

Gold Colloids: From Quasi-Homogeneous to Heterogeneous Catalytic Systems

LAURA PRATI* AND ALBERTO VILLA

*Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19,
20133-1 Milano, Italy*

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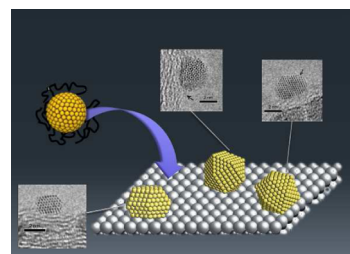
Ruby red colloids of gold have been used for thousands of years and in the past have attracted much attention due to their optical properties. Surface plasmon resonance (SPR) bands are responsible for gold colloid colors and typically appear for nanometer-sized gold nanoparticles (GNPs). These lie in the visible range and their position (and intensity) depends on the size, distribution of size, and shape of GNPs but also on their interaction with other materials (i.e., support).

Scientists consider colloids as quasi-homogeneous systems, but because of their intrinsic thermodynamic instability, they need different capping agents providing sufficient stability. The strength and the nature of the interaction between the protective (or functionalizing) molecule and the GNP surface is of utmost importance. It can determine the catalytic properties of the nanoparticles, as they mainly interact with the active sites, thus interfering with reactant. Therefore, the protective layer should contribute to the colloid stability, but at the same time, it should not be irreversibly adsorbed on the active site of the GNP surface providing convenient accessibility to reactant.

From a catalytic point of view, the milder the interaction is between the particle surface and the capping agent, the more the activity increases. Unfortunately, the reaction conditions often do not allow the required stability of GNPs, which constitutes a fundamental prerequisite for stable catalytic activity. Anchoring GNPs on suitable supports can circumvent the problem, and this technique is now considered a valuable alternative to classical methods to produce highly dispersed gold catalysts.

In this Account, we describe the advantages in using this technique to produce gold heterogeneous catalysts of high metal dispersion on a large variety of supports with the possibility of tuning to a large extent the size and (even partially) the shape of GNPs. We also review our recent progress on the sol-immobilization technique. Specifically, we highlight how, depending on its nature, the protective agent not only mediates the activity of GNPs in alcohol oxidation process but also actively participates in the anchoring process and to the stability of GNPs depending on the support surface. We can also use the modification of the metal surface operated by the capping agent to prepare bimetallic species and influence the surface potential, which modifies the intrinsic activity of the GNP.

In conclusion, this technique implies many contributions (sometimes not yet clarified factors) that are not simply concerning dimension and dispersion of GNPs or type of support. Chemists should make careful selection of the protective agent and reaction parameters depending on which support is used in which reaction.



1. Introduction

The peculiarity of gold as a catalytically active metal has only been recognized quite recently and is based on the pioneer works of M. Haruta and G. J. Hutchings that have laid the foundations for the development of new catalytic processes.^{1–3} It was apparent that it was necessary to have high metal dispersion to obtain an appreciable catalytic activity, but in the case of gold due its low melting point, this was not an easy task with the common procedures used for making heterogeneous catalysts. On the other hand, gold

colloids have been appreciated since the time of the Lycurgus Cup dated in 4th century AD for their beautiful colors, that reflect the peculiarity of their electronic state.⁴ Indeed, gold nanoparticles (GNPs) have historically received much attention in art and ancient medicine and currently in enhanced optoelectronics and photovoltaics and biomedicine.^{5,6} The techniques of metal colloid chemistry have been applied increasingly to the preparation of metals in highly dispersed form, leading in principle to a careful control of composition, size, and morphology of the

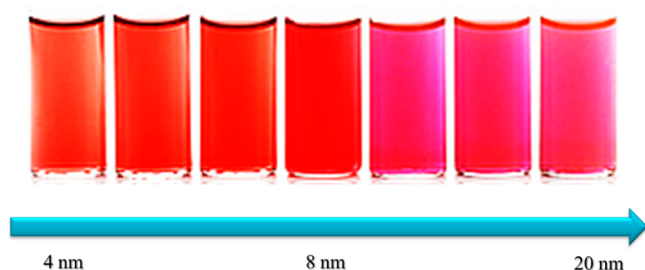


FIGURE 1. Differently sized gold colloids.

resulting particles.^{7–9} However, despite some attempts to directly use such particles in catalysis, limited stability under reaction conditions and recyclability problems make the preformed GNP interesting from an applicative point of view only as precursors of heterogeneous gold catalysts where the metal nanoparticles normally range in size between 1 and 30 nm and are immobilized on a suitable supporting material.^{10,11}

The advantage of using this technique appeared principally to be based on its applicability regardless of the type of support employed and the possible control over the particle size and distribution, an important factor governing the overall activity of catalysts (Figure 1).

However, from the first studies dealing with gold colloid immobilization and their catalytic tests, many other different parameters could be highlighted. Particularly relevant appeared the obligatory presence of molecules adsorbed on the metal particle surface, which not only provide thermodynamic stability of gold sols but also contribute to stability, catalytic activity, and selectivity of the final catalyst.¹²

In this Account, we critically discuss these three fundamental aspects of heterogeneous catalysis, focusing on the role of the capping agent in mediating the interaction between GNP and support surface and between the reactant and the active sites (on the metal or on the support). In order to be able to relate the influence of a particular coating to the catalytic activity and selectivity in a given reaction, not only a precise knowledge of the structural, morphological, and electrical properties of the GNP but also a view of the molecular dynamics during the reaction are required. Therefore, throughout this Account, we will show results of structural characterizations that allow us to clarify the active surface morphology and also *in situ* spectroscopic study (mainly infrared, IR) used for determining the dynamics of the adsorption and desorption of reagents. These studies become important in order to correlate the type of sol used (on a given support) with the activity and selectivity of the

catalytic material and then also to be able to predict what should be the best choice for a given reaction.

2. Preparation of Catalyst: Sol Generation and Immobilization

The method is based on the preparation of GNPs by reduction of gold precursor in the presence of a stabilizing agent (polymer, surfactant, polar molecule, etc.) and their subsequent immobilization on a support. The GNP is surrounded by a cloud of adsorbed ions or molecules whose presence is responsible for the stability of the colloid. Particles of colloidal gold carry a negative charge in water, due to surface adsorbed anions (mainly AuCl_4^-). A considerable advance in the understanding of the behavior of these systems was given by the theory of Derjaguin, Verwey, Landau, and Overbeek (DLVO).^{13,14} In this assumption, the stability of the particle consists of two components: the overlap of the electrical double layer, leading to repulsion, and the electromagnetic effects leading to van der Waals attraction.

At a finite distance, where the surfaces do not come into molecular contact, equilibrium is reached between electrodynamic attractive and electrostatic repulsive forces (secondary minimum). At smaller distances, there is a net energy barrier. Once overcome, the combination of strong short-range electrostatic repulsive forces and van der Waals attractive forces leads to a deep primary minimum. Both the height of the barrier and the secondary minimum depend on the ionic strength and electrostatic charges. The energy barrier is decreased in the presence of electrolytes (monovalent < divalent < trivalent) by compression of the double layer.¹⁵ Thus, the stability of a colloid is a function of the energy of interaction between the particles. The conventional strategies for the preparation of small precious metal nanoparticles in the presence of a protective agent have been mainly developed in the past decade.^{8,9} These can be divided into three main methodologies: (a) surface potential or charge density is increased by the adsorption of surface active long-chain ions (i.e., surfactants); (b) van der Waals forces are reduced by adsorption of relatively rigid hydrophilic macromolecules (i.e., dextrin, starch); (c) absorption of flexible polymers of sufficiently high molecular weight providing steric stabilization. The use of this latter method leads to polymer chains protruding from the particle surfaces (i.e., PVA and PVP). The slight interpenetration of these chains, elongating from colliding particles, keeps them at a distance too large to give a van der Waals interaction sufficient for coherence.¹⁶

Among all the stabilizers used for catalytic applications, polymeric materials are the most used. Brij35 (polyoxyethylene(23)-laurylether, MW_{avg} 1200), PVA (poly(vinyl alcohol), MW 13000–23000, 98% hydrolyzed), PEG (poly(ethylene glycol), reacted with bisphenol A diglycidyl ether, MW 15000–20000), and PVP (poly(vinyl pyrrolidone), MW_{avg} 55000), have been reported to produce highly stable GNPs by steric stabilization, with small particle size (2–6 nm). Moreover, long chain alcohols of 15000–20000 Da, like PVA, are suitable stabilizers for nanoparticles of 3–8 nm mean diameter.¹⁷ Dextrin has been investigated as a rigid hydroxyl protective agent, affecting the attractive van der Waals forces. Small sizes of nanoparticles have been obtained with dextrin stabilized sols (2–3 nm), but they have not greatly affected the catalysis.¹⁸ Better results have been achieved by increasing the surface potential or charge density by the absorption of ionic surfactants, such as polydiallyl ammonium chloride, PDPA (poly(diallyldimethylammonium) chloride), and the polyion PEU (poly[bis(chloroethyl)ether-*alt*-1,3-bis-[3-(dimethylamino)propyl]urea) and sulfobetaines, such as *N*-dodecyl-*N,N*-dimethyl-3-amino-1-propanesulfonate.¹⁸ Typically, the stabilizer/Au weight ratio is maintained at one, with a metal concentration ranging between 10^{-3} and 10^{-4} M. The use of higher values normally increases the stability of the GNPs.

A second parameter greatly affecting the GNP morphology is the nature of the reducing agent. Schmid introduced the diborane reducing agent for the synthesis of Au_{55} nanoclusters stabilized by phosphine ligands.¹⁹ The alcoholic reduction preparation, in the presence of PVP and PVA polymers, was developed mainly by Hirai and Toshima, exploiting the easy reduction of alcohol to aldehyde.²⁰ The use of *in situ* hydrolysis of tetrakis(hydroxymethyl)phosphonium chloride (THPC) as a reducing agent was introduced by Baiker and facilitates the synthesis of small monodispersed gold nanoparticles (2–4 nm).²¹ Moreover, the use of $NaBH_4$, a powerful reagent for the reduction of metal salts, has been developed within this past decade.¹⁸ The Au/BH_4^- molar ratio was optimized, and an excess corresponding to 1:4 (mol/mol) was used with respect to the overall stoichiometry. Chemical reduction obviously produces byproducts that are not always just spectators in catalysis. Therefore, final catalysts are often washed thoroughly in order to remove any possible byproducts.

A third (and crucial!) point is the immobilization of the GNP on the support. Very often this step was not considered as influencing the metal particle size. However, the morphology and the metal dispersion strictly depend on the surface

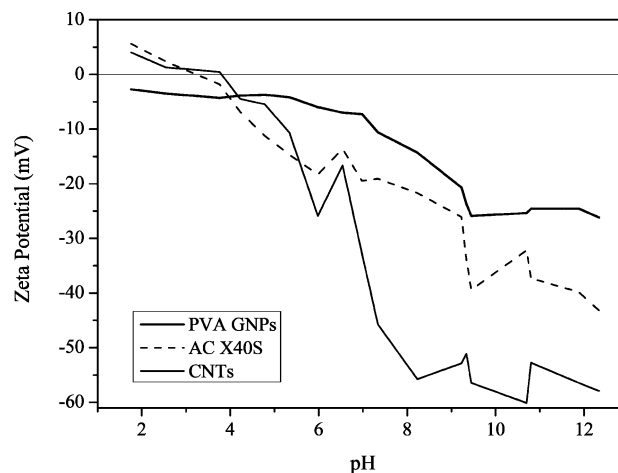


FIGURE 2. ζ Potential measurement of PVA GNPs, AC X40S, and CNTs.

properties and the morphology of the support.^{22,23} The immobilization is performed most often by simply dipping the support in the metal sol under vigorous stirring. The kinetics of the adsorption depends on the sol stabilizer and on the isoelectric point (IEP) of the support. Therefore, it can be tuned by varying the pH of the metallic sol. As an example, PVA stabilized gold sol is negatively charged within a large range of pH values (Figure 2) and should be more easily adsorbed on a positively charged surface, if no other interactions occur. The IEP of the support should be investigated first, before the adsorption step. For example, the electrostatic interaction between PVA GNPs and activated carbon or carbon nanotubes is favored only at a pH below 3, where the two supports present a positively charged surface.

Table 1 reports the variation of GNP mean size as a function of stabilizer/Au ratio (w/w) for commonly used stabilizing agents. Note that by increasing the relative amount of the stabilizer, the GNP mean size decreases. Another point of interest that already highlights the possible role of the stabilizer as a mediator between the metal particle and the surface of the support is the variation of the average GNP size obtained after immobilization by varying the support. Active carbon shows the highest tendency to make the particles grow with respect to the original GNP size, as shown in Table 1.²³ Indeed, among the tested protective agents, PVA appeared to be the only one able to preserve the sol particle dimension during the immobilization step on activated carbon.

Poly(vinyl alcohol) (PVA) was very efficient in keeping the original GNP size during the immobilization step, almost independently of the amount of capping agent. On the contrary, with the other stabilizers, an obvious growth of the GNP is observed comparing the unsupported and

TABLE 1. Effect of the Amount and Nature of the Protective Agent on the Growth of GNPs during the Immobilization on Different Supports^a

stabilizer	stabilizer/ Au (w/w)	particle size (sol)	support	particle size (nm) (supported)	ref	
THPC	0.8	4.0	AC	8.6	24	
			TiO ₂	4.1	24	
			Al ₂ O ₃	3.9	24	
	1	3.5	AC	8.2	24	
			TiO ₂	3.7	24	
			Al ₂ O ₃	3.8	24	
	2	2.7	AC	4.2	24	
			TiO ₂	4.2	24	
			Al ₂ O ₃	4.3	24	
	PVA	0.125	3.2	AC	4.1	25
				AC	3.9	25
				AC	3.6	25
0.25		3.1	NiO	3.8	26	
			nano-NiO	3.6	26	
			SiO ₂	4.0	26	
			MgO	3.8	26	
			TiO ₂	4.0	26	
			H-mordenite	3.8	26	
0.5		2.6	AC	3.5	25	
			graphite	5.4	27	
			CNTs	4.6	27	
			CNTs oxidized	3.8	28	
			CNFs PR24-LHT	3.5	29	
			CNFs PR24-PS	3.8	29	
			CNFs PR24-PS oxidized	3.7	28	
			N-CNFs PR24-PS 873 K	2.9	28	
			PEG	0.3	5.3	AC
AC	12.0	30				
1	5.2	AC		12.0	30	
		AC		12.0	30	
C ₁₂ E ₂₃	0.3	5.3		AC	8.2	30
				AC	7.0	30
dextrin	0.3	3.5	AC	7.0	30	
			AC	7.0	30	
			AC	7.0	30	
PDDA	0.1	3.6	AC	12.0	30	
			AC	8.4	30	
			AC	9.5	30	
0.3	2.8	AC	9.5	30		
		AC	27.0	30		
		AC	22.0	30		
0.65	2.6	AC	22.0	30		
		AC	15.0	30		

^aAC = activated carbon; PEG = poly(ethylene glycol); C₁₂E₂₃ = poly(oxyethylene dodecyl ether); PDDA = poly(diallyldimethylammonium bromide). Preparation method for GNPs: Au precursor = NaAuCl₄, 10⁻⁴ M, reducing agent = NaBH₄ 0.1 M (Au/NaBH₄ 1/4 mol/mol).

supported ones. This difference is more evident using a low amount of protective agent. In the case of THPC, the particle dimension in the sol is maintained only when a high THPC/Au ratio is used, especially in the case of carbon as the support.

Considering carbon materials as catalyst supports for metal nanoparticles requires control over porosity, defects, and the chemical state of the surface. These factors become critical parameters because they influence the active phase dispersion, which influences the catalytic activity of the metals.²² In recent studies, we showed that the internal bonding of the carbon support, that is, sp² vs sp³, and the crystallinity have an important effect on the immobilization of PVA supported GNPs and the selective oxidation of glycerol. Two catalyst supports were investigated, crystalline graphite (G) and more disordered activated carbon (X40S).²²

Analysis of XPS data revealed that the X40S contained a high concentration of C–O (531.3 eV) and C=O (533.8 eV) functional groups, but the graphite was oxygen-free. TEM studies showed that the growth of the PVA GNPs during the immobilization occurred to a higher extent on the less defected surface of the graphite (3 and 5.4 nm for Au/X40S and Au/graphite, respectively) (Table 1). Comparing the Raman D/G band ratios [Graphite (ID/IG 0.6) and AC (ID/IG 2.4)] allowed us to relate this effect to the graphitization degree.²⁷ Functional groups can be also artificially introduced onto the surface. For example, we demonstrate that by introducing oxygen functionalities onto CNFs and CNTs, (CNFs ox and CNTs ox, Table 1), it is possible to obtain better GNP dispersion compared with pristine CNFs. Furthermore, during the immobilization of Au preformed sol, oxygen functionalities also improve, with respect to an untreated support, the stabilization of Au nanoparticles, decreasing the discrepancy between the particle size in the sol and on the support after the immobilization step (Table 1). Moreover, oxygen functionalities increase the surface hydrophilicity, improving thus the surface wettability. Therefore, the interaction between the support and the metal precursors normally dispersed in the aqueous phase increases. In addition, the introduction of nitrogen-containing groups, by gas phase amination (N-CNFs PR24-PS 873 K) favorably affected the particle dispersion on the support (Figure 3), as observed in the case of oxygen-containing groups.²⁸

Further evidence of the active role that the protective agent plays in mediating the interactions among species in solution is represented by the preparation of bimetallic alloyed catalysts. The procedure developed by our group involved the use of PVA protected GNPs as nucleation centers for the other metal (Pd).³¹ After immobilization of a preformed gold sol on activated carbon, a sol of palladium was generated in the presence of Au/C using H₂ as reducing agent. The rate of Pd reduction was fundamental for avoiding Pd segregation or homogeneous nucleation that can result in a mixture of phases. By performing XEDS analysis on individual Au–Pd supported nanoparticles (Figure 4), no segregation of Au and Pd has been observed, and all the particles were homogeneous random alloys with a similar Au/Pd ratio. A small (3 nm) particle size with narrow size distribution was also reported.

Further studies proved that the PVA protective agent was fundamental for obtaining a pure alloy.³² Indeed, GNPs with only electrostatic stabilization, tetrakis(hydroxypropyl)phosphonium chloride (THPC), or no stabilization (magnetron sputtering) produced inhomogeneous alloys

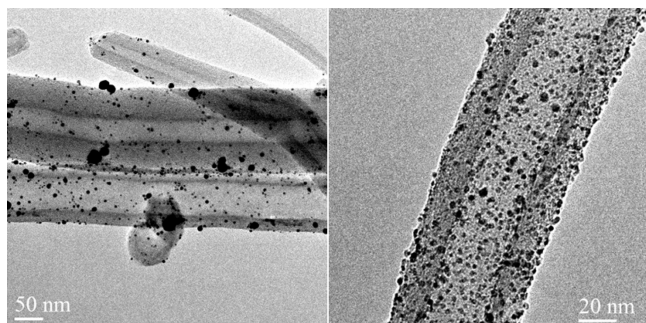


FIGURE 3. TEM images of (a) Au/CNF and (b) Au/N–CNF 873 K.

and segregation of the gold and palladium. Unprotected nanoparticles, as well as weakly stabilized gold nanoparticles, undergo reconstruction during the reduction/deposition of Pd and are not efficient seeds for alloying Pd. The result, in these two latter cases, was a considerable growth of metal particle size, as well as metal segregation or different alloy composition.

3. The Protective Layer Effect on Catalysis

We have seen the importance of the nature of the protective layer during the immobilizing step for obtaining good metallic dispersion. The control of the dimensions and the maintenance of sol size during the immobilization roughly depend on the metal/capping agent ratio, the optimum being determined by the nature of the support and the capping agent itself. The importance of using metallic sols as precursors of heterogeneous catalysts has received particular attention, because of the difficulty of obtaining a high metal dispersion on all types of support. However, from a catalytic point of view, the first drawback that can be easily figured out is the shielding of metals, which results from the presence of molecules, normally bulky, adsorbed on the surface of the metal particles and providing size stability during the immobilization step. In fact, the protective layer formed on the surface can limit the contact between the reagents and the active site. As usual, a compromise should be found between a high amount of protective agent (low metal/capping agent ratio), which ensures the size of the metal nanoparticle, and a low amount of protective agent (high metal/capping agent ratio), which reduces the shielding of the metal nanoparticles, thus enhancing their catalytic activity.

The shielding effect is not simply determined. In fact, the overall catalytic activity results from the merging of several factors not always easily disentangled. The single shielding effect could be highlighted by comparing the catalytic activity of GNPs of similar size on the same support, differing only

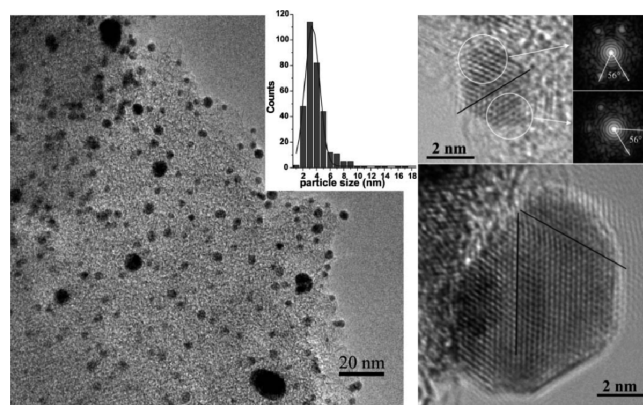


FIGURE 4. HRTEM images of AuPd bimetallic catalyst.

in the amount of capping agent. This procedure is not easily feasible, because the amount of capping agent and the size of the GNPs are directly correlated. The removal of the protective layer under mild conditions, which does not affect the metal dispersion on the support, indicated the presence of the shielding effect, even though this procedure could only determine the presence of the effect and was not able to quantify it at all. Accordingly, as shown in Table 2, GNPs generated in the presence of poly(vinyl alcohol) (PVA) as a protective agent and supported on active carbon have been shown to be transformed into a more active catalyst by washing away the PVA layer.²⁵

Protective agents can also be removed by heat treatment. However, as evidenced from Table 2, in this case the dimensions are modified and the catalytic activity drops due to particle coarsening. In order to have an indication of the different shielding effects caused by different protective agents, the catalytic activity of unsupported sols should be considered. In the liquid phase oxidation of glycerol, it was clearly shown that the more bulky the protective agent (PVA), the more the shielding effect is present.¹¹

Indeed, GNPs of similar dimensions (Table 3) but stabilized in one case mostly sterically (PVA) and in the other mostly electrostatically (THPC) presented very different catalytic activities.

The same comparison is less reliable for supported particles, because other factors could affect the activity, even if the same support is used. In particular, the surface exposure was shown to be relevant from a catalytic point of view when liquid phase reactions are carried out, because diffusional limitation can occur within the porous structure of the support.^{33,34} This parameter can be assessed by XPS, but it should be carefully considered, because it is a relative measurement and thus dependent on the particle size.

TABLE 2. Catalytic Activity of 1 wt % Au on AC Generated by PVA GNPs in the liquid phase Oxidation of Glycerol

treatment	GNP <i>d</i> (nm) [HRTEM]	catalytic activity ^a
none	3.6	236
washed with water at r.t.	3.7	355
calcined at 400 °C	15.0	89

^aExpressed as mol of alcohol converted (Au mol)⁻¹ h⁻¹, calculated after 15 min of reaction. Reaction conditions: alcohol/metal 1000/1 (mol/mol), 50 °C, pO₂ 3 atm, 1250 rpm.

The presence of a different protector can also be exploited to optimize this parameter, as in the case of GNPs stabilized by the presence of PVA or SB (dodecylbenzenesulfonic acid). When these particles were supported on active carbon, the increased chemical interaction of SB with the functional groups present at the surface of the support, compared with the PVA, causes (at constant average gold particle size) the resulting catalyst surface exposures to differ significantly (Table 4). This increased exposure could be correlated with a considerably higher activity in the ethylene glycol oxidation.

Very recently, we obtained an additional confirmation of the active role of the protective agent in the catalytic processes.²⁵ During glycerol oxidation, it was shown that a small amount of PVA has a positive influence on the activity of Au_{PVA}/TiO₂ and, in addition, is able to influence the selectivity of the reaction. Indeed, IR adsorption studies showed evidence of a direct interaction between PVA and the glycerol molecule, evidencing a different adsorption mode of glycerol on the active sites with or without PVA.

Finally, it should be mentioned that the presence of a protective agent is beneficial for the stability of the catalyst. Indeed, recycling tests revealed a better resistance of the catalyst obtained by protected particle deposition with respect to the catalyst obtained by the deposition–precipitation technique, where no protective agent is used. Figure 5 shows the trend in the case of 1 wt % Au_{PVA}/TiO₂ and 1 wt % Au_{DP}/TiO₂.

It should also be noted that PVA can be partially removed from the GNP surface during the recycling test. Indeed a small change in selectivity could be observed.²⁵

4. The Support Effect on Catalysis

Recent studies have shown that the support plays an important role in enhancing the activity and the selectivity of the gold catalyzed reactions.^{22,23} Indeed, the support properties can tune the interaction with the metallic particles, modifying both their electronic and their structural properties. As reported above, the metal colloids are commonly adsorbed by the support with a rate depending on sol

TABLE 3. Shielding Effect of Two Different Protective Agents

protecting agent	GNP <i>d</i> (nm) [HRTEM]	catalytic activity ^a
THPC	2.0	2478
PVA	2.2	715

^aExpressed as mol of alcohol converted (Au mol)⁻¹ h⁻¹, calculated after 15 min of reaction. Reaction conditions: alcohol/metal 1000/1 (mol/mol), 50 °C, pO₂ 3 atm, 1250 rpm.

stabilizer and on the IEP and surface area of the support.³⁵ The final GNP dispersion is therefore, strictly correlated with the presence of functional groups on the surface, being normally higher for support with high surface area and functionalities that act as anchoring sites.

Even in the case of the sol immobilization technique, a strong support effect not ascribed to different metal dispersion or size was revealed. Indeed, we recently reported that PVA-GNPs supported on nanosized NiO (Table 5) showed higher activity in the benzyl alcohol oxidation than supported ones on MgO and TiO₂ even though the GNP sizes were similar (3.6, 4.0, and 3.7 nm for nano-NiO, TiO₂, or MgO, respectively).

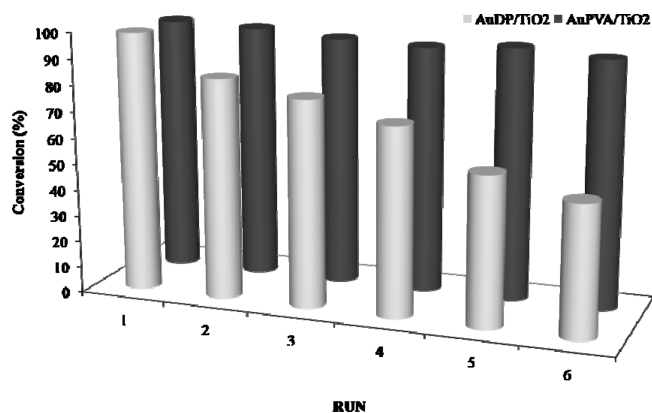
This effect was ascribed to an electronic interaction revealed by an XPS Au binding energy evaluation and established between GNPs and the nano-NiO surface. Most probably, this interaction is mediated by the protective agent. In fact, when THPC protected GNPs (an electrostatic capping agent) were used, the influence of the support was more evident.³³

It is to be noted that the structure of the support can also modify the structure of the GNP. Indeed, by using carbon nanofibers with different degrees of graphitization (CNFs PRPS-24 and PR-LHT from Applied Science) as support for PVA GNPs, it was shown that in the immobilization step we can have a restructuring of the GNPs.²⁹ In contrast to PR24-PS, PR24-LHT exhibited a more graphitized surface of more ordered layer. HRTEM analyses revealed that the distribution and the size of the GNPs were similar on the two supports (3.8 and 3.5 nm for PR-24 and PR-LHT respectively) but showed that the final shape of the Au particles was related to the surface structure of the support, although the Au particles were preformed in the sol. In particular, GNPs were attached to the CNFs PR24-PS without a distinguishable orientation relation between the Au low-index crystallographic planes and the CNF surface. Among the examined particles, 21.6% of the GNPs were found to have one set of {111} planes parallel to the CNF surface and the rest were randomly oriented. Most of the particles exhibited a polyhedral shape, for example, cuboctahedron and icosahedron (Figure 6a,b).

TABLE 4. Effect of the Protective Agent on the Catalyst Surface Exposure and the Catalytic Activity in the Ethylene Glycol (EG) Oxidation

protecting agent	atom % Au(4f)/C(2s) [XPS]	GNP <i>d</i> (nm) [HRTEM]	catalytic activity ^a
PVA	0.49	4.3	260
SB	2.42	4.8	1586
PVA	2.52	5.5	580
SB	3.26	5.5	1620

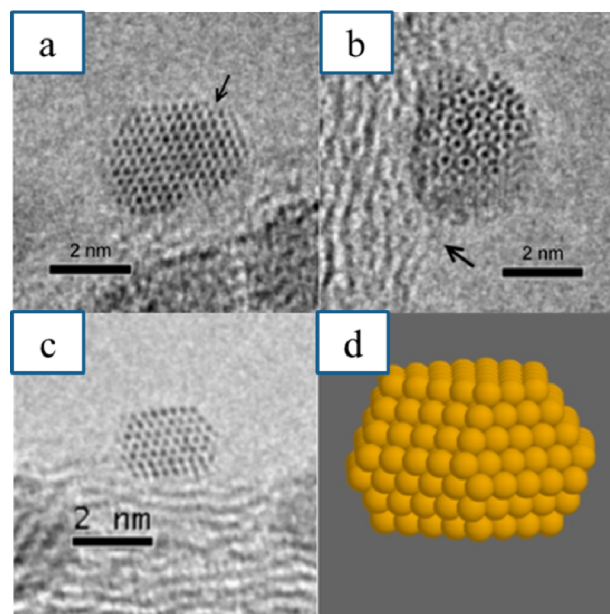
^aExpressed as mol of alcohol converted (Au mol)⁻¹ h⁻¹, calculated after 15 min of reaction. Reaction conditions: [EG] = 0.5 M; EG/M = 1000 (mol/mol); EG/NaOH = 1 (mol/mol); pO₂ = 3 atm; T = 343 K.

**FIGURE 5.** Recycling test using Au_{DP}/TiO₂ and Au_{PVA}/TiO₂.**TABLE 5.** Activity of Au Base Catalysts in Benzyl Alcohol Oxidation

catalyst ^a	Au particle size (nm)	conversion (%) after 6 h
Au _{PVA} /NiO	3.8	6
Au _{PVA} /nano-NiO	3.6	55
Au _{PVA} /SiO ₂	4.0	3
Au _{PVA} /MgO	3.8	6
Au _{PVA} /TiO ₂	4.0	6
Au _{PVA} /H-mordenite	3.8	14

^aData from ref 26. Reaction conditions: benzyl alcohol/cyclohexane = 50/50 wt/wt, alcohol/metal = 1000 mol/mol, pO₂ = 0.3 MPa, T = 80 °C.

The {111} planes of Au particles on PR24-LHT are more frequently observed to be parallel to the CNF surface than in the case of PR24-PS. Among these particles, 46.8% of the GNPs were found to have one set of {111} planes parallel to the CNF surface. Figure 6c shows a representative particle with one set of {111} lattice planes on the CNF surface. The particle has a configuration similar to the cuboctahedron shape with {111} and {100} surfaces exposed. A structural model was constructed and is displayed in Figure 6d. The particle has a relatively large (111) base plane contacting the supporting CNF. The catalytic test for glycerol oxidation evidenced that the catalytic activity depends only on the particle size. On the basis of experimental evidence, it is now accepted that the larger the GNP size, the more the activity decreases.³⁶ The selectivity of the reaction toward C3 products (glyceric, tartronic acids) appears to be related to the

**FIGURE 6.** Aberration-corrected TEM images of GNPs supported on CNFs-PR24-PS with (a) modified cuboctahedral configuration and (b) icosahedral configuration and of GNPs supported on PR24-LHT. (c) A representative 2–4 nm particle with {111} surface epitaxially parallel to the graphitic layer of CNF. (d) Structure model derived from the image in part c.

particle size, as well as the activity, but in the opposite sense. The two catalysts indeed showed a similar activity (TOF of 948 and 982 h⁻¹ for Au/PR24-PS and Au/PR24-LHT, respectively), in good agreement with the similar particle size (3.8 and 3.5 nm for Au/PR24-PS and Au/PR24-LHT, respectively). However, the different product distribution obtained revealed that the particle size is not the only parameter determining the selectivity. With Au/PR24-PS, 56% C3 products and 45% C2+C1 products were obtained, whereas with Au/PR24-LHT, 22% C3 products and 77% C2+C1 were obtained. The direct contact between PR24-LHT and the {111} surface of PVA GNPs led to the exposure of low index Au surfaces, suggesting that the active sites on these surfaces could promote the C1 and C2 products, derived from the C–C bond cleavage.

5. Concluding Remarks

The use of the immobilization of a preformed metal sol has aroused great interest in the scientific community for the preparation of catalysts based on gold. Indeed, the immediate advantages that were expected from the use of this technique were the control of the size of the GNPs in a catalytically active range and the generality of its applicability regardless of the support material. The size of the GNPs is indeed tunable in a wide range of dimensions

and distribution, thanks to the well-established and vastly proven knowledge of colloid chemistry. However, in this Account, we emphasized that the application to catalysis of colloids and even more of supported colloids must take into account many other aspects.

First of all, metal sols require for their stability the presence of molecules that, by adsorbing on the surface of GNPs, decrease their tendency to collapse. It has been shown that the impact of these molecules on the catalytic activity of the final catalyst is not simple to evaluate and depends on both their structure and their amount. The first step in which we highlight these effects is the immobilization on a support and their influence on the metal dispersion. In fact, having a high metal dispersion is a fundamental prerequisite for an active catalyst. We have shown that contrary to what is commonly believed, an increase of the particle size occurred depending not only on the nature and amount of the protective agent but also on the nature of the support. The size of the GNP was more stable when more stabilizing agent was used, and the metal dispersion increases when the presence of functional groups on the support is increased. The match between the functionalities over the particles and the support could also determine the allocation within the support porous structure, varying the metal site exposure. Moreover, the support itself can actively participate to reconstruct the metal nanoparticle. Obviously an impact on the catalytic activity is expected.

The catalytic activity increases upon decrease of the GNP size, but in turn the size decreases upon increase of the amount of protective agent, which thus causes a shielding effect. This shielding was detrimental from an activity point of view, but can also act as a stabilizing effect in terms of durability of the catalysts.

The most recent and challenging feature in metal sol immobilization is represented by the discovery of additional effects caused by the protective layer other than those highlighted. An effect of promoting the activity, although present in small amounts, and an effect of mediation between the reagent and the active site have been disclosed. These aspects of the research are not only of great importance for a better understanding of the elementary parts of a catalytic process but also constitute a step toward a more targeted design of heterogeneous catalysts.

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BIOGRAPHICAL INFORMATION

Laura Prati, after Specialization in “Analytical technique applied to fine chemicals” at Politecnico of Milan in 1985, was awarded a Ph.D. in Industrial Chemistry in 1988. She became Associate Professor of Inorganic Chemistry at the Università degli Studi di Milano in 2001. Her scientific interests focus principally on catalytic hydrogenation and oxidation reactions and specific design of heterogeneous catalysts. She has been involved in catalytic applications for gold since 1986.

Alberto Villa received his Ph.D. from the Università degli Studi di Milano in 2007 after carrying out a thesis on the development of gold based catalysts for liquid phase transformation under the guidance of Prof. Laura Prati. After 2 years as a postdoctoral fellow at Fritz Haber Institut der Max Planck Gesellschaft (FHI-MPG)-Berlin (Germany), he joined Prof. Laura Prati's group at the Università degli Studi di Milano in 2009. His current research focuses on the development of heterogeneous catalysts for biomass transformation.

FOOTNOTES

*Corresponding author. E-mail: Laura.Prati@unimi.it.
The authors declare no competing financial interest.

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