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The wet synthesis and quantification of ligand-free sub-nanometric Au clusters in solid matrices†

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The synthesis of ligand-free sub-nanometric metal clusters on a large scale suffers typically from very low yields (<5% yield) and needs very high dilutions. Here we show that Au clusters can be prepared with ethylene-vinyl alcohol copolymers (EVOH), charcoal, and different metal oxides (CeO₂, Al₂O₃, TiO₂ and ZnO) in >15% yields, as unambiguously determined using a very simple and extremely sensitive analytical reaction test.

Sub-nanometric, ligand-free clusters of few metal atoms (13 or less) show remarkable catalytic,^{1–4} electrochemical,⁵ optical⁶ and biological properties.⁷ In contrast to nanoparticles (NPs), the small size of the clusters pinpoints all the metal atoms on the surface and enables high accessibility to external reagents, provided that strong ligands do not cover the surface.⁸ However, the bottleneck for the general use of ligand-free small metal clusters in any application is their synthesis and storage for long periods. To date, the main synthetic method for preparing sub-nanometric metal clusters in solution, without the aid of ligands, consists of the electrochemical etching of metallic plates in high-diluted solutions (10^{–6} M) with typical yields of <5%.⁷ Other alternatives, based on mass-selected soft-landing techniques on solids⁹ or the controlled chemical treatment of solid-supported metal precursors,¹⁰ do not significantly alleviate the inherently low yield of clusters during large scale synthesis.

An additional drawback when preparing and using sub-nanometric metal clusters is readily differentiating the clusters from the remaining metal salts and NPs. For that, a combination of techniques, including high resolution transmission electronic

microscopy (HRTEM) and near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) techniques, together with mass spectrometry (MS), and ultraviolet-visible absorption (UV-vis) and emission (fluorescence) spectrophotometry, are employed. Despite the valuable information given by these techniques, their instrumental, economic and time-consuming limitations, and the potential modification of the sample during *ex situ* analysis, make it difficult in some cases to ascertain accurately the number of clusters. Thus, it seems that more simple and routine methodology to precisely probe sub-nanometric metal clusters would be of interest.

Here, a simple reaction test based on the one-pot acylation-ester assisted hydration of alkynes, which is a reaction exclusively catalyzed Au clusters of 3 to 7 atoms (Au_{3–7}) that are stable during the reaction,^{2,11,12} is developed as an analytical tool to unambiguously differentiate and quantify sub-nanometric Au clusters from salts and NPs. The test is first validated with different samples of sub-nanometric Au clusters on nanoceria (Au-*n*CeO₂), and then applied to a series of new solids containing sub-nanometric Au clusters. These solids are prepared from simple Au precursors using bottom-up and top-down approaches, with a >10% yield of sub-nanometric Au clusters. In the bottom-up approach, a biocompatible ethylene-vinyl alcohol (EVOH) copolymer encapsulates and mildly reduces a Au salt inside the polymer matrix, to give sub-nanometric clusters. In the top-down approach, I₂ solutions dislodge Au NPs supported on charcoal, Al₂O₃, TiO₂ and ZnO, into sub-nanometric Au clusters and isolated atoms.

First, the synthesis and determination of Au clusters supported on nanoceria (*n*CeO₂) was accomplished. *n*CeO₂ has a high number of vacancies to stabilize catalytically active Au species,^{13,14} and the amount and nature of these Au species depends on the metal precursor and the reducing treatment employed.^{15–18} Hydrogenation at 200 °C of *n*CeO₂ properly impregnated with HAuCl₄ gives, according to X-ray photoelectron spectroscopy (XPS, see ESI,† Fig. S1) and carbon monoxide-probe infrared spectroscopy (CO-IR, Fig. S2, ESI†), up to ~15% of cationic Au species. These species, originally assigned as Au⁺ and Au³⁺ cations, can however be better ascribed to sub-nanometric cationic Au clusters,

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according to further characterization¹⁹ and reactivity^{11,20} studies. To confirm that the cationic species in Au-*n*CeO₂ corresponds to Au clusters and not to isolated Au atoms, cyclic voltammetry measurements were obtained, and the results (Fig. S3, ESI†) show that two consecutive cathodic processes at potentials close to those for the alteration of Au^{δ+} to Au^{δ-x}, and then to Au(0), occur, with the height of these signals significantly decreasing or even disappearing under the application of more severe reductive treatments.^{21,22} These electrochemical results further support that small Au^{δ+} clusters, and not isolated Au cations, are formed on Au-*n*CeO₂ after hydrogenation at 200 °C; however, as with the above-mentioned characterization techniques, they do not unambiguously discriminate and quantify the amount of sub-nanometric Au clusters in Au-*n*CeO₂. Since other complementary methods to characterize very small Au clusters, such as HR-TEM and UV-vis, are severely hampered for Au-*n*CeO₂, the former due to the heavy Ce atom framework and the latter because absorption in *n*CeO₂ occurs just where sub-nanometric Au clusters absorb (Fig. S4, ESI†), a simple reaction test was developed in order to unambiguously assess the presence and amount of Au^{δ+} clusters in Au-*n*CeO₂.

Fig. 1 shows the reaction test, which consists of a specific reaction catalyzed by Au clusters, *i.e.* the one-pot acylation-ester assisted hydration of alkynes under standard reaction conditions (25 °C, 1 M).[‡] The kinetic profile of the reaction clearly discriminates isolated Au atoms, sub-nanometric Au clusters and Au NPs. For instance, Au salts, including AuCl, AuCl₃ and Au(OH)₃, transform into catalytically-active sub-nanometric Au clusters after an induction time of up to 8 h, under the reaction conditions of the test, to give a clear sigmoidal curve; in contrast, Au₃₋₅ and Au₅₋₇ clusters, stabilized²³ or not^{24,25} with PAMAM-OH dendrimers in aqueous solutions, give a clear first-order curve, and commercially-available colloid solutions of 5 or 10 nm Au NPs do not transform into sub-nanometric Au clusters and remain mainly inactive. Thus, after calibration with exact amounts of pure Au₃₋₇ clusters, it is now possible to correlate the number of clusters in Au-supported solids with the initial rate from the reaction test.

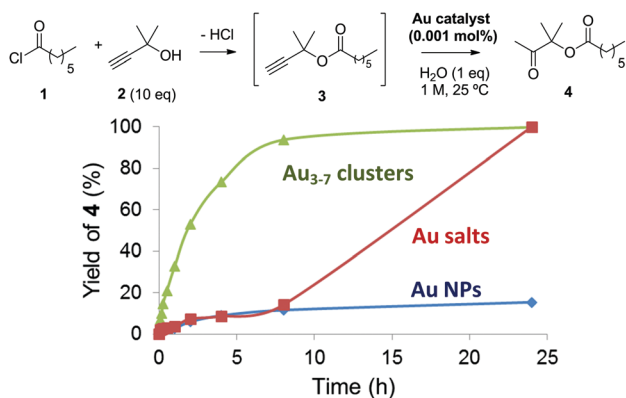


Fig. 1 Reaction test with 0.001 mol% of representative Au catalytic species: Au₃₋₇ clusters prepared using the electrochemical method (green triangles), AuCl (red squares), and colloidal Au NPs of ~10 nm (blue diamonds). The lines are a guide for the eye.

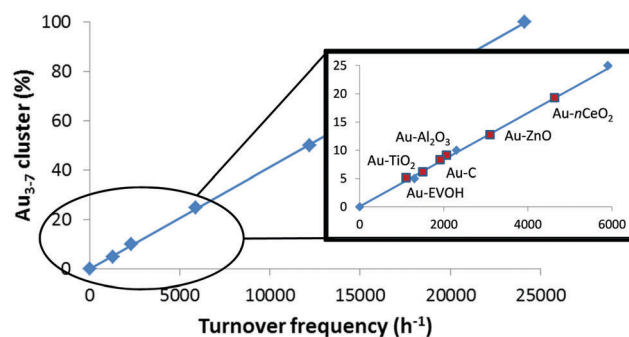


Fig. 2 Calibration line obtained for neat Au₃₋₇ clusters with respect to their initial turnover frequencies, and the quantification of sub-nanometric Au clusters in the different Au-supported solids prepared herein (inset) according to the test.

Fig. 2 shows the calibration line and the results obtained for different Au-supported solids. The sample of Au-*n*CeO₂ hydrogenated at 200 °C shows a catalytic activity that corresponds to 18% Au₃₋₇ clusters, with respect to the total Au in the solid (see also Fig. S5, ESI†). This value nicely fits the 15% Au^{δ+} found using XPS. Other samples of Au-*n*CeO₂, including a sample reduced with hydrogen at 500 °C and a sample reduced with phenylethanol,¹⁸ were tested, and a clear linear correlation between the amount of Au₃₋₇ clusters found using the reaction test and the corresponding relative Au^{δ+} area from XPS was found (Fig. S6, ESI†). Different batches of Au-*n*CeO₂ samples, prepared under similar conditions, gave identical results.

The removal of the Au-*n*CeO₂ solid using filtration after a few minutes does not change the reaction profile, which indicates that the support merely leaches Au clusters into solution during the reaction test (Fig. S7, ESI†). A sample of Au-*n*CeO₂ with 15% Au clusters, a sample of *n*CeO₂ impregnated with 15% neat Au₃₋₇ clusters, and 15% neat Au₅₋₇ clusters in solution, all give similar catalytic activity (~4000 h⁻¹), which confirms that the supporting *n*CeO₂ does not interfere in the reaction test, and just provides Au clusters for the reaction. If the reaction test is performed with ester 3 as the starting material instead of 1 and 2, the initial reaction rate is very similar, and the reaction proceeds with a similar kinetic profile (Fig. S8, ESI†) with Au@EVOH as a catalyst (see below). These results indicate that the HCl liberated during the reaction test does not cause any modification of the solid catalyst and does not generate additional Au clusters. Thus, it seems that the reaction test can be expanded to other Au-supported solids, regardless of the amount of Au supported or the amount of available solid, since the extremely sensitivity of the analytical reaction allows the test to be run with less than 1 milligram of Au catalyst.

The synthesis of Au clusters was then attempted in polymers. EVOH co-polymers are a family of semi-crystalline random materials widely used in the food-packaging sector, due to their outstanding gas barrier properties against oxygen and organic compounds (solvents and food aromas), as well as their considerable chemical resistance and high transparency. It has been recently reported that Cu salts mildly reduce to clusters during EVOH film preparation, in such a way that solid films with similar properties to the pristine

polymers, but with Cu clusters within their structure, are obtained.²⁶ With this in mind, the formation of Au clusters within an EVOH co-polymer was carried out through dissolving $\text{AuCl}_3 \cdot 3\text{H}_2\text{O}$ in a co-polymer hydroalcoholic solution and forming a film at 80 °C. Fig. 3 shows an aberration-corrected HR-TEM image of the Au@EVOH material obtained, cut with a microtome, where the successful formation of sub-nanometric Au clusters inside the polymer can be observed and analyzed using energy-dispersive X-ray spectroscopy, together with some Au NPs.

The Au@EVOH material admits up to 0.2 wt% Au without appreciable Au NP formation, and contains 5% of Au_{3-7} clusters according to the reaction test (see Fig. 1). UV-vis and fluorescence spectrophotometric measurements of the leached Au clusters, combined with MS and dynamic light-scattering (DLS) techniques, confirm that cationic Au_{3-7} clusters are mainly present inside the co-polymer, regardless of the thickness of the film processed, the ethylene molar percentage of EVOH copolymer used, and the use of UV radiation during the curing process (Fig. S9, ESI†). For the sake of comparison, the synthetic procedure was carried out with carvacrol, a known mild reducing agent, and Fig. 3 shows that mainly Au NPs are formed in this case (red film), showcasing the exquisite aggregation control exerted by EVOH to form sub-nanometric Au clusters (yellow film).

After synthesizing $\text{Au}-n\text{CeO}_2$ and Au@EVOH using bottom-up approaches, starting from different Au salts, attention was turned to charcoal and other inorganic oxide supports. However, solids without vacancies are not so prone to stabilizing Au species below 1 nm *via* the reduction of supported Au cations. Indeed, statistical analysis on the size of Au particles over 30 different Au-supported solids described in the literature²⁷⁻³³ (Fig. S10, ESI†) shows that, within the resolution limit of conventional HR-TEM instruments, the probability of having sub-nanometric Au entities after the hydrogenation of Au atoms supported on a solid is <5%, and this value only becomes significant for some transition metal oxides. This statistical analysis was carried out following normal and lognormal distributions, the most accepted and suitable statistical approaches to describe the formation of metal particles from monoatomic precursors.^{34,35} Thus, a top-down approach starting

from Au NPs seems more suitable to generate sub-nanometric Au clusters in conventional solids, such as aluminosilicates or carbonaceous materials.

It has been recently reported that iodoalkanes are able to re-disperse Au NPs into isolated Au atoms and sub-nanometric Au clusters when supported on charcoal or inorganic oxide supports.^{36,37} The re-dispersion of Au NPs occurs because the C-I bond dissociation energy (BDE), which ranges from 190 kJ mol^{-1} in Cl_4 to 270 kJ mol^{-1} in $\text{C}_6\text{H}_5\text{-I}$, is favorable for the formation of Au-I bonds.^{38,39} With this in mind, it was envisaged that the non-toxic and cheap I_2 , with a I-I BDE of 152 kJ mol^{-1} , should re-disperse Au NPs more efficiently.

Fig. 4 shows that different commercially available Au NP-supported solids (1 wt% Au, ~3.0 nm average size), free of sub-nanometric clusters, become catalytically active for the reaction test with starting material 3 when pre-treated with I_2 solutions in dichloromethane (DCM), and the catalytic activity is higher than when pre-treated with a representative iodoalkane, such as neat CH_3I . The amount of Au_{3-7} clusters generated in each solid with I_2 is 12, 9, 8 and 6% for Au-ZnO, Au- Al_2O_3 , Au-C and Au- TiO_2 , respectively (see Fig. 1). The same result is obtained with a specifically prepared sample of Au- TiO_2 with a higher loading (1.5 wt%) and average Au NP size (4.3 nm, Fig. S11, ESI†).⁴⁰ UV-vis and MS measurements confirm the generation of sub-nanometric Au clusters, and analysis using X-ray fluorescence of the I_2 -treated solids shows that Au mainly persists on the solid after re-dispersion (Au- TiO_2 : 1.08 wt%; Au-ZnO: 0.89 wt%; average of 3 samples). Treatment of Au- Al_2O_3 , Au- TiO_2 and Au-ZnO with aqueous, rather than DCM, I_2 solutions was also tested and, according to the reaction test, the generation of sub-nanometric Au clusters also occurred in some cases (Fig. S12, ESI†).

In conclusion, supported, ligand-free, sub-nanometric Au clusters have been prepared using different synthetic methods including: (1) the hydrogenation of Au atoms on $n\text{CeO}_2$; (2) the endogenous reduction of Au salts on EVOH co-polymers; and (3) the re-dispersion with I_2 of supported Au NPs on charcoal and inorganic oxides; all with higher yields (up to 15%) than previously reported for large scale wet methodologies. These supported Au_{3-7} clusters

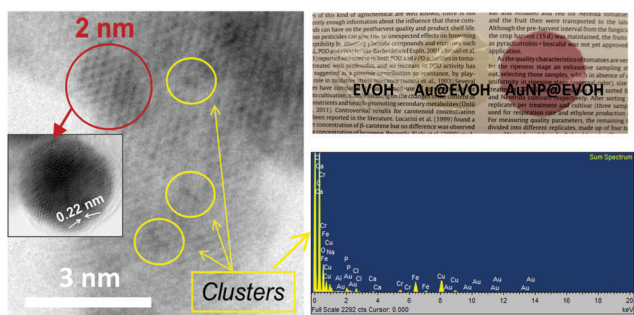


Fig. 3 Left: Aberration-corrected HR-TEM micrograph of Au@EVOH; the circles in yellow indicate Au clusters, the circle in red indicates a 2 nm Au NP, and the inset shows the interplanar crystallographic distance for Au. Top right: Photograph of neat EVOH (left, colorless), Au@EVOH (middle, yellow) and the material synthesized with carvacrol, which leads to plasmonic Au NPs (right, red). Bottom right: A representative EDX spectrum of the area indicated for clusters, showing the presence of Au.

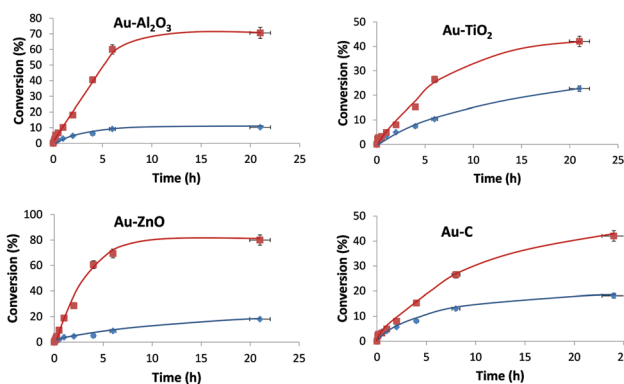


Fig. 4 Kinetic profiles for the ester-assisted hydration of the alkyne 3 catalyzed using commercially available Au- Al_2O_3 , Au- TiO_2 , Au-ZnO and Au-C supported NPs, before (black squares) and after (red circles) treatment with I_2 solutions; average of three experiments; error bars account for 5% uncertainty. Lines are a guide for the eye.

can be quantified using a new, extremely cheap and extremely sensitive (ppm) reaction test.

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Notes and references

‡ Reaction test: Au catalyst (0.01 mol%), heptanoyl chloride **1** (1 mmol) and propargylic alcohol **2** (10 mmol) were placed in a 2 ml vial equipped with a magnetic stir bar. The vial was sealed and the resulting mixture was magnetically stirred for 30 min at 25 °C. Then, water (1 mmol) was added and aliquots of 25 μ l were periodically taken, diluted in *n*-hexane, and analyzed using GC in order to follow the reaction, using dodecane as an external standard. Alternatively, the test can be run directly from intermediate **3**, in order to avoid HCl generation.

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