

# Green synthesis of noble metal and bimetal nanosols and their applications as catalysts

M. Blosi\*, S. Ortelli\*, S. Albonetti\*\*, A. L. Costa\*, L. Ortolani\*\*\*, M. Dondi\*

\* - ISTECCNR, Institute of Science and Technology for Ceramics, National Research Council, Via Granarolo 64, 48018, Faenza (Italy)

\*\* - Department of Industrial Chemistry "Toso Montanari", INSTM, Research Unit of Bologna

\*\*\* - IMM-CNR Bologna - Via Gobetti 101, 40129 Bologna (Italy)

## ABSTRACT

Bimetallic nanoparticles with various noble metals (AuCu, AuAg, PdCu, PdAu) as well as the respective monometallic nanoparticles protected by PVP shell were synthesized following the developed strategy. A deep characterization was performed on prepared sols using HR-TEM, XEDS, UV-vis, ICP-OES and XRD. Microwave heating has been shown to provide more homogeneous particle nucleation and shorter synthesis time than traditional heating. This synthesis route showed several advantages with respect to other methods, in fact it is simple, eco-friendly, carried out at low temperature and easy transferable on large scale production. Particle size-control, total reaction yield, high solid loading and long time stability of colloids, were achieved thanks to an accurate reaction optimization. Prepared nanoparticles acted as effective catalysts in the reduction of 4-nitrophenol with NaBH<sub>4</sub>, a typical probe reaction.

**Keywords:** colloidal nanosols, green synthesis, microwave, noble metals, bimetals

## 1 INTRODUCTION

Recently a great interest has been addressed toward the synthesis of noble metal nanoparticles in order to explore their special features, due to their typical chemico-physical properties.

Integration of green chemistry principles into nanotechnology and nanoscience have attracted much attention over the past decade aiming at the design of more sustainable processes synthesis. Most of the synthetic routes reported in the literature are based on organic solvents thus implying a complex environmental path to the industrial production. So far, some expensive and toxic chelating agents (thiols, oleic acid, hexadecylamine, trioctylphosphine oxide) together with hazardous reducing agents are employed (hydrazine, sodium borohydride, dimethyl formamide) making these processes less promising for a subsequent industrial scale up.

In this work, we report an environmentally benign approach to the production of stable metal nanosols. Water has been chosen as environmentally benign solvent, glucose serve as a mild, renewable and non-toxic reducing agent and microwave irradiation was used as heating method. The so-obtained sols were characterized and used in a catalytic probe reaction, showing interesting catalytic properties. Moreover the versatility of these products makes them useful for different applications. In fact AuAg sols were tested as ceramic inks for ink jet printing technology [2], supported catalysts for different reactions of interest were prepared by immobilization of these preformed colloids [3], while Ag-antibacterial characterization are now ongoing.

## 2 EXPERIMENTAL PROCEDURE

### 2.1 Synthesis of nanosols

All the chemical reagents used in this experiment were analytical grade (Sigma Aldrich). Metallic nanoparticles were prepared following a patented procedure [4], which provides stable nanosols.

**Monometallic colloids** - PVP (from 0.35 to 5.66 g), glucose (from 0.20 to 7.2 g) and NaOH solution were mixed in a round bottom flask containing water and the solution was microwave heated at ambient pressure to a temperature ranging from 70 to 90 °C. At this temperature the precursor salts (HAuCl<sub>4</sub>, AgNO<sub>3</sub>, CuSO<sub>4</sub>, PdCl<sub>2</sub>) were added to the flask and stirred for a time ranging from 2.5 to 40 min. After reaction, a stable suspension of metal nanoparticles with a solid loading ranging from 0.1 to 4 %wt was obtained. In order to optimize the system for each metal the following synthesis parameters were evaluated: synthesis temperature, synthesis time, glucose/metal and NaOH/metal molar ratios.

SAMPLE	%Me1 (mol/mol)	%Me2 (mol/mol)	Metals Conc [mM]
Au	100	0	11
Ag	100	0	50
Cu	100	0	16.5
Pd	100	0	11
(Au)Ag01	67	33	15
(Au)Ag02	40	60	8.3
(Au)Ag03	18	82	6.1
Au <sub>1</sub> Cu <sub>1</sub>	50	50	5
Au <sub>1</sub> Cu <sub>3</sub>	25	75	5
Au <sub>1</sub> Cu <sub>6</sub>	14	86	5
Pd <sub>1</sub> Au <sub>1</sub>	50	50	5
Pd <sub>1</sub> Au <sub>3</sub>	25	75	5
Pd <sub>1</sub> Au <sub>6</sub>	14	86	5
Pd <sub>1</sub> Cu <sub>1</sub>	50	50	5
Pd <sub>1</sub> Cu <sub>3</sub>	25	75	5
Pd <sub>1</sub> Cu <sub>6</sub>	14	86	5

Table 1 – Prepared samples: monometals and bimetallic nanoparticles.

**Bimetallic colloids** - The Au-Ag core-shell structures were prepared by a two-step process [ref], both Au and Ag sols were used as core, acting as seed for the shell nucleation. The reactions were carried out in few minutes at low temperature, 70°C for Ag or 90°C for Au.

The bimetallic alloys, AuCu, AuPd, PdCu were obtained through the MW assisted co-reduction of H<sub>2</sub>AuCl<sub>4</sub> and CuSO<sub>4</sub> for AuCu, of H<sub>2</sub>AuCl<sub>4</sub> and PdCl<sub>2</sub> for PdAu and of PdCl<sub>2</sub> and CuSO<sub>4</sub> for PdCu. In a typical reaction for AuCu colloids, PVP, NaOH and glucose were mixed in a round bottom flask containing water and the solution was heated at ambient pressure to 90°C using microwaves. At this temperature a solution containing both H<sub>2</sub>AuCl<sub>4</sub> and CuSO<sub>4</sub> with a Cu/Au molar ratio ranging from 1 to 6 was added to the flask and the temperature was maintained for 40 min. After reaction, a brown, stable suspension of bimetallic nanoparticles was obtained.

The bimetallic colloids, AuPd and PdCu were obtained with the same procedure of co-reduction, by adding simultaneously H<sub>2</sub>AuCl<sub>4</sub> and PdCl<sub>2</sub> or CuSO<sub>4</sub> and PdCu, with a molar ratio Pd/Au or Pd/Cu ranging from 0.5 to 6.

In Table 1 the characteristics corresponding to the synthesized samples are shown. For AuAg core metals are in brackets, molar ratio and total metal concentration are reported.

## 2.2 Apparatus

The microwave system used is a Milestone MicroSYNTH plus, whose reaction chamber is provided with magnetic stirring, reflux system and an optical fiber temperature controller. The microwave power is generated by 2 x 800 W magnetrons, with frequency 2.45 GHz. In order to respect the scheduled heating ramps, the power is continuously supplied and automatically modulated by a

software; for each ramp only the maximum deliverable power can be imposed. The power is automatically changed by the instrument to follow the temperature profile.

## 2.3 Analytical characterization

UV-VIS extinction spectra were measured with a Lambda 35 spectrophotometer (Perkin Elmer, UK), using a quartz cuvette as sample-holder. Samples for UV-VIS spectroscopy were prepared by diluting the as prepared colloidal suspension with water in order to get into the cuvette the same metal concentration for every sample. Particle size distribution, based on hydrodynamic diameter, was evaluated by Nano S (Malvern, UK), a dynamic light scattering analyzer (DLS), taking care to dilute and pour it in a polystyrene cuvette before measurement. Hydrodynamic diameter includes the coordination sphere and the species adsorbed on the particle surface such as stabilizers, surfactants and so forth. Unreacted metal cations were detected by ICP-AES analysis in order to determine the reaction yield. Samples were prepared as follow: 50 ml of synthesized colloid was poured into a semi-permeable osmotic membrane (Visking tube), which was submerged in a de-ionized water bath. Osmotic pressure caused the exchange of unreacted cations into the external water and the water entrance into the tube. After three hours, the equilibrium was attained and the external liquid underwent ICP (Liberty 200, Varian, Australia) quantitative analyses. Suspensions were dropped and dried on a copper grid, then observed by high resolution transmission electron microscopy (HRTEM) (Tecnai F20).

## 2.4 Catalytic reaction

The catalytic reduction of 4-nitrophenol by NaBH<sub>4</sub> was studied at room temperature (25°C) in a standard quartz cuvette with 1 cm path length and about 3 ml volume. The prepared samples were properly diluted with distilled water in order to achieve a metal concentration of 1.1x10<sup>-2</sup> mM. Thus 10 ml of diluted suspensions were mixed with 5 mL of a 4-nitrophenol solution (9.0x10<sup>-2</sup> mM) and with 1 mL of a NaBH<sub>4</sub> aqueous solution (0.72 M). An aliquot of the solution was poured into the quartz cuvette and the absorption spectra were collected by a Lambda 35 spectrophotometer (Perkin Elmer, USA) in the range between 250 and 500 nm. The rate constants of the reduction process were determined by measuring the change in absorbance at 400 nm, corresponding to the 4-nitrophenolate ion, as a function of time.

# 3 RESULTS AND DISCUSSION

## 3.1 Nanoparticles synthesis and characterization

Metals nanoparticles were obtained by developing the green approach and changing some fundamental parameters: NaOH/metal and glucose/metal ratios, temperature and reaction time. Since the glucose is a weak reducing agent [5] but its reducing power can be drastically enhanced in alkaline conditions. For this reason the right matching of the two molar ratios, NaOH/metal and glucose/metal, represents a key parameters for the reaction, allowing a total reaction yield. Furthermore, in order to obtain small particle size the reduction should be very fast so favoring particle nucleation on particle growth.

For each metal the study of the reaction was carried out and the optimization of all the parameters were achieved. While the bimetallic nanoparticles were produced exploiting the conditions optimized for the single metals.

ICP analysis on external water containing the unreacted cations confirmed for all samples reaction yields higher than 98%, indicating that the so-optimized synthesis allows the complete reduction of precursors.

Table 2- Particle size by DLS and TEM. The UV-VIS maximum wavelength absorption of the sols is also

SAMPLE	ØDLS (nm)	PDI	ØTEM (nm)	λ <sub>max</sub> (nm)
Au	17	0.2	7±3	521
Ag	67	0.1	20±7	409
Cu	314	0.4	3±1	590
Pd	23	0.3	-	-
(Au)Ag01	29	0.3	6±2	513
(Au)Ag02	32	0.2	9±4	442
(Au)Ag03	36	0.2	12±4	423
Au <sub>1</sub> Cu <sub>1</sub>	23	0.3	3±2	550
Au <sub>1</sub> Cu <sub>3</sub>	61	0.3	-	-
Au <sub>1</sub> Cu <sub>6</sub>	80	0.5	-	-
Pd <sub>1</sub> Au <sub>1</sub>	25	0.4	-	-
Pd <sub>1</sub> Au <sub>3</sub>	71	0.3	-	-
Pd <sub>1</sub> Au <sub>6</sub>	34	0.2	-	503
Pd <sub>1</sub> Cu <sub>1</sub>	79	0.4	-	-
Pd <sub>1</sub> Cu <sub>3</sub>	88	0.2	-	-
Pd <sub>1</sub> Cu <sub>6</sub>	99	0.3	-	-

reported.

Except for Cu sample, which evidenced precipitation after 24 hours, all the prepared sols showed an excellent time stability up to several months of storage, even the bimetallic samples containing copper (AuCu, PdCu). Probably in these cases the presence of Au and Pd alloyed with copper, provided a good stability to the bimetallic sols. From the data in table 2 a systematic mismatch between TEM and DLS size can be observed. This frequent behavior is due to various reasons. Firstly, the laser scattering technique measures the hydrodynamic diameter comprehensive of PVP and coordinated molecules. Furthermore, since dispersed particles can aggregate locally, the coarsest sizes in the DLS distribution consist of agglomerates which strongly influence the mean size, which becomes greater than the average primary particle size calculated from TEM image.

However, HRTEM performed for all monometallic samples indicated that nanoparticles are typically spherical and polycrystalline

The difference between TEM and DLS measure is particularly clear for Cu sample, which showed a TEM mean diameter of 3 nm (Fig 1). In this case the strong aggregation phenomena occurring within the suspended nanoparticles affected the final hydrodynamic diameter. Maybe, for this kind of sample DLS results were not a reliable expression of particle size but only an index of the aggregation phenomena.

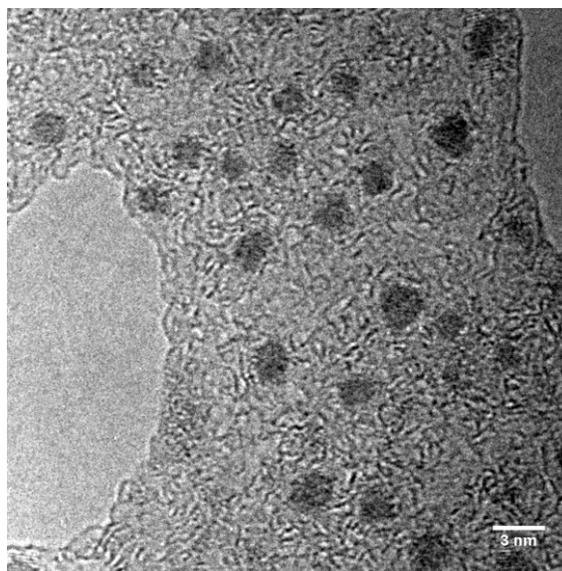


Figure 1 - TEM micrograph of Cu nanosol

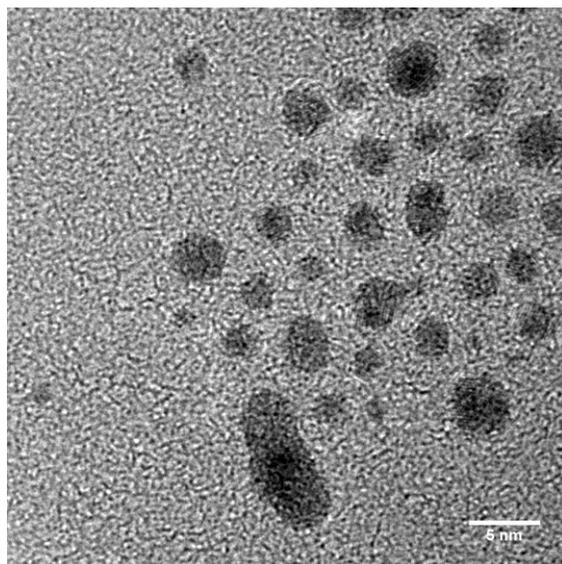


Figure 2 - TEM micrograph of Au<sub>1</sub>Cu<sub>1</sub> nanosol

DLS analyses performed on bimetallic nanosols, evidenced a progressive increase in the hydrodynamic diameter for the samples AuAg (core-shell), increasing the amount of silver. Furthermore in this case it was clearly observed that the

diameter of the particle used as seed influenced the final core-shell size.

Likewise, the bimetallic nanoparticles containing an increasing amount of copper, AuCu and PdCu, evidenced a particle size enlargement, due to the copper tendency of aggregation. Figure 2 showed an image of the sample Au<sub>1</sub>Cu<sub>1</sub>.

XRD spectra proved the presence of the metallic phases with the peak enlargement typical of nanometric crystallites, for all the monometallic samples.

Concerning the bimetallic structures, the formation of AuAg core-shell nanostructures were previously hypothesized by both EDX line scan across nanoparticles and UV-Vis spectroscopy [2], while the alloy formation on AuCu samples was detected by the electron diffraction pattern and by XRD, which showed a shift of the mean peak changing the metal composition. The XRD peak shift was observed also for PdAu and PdCu (table 3).

Sample	2θ
Pd	39,774
Pd <sub>1</sub> Au <sub>1</sub>	38,705
Pd <sub>1</sub> Au <sub>3</sub>	38,488
Pd <sub>1</sub> Au <sub>6</sub>	38,351
Au	38,270

Table 3 - Shift of the main peak of Pd increasing the Au amount.

### 3.2 Catalytic behavior

All the synthesized nanocrystals as effective catalyst for the hydrogenation of p-nitrophenol in the presence of NaBH<sub>4</sub>. Since NaBH<sub>4</sub> was added in large excess, the reduction rates can be regarded as being independent by its concentration. The peak of 4-NP at 400 nm decreased, while at 290 nm a new peak, assigned to 4-AP, appeared. The pseudo-first-order rate constants reported in table 4, were calculated by the decreasing of the band of 4-NP, considering the slope of the ln(A<sub>t</sub>/A<sub>0</sub>) function of time. The final kinetic constants resulted similar to literature values.

As reported by other groups working on polymer supported nanoparticles [6], also our tests evidenced the best activity for the palladium sol, probably due to its intrinsic characteristics of efficient hydrogen relay. In fact, due to the high reactivity of the Pd sol, the tests were performed lowering the concentration of catalyst, to better follow the reaction. For this reason the k value for Pd was not comparable with the others. Anyway the direct comparison within the catalysts can be carried out on the basis of the turnover frequency, TOF.

In agreement with the literature the observed ranking in the hydrogenation of 4-NP was the following: Pd>Au>Ag>Cu. Concerning the bimetallic structures, Ag produced a decreased activity of Au. Au<sub>1</sub>Cu<sub>1</sub> showed a slight increase

of Au, while PdAu for a composition of Pd<sub>1</sub>Au<sub>1</sub> evidenced a strong improvement with respect to both single metals. Further study are now ongoing in order to better understand the behavior of these alloys.

SAMPLE	Kinetic Constant (s <sup>-1</sup> )	TOF
Au	1.70	1.30
Ag	0.21	0.67
(Au)Ag01	0.71	-
Cu	0.20	0.26
Au <sub>1</sub> Cu <sub>1</sub>	1.80	-
Pd	1.95	26.00
Pd <sub>1</sub> Au <sub>1</sub>	2.29	-

Table 4 – Calculated kinetic constants of the monometallic nanoparticles and of some bimetallic nanoparticles

### 3.3 Conclusions

Stable monometallic and bimetallic nanoparticles were synthesized by a microwave assisted route, by using an eco-friendly method that provided a total reaction yield, with excellent stability of the sols. Both DLS analyses and microscopy data confirmed the formation of nanometric sizes. The formation of bimetallic nanostructures are hypothesized on the basis of both electron diffraction analysis and of XRD peak shift. The performed catalytic tests showed that prepared nanostructure act as effective catalyst in the hydrogenation of p-nitrophenol, with a ranking for monometals in agreement with literature data, but with outstanding properties observed for Au<sub>1</sub>Cu<sub>1</sub> and Pd<sub>1</sub>Au<sub>1</sub> nanostructures.

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