5/TiO_2$ and $Au5Pt5/TiO_2$, as compared with $Au2.5Pt2.5/TiO_2$, is due to the increased Pt/Au ratio (1.22 and 0.98, respectively, instead of 0.22), rather than the increased metal loading. This explanation (Pt deposition on Au seeds) is consistent with the absence in the Pt-containing catalysts of the large metal aggregates found on the monometallic $Au5/TiO_2$ catalyst (Fig. 3 of the paper, **https://doi.org/10.1039/d2fd00094f**), and the occurrence of size control of Au NPs by Pt *via* the Pt–Au interface.

Magnetic and optical properties of nanoalloys, part 2

Alessandro Fortunelli opened a discussion of the paper by Christine M. Aikens: You showed that Pt doping does not increase the luminescence of Au_{25} Monolayer Protected Clusters (MPC): did you try other dopants (such as Cd as you also mentioned)? Or do you think that ligands (in particular conjugated ligands) can play a beneficial role?

Christine M. Aikens replied: Yes, we have looked at a few other dopants such as Cd. If the system maintains the superatomic electron count of 8 (as it does with Cd or Ag dopants), then the luminescence mechanism is essentially the same as the pure $Au_{25}(SR)_{18}^-$ nanoparticle. The actual emission frequency shifts somewhat, but those systems are still luminescent. On the other hand, the systems with 6 superatomic electrons such as the Pt-doped system do not show emission, which we attribute to this very fast relaxation due to intersystem crossing.

There has been some interesting experimental work that suggests that conjugated ligands can help with the luminescence. This is not too surprising, since aromatic ligands seem to have a stronger interaction with the nanoparticle core (perhaps through better wavefunction overlap). We have not personally examined luminescence of these aromatic ligands on $Au_{25}(SR)_{18}^-$, however.

Alessandro Fortunelli said: Nice work. I have a technical question on how you deal with the problem of conical intersections, and if you have found cases in which your approach does not work.

Christine M. Aikens answered: Thank you. As a community, we know that density functional theory is not the best for treating conical intersections. In our work (**https://doi.org/10.1039/d2fd00110a**), we are not trying to characterize the conical intersections themselves. Our approach is to excite a particular excited state and follow its potential energy surface down in energy until it reaches a point where the energy of that state is equal to the energy of the state below it (the calculations may or may not reach a minimum (with a zero gradient), or they may stop with an error due to these degeneracies). The degeneracies indicate the presence of a conical intersection. We then start an optimization of the lower energy state and proceed in this manner until we find a minimum that is well-separated from the next lower energy state (if possible; most states reach degeneracy with the next lower state). This approach of following a potential energy surface down its steepest descent should be distinguished from a true nonadiabatic dynamics approach in which the system is able to switch between states as needed (going up or down in energy) and does not necessarily follow the path of steepest descent. These nonadiabatic dynamics would be needed if we were interested in *e.g.* branching ratios. With our approach, we have been able to find a number of excited state minima, and can explain some cases of dual emission. However, this does not guarantee that we have found all of the excited state minima present for a particular system.

Hans-Christian Weissker asked: For the gold cluster you look at, is it realistic to carry out surface hopping calculations in order to capture the full dynamics? Or would that be too heavy computationally?

Christine M. Aikens responded: We have carried out surface hopping calculations using the classical path approximation with the Prezhdo group approach on the pure $Au_{25}(SR)_{18}^-$ nanoparticle[1,2] and the silver doped system,[3] but we have not reported any dynamics on Pt-doped systems yet. Full surface hopping calculations without the classical path approximation would indeed be too computationally expensive right now.

[1] R. D. Senanayake, A. V. Akimov and C. M. Aikens, *J. Phys. Chem. C*, 2017, **121**(20), 10653–10662.

[2] R. D. Senanayake and C. M. Aikens, *Phys. Chem. Chem. Phys.*, 2020, **22**, 5272–5285.

[3] P. Pandeya, R. D. Senanayake and C. M. Aikens, *J. Chem. Phys.*, 2021, **154**, 184303.

Didier Grandjean remarked: You report that the type of ligands around the $Au_{24}Pt$ cluster can directly affect the structure and electronic properties and shift the absorption energy.

Do they also play a direct role in the cluster luminescence? Can the observed shift of the absorption energy be linked to a crystal field effect created by the ligands? How could these effects be quantified?

Christine M. Aikens answered: We have previously looked at ligand effects on the pure Au_{25} system, and we see that the ligands can affect the specific emission energy, but they do not change the basic underlying physics (*i.e.* excitations among superatomic orbitals and the Jahn–Teller splitting that occurs). The degree of geometrical distortion that occurs in the optimized excited state does change to some extent with the chosen ligand. We have not considered possible crystal field effects, although a simple crystal field model does indeed lead to the observed splitting between D orbitals that is known for Au_{25}. It may be possible that aromatic ligands, which interact more strongly with the core, could lead to new effects in the emission mechanism, but we have not looked at these systems yet.

Alessandro Fortunelli asked: Still on the problem of increasing luminescence, do you know the work on silver doped Au_{25} Mono-layer Protected Clusters (MPC) and what do you think of this possibility?

Christine M. Aikens replied: We have been interested in silver/gold doping effects on photoluminescence for some time. We found that doping gold with silver (or silver with gold) does affect the emission energy and radiative lifetimes; again the basic physics for the process is essentially the same as for the pure Au_{25} system, so these are quantitative but not qualitative changes.[1] We have separately looked at the nonradiative dynamics of these systems.[2] This work shows us some of the factors that may be involved in the improved quantum yields (such as changes in the HOMO–LUMO gaps), although we are not actually able to calculate the experimental quantum yields.

[1] K. L. Dimuthu, M. Weerawardene and C. M. Aikens, *J. Phys. Chem. C*, 2018, **122**(4), 2440–2447.

[2] P. Pandeya, R. D. Senanayake and C. M. Aikens, *J. Chem. Phys.*, 2021, **154**, 184303.

Hans-Christian Weissker commented: In your calculation, you look at different transitions, and you say that you have in the absorption several very weak transitions from the d-band. But then, when you calculate the emission, you seem to talk only about the super-atom states. Would that not risk potentially missing some dark states that might be important for your emission?

Christine M. Aikens responded: We did actually look at the low energy transitions from the d-band in addition to the ones from the superatomic orbitals. These states are very dense, and so they tend to quickly reach a point at which the state is degenerate with the next lower energy state, and we expect fast intersystem crossing through this manifold of d-band states. Of note, the one state (S_3) that we found that has a reasonable gap to the next lower energy state arises from a d → P transition, whereas the first and second excited states arise from P → P. So, it may be possible to observe this state, given an appropriate experimental detector.

Stephan Barcikowski asked: If you threw away all ligands (still having 24 core atoms), would the core behave the same after Pt doping if it was surrounded by water (*e.g.* with hydroxy adsorption)?

Christine M. Aikens replied: The behavior of the system will greatly depend on its geometric and electronic structure. Without the thiolate ligands, it is possible that all 25 metal atoms would have a compact core (rather than a 13-atom core with 12 atoms forming gold-thiolate motifs). It is critically important to know how a new ligand (such as water or hydroxy) interacts with the core: what the binding motifs are, how many electrons are extracted from the total count, *etc.* The pure gold nanocluster is likely to have its behavior strongly affected.

Fuyi Chen communicated: In the Computational details section of the paper (**https://doi.org/10.1039/d2fd00110a**), why is $Au_{24}Pt(C_3H_7)_{18}$ optimized by using the lowest energy isomer with single-atom substitution as the initial input structure, while for $Au_{24}Pt(SH)_{18}$, single-atom Pt substitution is used as the input structure for all calculations?

Christine M. Aikens communicated in reply: Thank you for the opportunity to clarify. For both systems, a slightly flattened (oblate) core is needed for the doped cores due to the superatomic electron count of 6 compared to the crystal structure of the pure system. For the system with propyl ligands, we considered a wide variety of propyl group orientations (which came from various pure crystal structures, as referenced in the paper, **https://doi.org/10.1039/d2fd00110a**) in order to determine the lowest energy isomer, whereas the SH ligands did not have this degree of orientational flexibility, so only the Au_{25} anion crystal structure was used.

Ewald Janssens opened a discussion of the paper by Junpeng Wang: You use an interesting laser ablation technique with Ag strips on a Pt target to make the PtAg nanoalloys. Using EDX characterization of the materials, you could determine the composition of the particles afterwards (Fig. 3f of the paper, **https://doi.org/10.1039/d2fd00102K**). Is there a one-to-one relation between the Ag and Pt surface areas in the laser ablation target and the final composition of the PtAg nanoalloys? The ablation yields of Ag and Pt are not identical.

Fuyi Chen answered: There is not a one-to-one relation between the Ag and Pt surface areas in the laser ablation target. The Ag surface area in the laser ablation target is less than that of Pt. We adjusted the number of Ag strips according to analyzed yields of Ag and Pt.

Jonathan Quinson asked: Maybe I missed it but did you have any stirring or bubbling during the electrochemical experiments? Given the "porous" like structure you obtained, I wonder how much of the different catalytic activity you observe could be due to mass transport and size of the pores and how much was actually due to composition effects (excluding a composition–size relationship), especially for $Pt_{75}Ag_{25}$ and $P_{50}Ag_{50}$ and maybe $Pt_{25}Ag_{75}$ since you stressed the importance of diffusion control (*e.g.* on page 17 of the paper, **https://doi.org/10.1039/d2fd00102K**).

Fuyi Chen replied: I did not have any stirring or bubbling during the electrochemical experiments. "How much of the different catalytic activity was due to mass transport and size of the pores and how much was actually due to composition effects" is an interesting question; we will explore how much of the different catalytic activity was due to mass transport and size of the pores and how much was actually due to composition effects in our next work.

Jonathan Quinson enquired: Could you clarify Fig. 9e of the paper (**https://doi.org/10.1039/d2fd00102K**)?

In particular I wonder what is behind the two arrows at 2000 and 4000 seconds. The caption states "replacement" of electrolyte but the Experimental section (pp. 5–6 of the paper) states that 2 different treatments were performed, one to "clean" and one to "activate". I understand you changed the electrolyte. But did you add fresh electrolyte or actually change the whole electrolyte? Were both CV treatments re-performed or was only one re-performed at 2000 and 4000 s? Thanks.

Fuyi Chen responded: We performed cyclic voltammetry (CV) four times from 0.03 V to 1.53 V *vs.* RHE to reactivate the catalyst. The arrows indicated the CV action.

Didier Grandjean opened a discussion of the paper by Emmanuel Cottancin: You mentioned several promising strategies to keep nanoalloys including non-noble metals stable in air in the long-term but most of them are still not fully efficient and oxidation generally occurs after some time.

Do you still believe that these type of nanoparticles, in particular the plasmonic ones, will be able to compete with the stability of noble metal nanoalloys in future applications?

Are there other approaches available against aging oxidation?

Emmanuel Cottancin answered: This work is very exploratory (there are very few publications on such systems) and our results are encouraging because we observed the presence of metallic Al (or In) inside the BNPs, even after aging. Nevertheless, we are aware of the difficulties to overcome to obtain systems stable against oxidation with LSPR far in the UV range.

We do not know if our proposed strategies will be successful, but we hope that some of them will work. If we can elaborate larger BNPs, the thickness of the oxide shell should be sufficient to protect the metallic cores from oxidation, if the oxide shell remains impermeable! Studies with other matrices should also be carried out, which is also time consuming. But if BNPs with intermetallic or ordered alloyed phases can be stabilized in impermeable matrices, we will have succeeded.

Finally, regeneration after annealing can also be an alternative. We indeed obtained during the thesis work of Élise Camus a sample (Al–Ag in a silica matrix) which remained stable over a long time (one year) after a series of annealing treatments under a reducing atmosphere at various temperatures with LSPR at

375 nm (see the figure below or page 86 of her PhD thesis, "Propriétés optiques et structurales de nano-alliages bimétalliques et spectroscopie *in situ* de nano-objets individuels" by Élise Camus, available in a few months on HAL). Unfortunately, we do not know the size of the BNPs after annealing nor their structure. It is also very time consuming work.

D) Recuits supplémentaires sur $Ag_{50}Al_{50}$

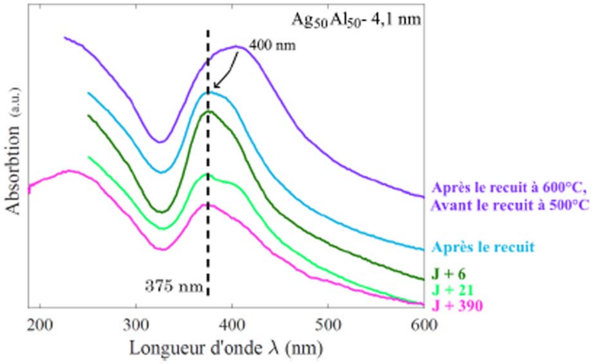

FIGURE 4.19 – Spectres d'absorption expérimentaux d'absorption d'agrégats $Ag_{50}Al_{50}$ - $\phi = 4{,}1$ nm en matrice de SiO_2 avant recuit, et après un second recuit à 500 °C (1h30) puis après plusieurs jours de vieillissement.

Trivalent-based BNPs are the only systems with LSPR in the UV range. With noble NPs it is not possible to go below 400 nm. Depending on the type of applications, such systems should indeed compete with noble metal-based NPs provided they remain stable against oxidation.

Kobe De Knijf asked: What are the parameters or particle properties that affect the rate of oxidation for the studied nanoparticles?

Emmanuel Cottancin replied: The metals (Al, In, Ag and Au) in the BNPs are differently sensitive to oxidation, with aluminium being the most sensitive (see Ellingham diagrams). The rate of oxidation is therefore primarily related to the nature of the metals constituting the BNPs. In our paper (**https://doi.org/10.1039/d2fd00109h**) we showed that aluminium-based BNPs were more rapidly oxidized than indium-based BNPs, with oxidation occurring even under ultra-high vacuum (see the ESI of the paper). However, after long-term air exposure, the nature of the matrix will also play a key role. Silica protects for a few tens of minutes, while alumina or carbon can prevent oxidation for longer. Other matrices should also be tested in the near future.

Christian Kuttner enquired: Is the porosity of the SiO_2 shell the main problem or are there other reasons for switching to a protective Al_2O_3 shell?

Emmanuel Cottancin responded: The porosity of silica remains indeed the main problem, since the produced BNPs (preformed in the gas phase) are initially metallic. However, alumina is probably not the best candidate as it is also porous and oxygen permeable. Other matrices should be tried and the influence of the temperature of the substrate during co-deposition will also be investigated.

Marcelo M. Mariscal commented: Fig. 5a of your paper (**https://doi.org/10.1039/d2fd00109h**) shows the theoretical absorption spectrum of Au@Al@Al_2O_3 (dashed line), I think it was calculated using the phenomenological Mie theory? A couple of years ago, we published in ref. 1 a paper (using time-dependent DFTB) where we studied the effect of oxidation of Al NPs and we observed that the oxide layer produces an optical response that is characterized by a red-shift, a broadening and a decrease in the intensity of a dipole SPR band associated with aluminum nanostructures.

1 O. A. Douglas-Gallardo, G. J. Soldano, M. M. Mariscal and C. G. Sánchez, *Nanoscale*, 2017, **9**, 17471.

Emmanuel Cottancin answered: Indeed these calculations were conducted with the Mie theory in the dipolar approximation. In our case, we have two metals (a particle made of a gold core surrounded by a metallic inter-shell of aluminium and an outer-shell of Al_2O_3 embedded in the matrix of silica). When the aluminium is partly oxidized, the size of the core is reduced, but it still contains the pure metallic gold core with a metallic aluminium inter-shell leading to LSPR at about 511 nm. In your paper,[1] a pure aluminium cluster in a vacuum is considered and the effect of oxidation induces the redshift, broadening and even disappearance of the LSPR when all the aluminium is oxidized. Even if your model is more accurate, Mie calculations within the dipolar approximation on a pure aluminium sphere (progressively oxidized) lead to similar results. We have already performed such calculations on the oxidation of a pure indium sphere within the dipolar approximation (see Fig. SI1 of ref. 2) showing the progressive redshift, broadening and damping of the LSPR with increasing oxidation level; calculations with aluminium should give the same results in agreement with the results of your paper.

1 O. A. Douglas-Gallardo, G. J. Soldano, M. M. Mariscal and C. G. Sánchez, *Nanoscale*, 2017, **9**, 17471.
2 E. Cottancin, C. Langlois, J. Lermé, M. Broyer, M.-A. Lebeault and M. Pellarin, *Phys. Chem. Chem. Phys.*, 2014, **16**, 5763–5773.

Vincenzo Amendola remarked: Thank you for your talk and original work.

Concerning the problems of oxidation, it would be useful to reduce the permeability of the matrix to atmospheric oxygen and prolong the observation time for the study of optical properties. To this end, is your synthetic procedure compatible with the use of a polymeric matrix or a crystalline transparent salt crystal instead of porous alumina?

Emmanuel Cottancin replied: It is indeed a good idea to use other matrices to reduce the porosity to oxygen, and this is exactly what we want to do. We have already worked with other matrices such as LiF or MgF_2 instead of alumina, but the results were not convincing. Assays will be performed with other matrices such as Si_3N_4. Using polymers can also be a good idea if they can easily be evaporated under high vacuum. They also have to be transparent in the UV range.

However, previous work in our group concerning silver NPs in polymers showed that polymers are more difficult to evaporate and often non-protective.[1,2]

Another way might be to maintain the substrate at high temperature during co-deposition and let it cool down very slowly under high vacuum. We indeed obtained stable copper metallic NPs embedded in alumina in this way while the NPs were oxidized if the co-deposition was performed at room temperature.[3]

1 R. C. Hensel, M. Moreira, A. Riul Jr., O. N. Oliveira Jr., V. Rodrigues and M. Hillenkamp, *Appl. Phys. Lett.*, 2020, **116**, 103105.

2 R. C. Hensel, M. L. Braunger, B. Oliveira, F. M. Shimizu, O. N. Oliveira Jr., M. Hillenkamp, A. Riul Jr. and V. Rodrigues, *ACS Appl. Nano Mater.*, 2021, **4**, 14231–14240.

3 G. Celep, E. Cottancin, J. Lermé, M. Pellarin, L. Arnaud, J. R. Huntzinger, J. L. Vialle, M. Broyer, B. Palpant, O. Boisron and P. Mélinon, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **70**, 165409.

Hans-Christian Weissker asked: Is there a way to do valence photoemission on these clusters?

Emmanuel Cottancin answered: Yes it should be possible to perform photoelectron spectroscopy experiments to probe the density of states near the Fermi level, but for deposited NPs, we will get the signal of both the NPs and the carbon substrate. It will be difficult to extract the density of states from the NPs only.

Fuyi Chen communicated: What is the distribution of oxygen in the energy dispersive X-ray spectroscopy for $Au_{0.33}Al_{0.67}$ NPs after exposure to air?

Emmanuel Cottancin communicated in reply: Unfortunately, after exposure to air, oxygen is probably almost everywhere on the substrate and it is therefore impossible to obtain its distribution inside the nanoparticle.

Francesca Baletto commented: Usually TD-DFT methods estimate single transitions. I'm wondering whether numerical methods can distinguish between single and multiple excitations (eventually not plasmonic) and whether experiments can differentiate between single and multiple transitions.

Emmanuel Cottancin responded: As far as "numerical calculations" concern our classical calculations to simulate the optical response of the considered nanoalloys in the publication, they do not distinguish between single and multiple excitations. Concerning the semi-quantal calculations performed in our group, please see the answer to the next question. In our experiments we cannot differentiate between single and multiple excitations. Several methods to discriminate between collective (metallic) and single-electron (molecular) behaviour are described *e.g.* in ref. 1.

1 M. Zhou, T. Higaki, Y. Li, C. Zeng, Q. Li, M. Y. Sfeir and R. Jin, *J. Am. Chem. Soc.*, 2019, **141**(50), 19754–19764, DOI: 10.1021/jacs.9b09066.

Ewald Janssens addressed Christine M. Aikens and Emmanuel Cottancin: With increasing particle size, molecular-like excitations in calculated absorption spectra bunch around the plasmonic response. Can you explain how it is possible that calculated single electron excitations contain information about a plasmonic response, which is per definition a many-body effect?

Christine M. Aikens replied: This is a question that has motivated much of our group's work on plasmonic systems. In TDDFT, RPA, and related methods, an excited state is able to be represented as a multideterminantal wavefunction. A given number of determinants (which represent single-particle transitions) leads to the same number of excited states; for example, three single-particle transitions with the same symmetry (such as "HOMO to LUMO+2", "HOMO−1 to LUMO+1", and "HOMO−2 to LUMO") will lead to three excited states of the same symmetry. However, it is possible for one of the excited states to pick up all of the oscillator strength of all three transitions, in a phenomenon known as "oscillator strength borrowing". The mathematics for this are relatively straightforward (two recommended references are ref. 1 and 2). The more single-particle transitions involved, the higher the oscillator strength can become. Plasmonic excitations typically have strong coupling between the single-particle transitions, which enables this process. Interestingly, the strong peak has all of the characteristics typically expected of a plasmonic excitation, such as the oscillation of electrons from one side of the nanoparticle to another. The many-body effects arise because of the multideterminantal nature of the excited state and the fact that the excited state picks up the oscillator strength from multiple determinants (representing single-particle transitions).

1 E. B. Guidez and C. M. Aikens, *Phys. Chem. Chem. Phys.*, 2014, **16**, 15501.
2 E. B. Guidez and C. M. Aikens, *Nanoscale*, 2014, **6**, 11512.

Emmanuel Cottancin responded: One way to look at it is within the semi-quantal model we have used in our group for many years. Here a jellium-like description of the ionic background potential gives rise to a harmonic Hamiltonian describing the centre-of-mass oscillation of the electron cloud (corresponding to the collective plasmonic movement). The non-harmonic corrections at the particle surface introduce additional terms, which ensure coupling of the collective centre-of-mass motion and the single electron excitations. Thus, the (spectrally) narrow plasmon excitation coupled to the multitude of single-electron excitations forms the expected slightly red-shifted Lorentz profile (see ref. 1). From an atomistic, bottom-up point of view one can consider a concentration of single electron excitations within a narrow spectral region; the larger the particle, the larger the number of excitations. If the particle is metallic, *i.e.* the valence electrons are delocalized over the entire particle, the corresponding centre-of-mass movement can be defined and corresponds to the coherent excitation in the external field.

1 J. Lermé, C. Bonnet, M.-A. Lebeault, M. Pellarin and E. Cottancin, *J. Phys. Chem. C*, 2017, **121**, 5693–5708.

Hans-Christian Weissker commented: The ligands are stabilizing the structures and the interfaces are very complex. In particular, in the staple motifs, a gold ad-atom is held between each pair of thiolates. When you remove the ligands, what is happening to the structure, in particular, what is happening with the ad-atoms which obviously will not be stable in the same positions when the ligands are removed?

Noelia Barrabés replied: This is an open question. In previous work using CeO_2 as a support, we observed the collapse of the staple motifs with the gold core during pretreatment at moderate temperatures. Thereafter, at higher temperatures, the migration of the staple motifs to the surface was observed and they strongly interact with the surface.[1,2] This resulted in some Au atoms being isolated from the staple on the support surface or forming small clusters (2–3). However, a clear indication of ligand migration was not observed for bimetallic clusters and for other supports; in these cases, migration of metal atoms from the staple to the Au core was more likely, but complete experimental evidence related to the Au atoms from the staples has still not been obtained.

1 B. Zhang, A. Sels, G. Salassa, S. Pollitt, V. Truttmann, C. Rameshan, J. Llorca, W. Olszewski, G. Rupprechter, T. Bürgi and N. Barrabés, *ChemCatChem*, 2018, **10**, 5372–5376.
2 S. Pollitt, V. Truttmann, T. Haunold, C. Garcia, W. Olszewski, J. Llorca, N. Barrabés and G. Rupprechter, *ACS Catal.*, 2020, **10**(11), 6144–6148.

Alessandro Fortunelli remarked: I agree with the comments by Noelia Barrabés and I agree that the experience acquired in the field of mono-layer-protected clusters proves that the interface is critical. In this sense, I wonder whether in the systems investigated by Emmanuel Cottancin it is possible to obtain information on the structure of the interface between the metal core and the oxide protecting layer: this could help in designing or stabilising the interface so as to avoid oxidation and aging processes that in this case deteriorate the plasmonic response.

Emmanuel Cottancin responded: Using transmission electron microscopy (HR-(S)TEM) may be a possibility for probing the chemical elements and their structure at the interface, but obtaining high-resolution between the core and the shell is more challenging. This is related to the fact that the particle must be stable under the electron beam. The use of low-dose electron microscopy could allow high-resolution at the interface on beam sensitive material structures.

Complementarily, average spectroscopic techniques, like photoemission spectroscopy could give chemical information about the oxidation state with a good accuracy, if the oxide layer is limited to one or two monolayers around the particles, maybe in addition to EXAFS measurements sensitive to the interface oxidized structure.

Miguel Jose Yacaman answered: I agree that HREM of the core–shell interface is very difficult to obtain. Normally the beam will be focused at the surface of the shell. Focusing on the core–shell interface will induce interference problems between the top surface and the interface.

Francesca Baletto commented: As a general point, in the last few decades, the nanoalloys field has expanded and showed its potential for various technological applications. Nonetheless, a picture of the complex interplay between nanoalloys and the environment is still missing. I am referring to the role of ligands (innocent or not); the effect of water during the formation processes; the role of an atmosphere rich in hydrogen and oxygen during chemical reactions.

Stephan Barcikowski remarked: Slides were presented on the stability (and photoluminescence) of gold and platinum doped gold atom clusters without ligands. Does this represent peeled apples, or pears?

Noelia Barrabés responded: The monolayer protected clusters, for example in the case of Au, the core structure is stabilized by staple motifs, which can have different configurations. It has already been investigated that the electronic configuration is influenced by the staple motifs, which also affects properties such as photoluminescensce, reactivity or chirality. Once the ligands are removed, these properties also changed. Furthermore, not only the staple motif affects the properties, but also the type of ligands attached. An exampleof this is the chirality induced into the metal structure by chiral ligands. Therefore, I would say we are speaking about apples and pears when we compare"bare" metal clusters with ligands protected metal clusters.

Alessandro Fortunelli replied: I agree with the comments by Noelia Barrabés that ligand-protected and unprotected clusters are like apples and pears. Luminescence can nevertheless occur in both systems. One of the cleanest cases for bare clusters is Au_{20} embedded in a rare-gas matrix as investigated by Harbich.[1]

1 C. Yu, W. Harbich, L. Sementa, L. Ghiringhelli, E. Aprá, M. Stener, A. Fortunelli and H. Brune, *J. Chem. Phys.*, 2017, **147**, 074301.

Conflicts of interest

There are no conflicts to declare.