

Au, Ag and Au-Ag nanoparticles: microwave-assisted synthesis in water and applications in ceramic and catalysis

M. Blosi^{*}, S. Albonetti^{**}, F. Gatti^{**}, M. Dondi^{*}, A. Migliori^{***}, L. Ortolani^{***}, V. Morandi^{***}, G. Baldi^{****}

^{*} ISTECCNR, Institute of Science and Technology for Ceramics, National Research Council, Via Granarolo 64, 48018, Faenza (Italy), magda.blosi@istec.cnr.it

^{**} Department of Industrial Chemistry and Materials, Bologna University, Viale del Risorgimento 4, 40136 Bologna (Italy), stalbone@fci.unibo.it

^{***} IMM-CNR Bologna - Via Gobetti 101, 40129 Bologna (Italy), morandi@bo.imm.cnr.it

^{****} CERICOL, Via Pietramarina 123, 50053 Sovigliana Vinci (Italy), baldi@colorobbia.it

ABSTRACT

A simple, microwave-assisted route for producing Au/Ag concentrated sols by glucose reduction in water was developed. Ag-Au bimetallic nanoparticles stabilized by polyvinylpyrrolidone (PVP) were characterized and their catalytic activity was studied in the reduction of 4-nitrophenol (4-NP) with NaBH₄. Moreover they were tested as red ceramic inks for ink-jet printing technology. Since the research was developed in collaboration with a company interested in the large scale production of the suspensions, some fundamental properties for an industrial scale up were developed: high metal concentration, long time stability. The Au-Ag core-shell structures were prepared by a two-step process. Particle size-control and colloidal stability were achieved thanks to the accurate reaction optimization, combined with microwave heating, that allows the intensification of process even on large scale production. Prepared Au, Ag and Au/Ag nanocrystals acted as effective catalyst for the reduction of 4-NP.

Keywords: Au, Ag, microwave, bimetallic sols, nanoparticles, water media.

1 INTRODUCTION

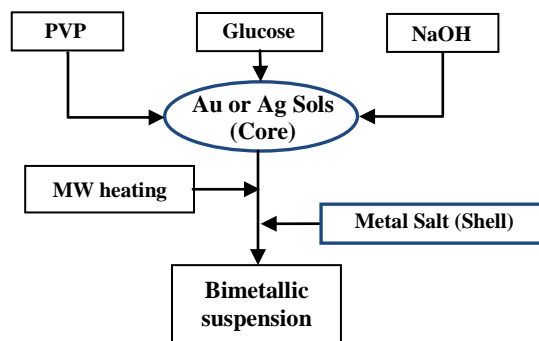
In recent years, colloidal suspensions of different metals have found applications in various fields, catalysis [1], cancer therapy, thermal nanofluids and also as special inks [2-4]. In particular, alloy and core-shell metallic nanoparticles have received special attention due to the possibility of tuning the optical and electronic properties over a broad range by simply varying the composition [5]. For example, current technology of ceramic inks, consisting in the synthesis of gold nanoparticles or their in situ formation in glazes from Au precursors, can take advantage from the use of AuAg core-shell structure of nanoparticles modulating colour and reducing the cost. Moreover metallic nanoparticles show high catalytic activity in different

reactions because a large fraction of the catalytically active metal sites is exposed to the reactants.

2 EXPERIMENTAL PROCEDURE

2.1 Bimetallic Synthesis

All the chemical reagents used in this experiment were analytical grade (Sigma Aldrich). The Au-Ag core-shell structures were prepared by a two-step process, both Au and Ag sols were used as core, acting as seed for the shell nucleation (Scheme 1). Au-core and Ag-core sols were synthesized separately by using the reduction of HAuCl₄ or AgNO₃ by glucose in alkaline water. PVP-coated metal seeds (nPVP/nMetal = 5.5) were synthesized in 5 minutes following a patented procedure [6] by using microwave heating. The reactions were carried out in few minutes at low temperature, 70°C for Ag or 90°C for Au. In order to control the particle size, the glucose amount and the solution pH were carefully optimized for each metal ($1 < n_{\text{Glucose}}/n_{\text{Metal}} < 2$; $1 < n_{\text{NaOH}}/n_{\text{Metal}} < 8$). In Table 1 the characteristics corresponding to the synthesized samples are shown. Core metals are in brackets, Ag/Au molar ratio and total metal concentration are reported



Scheme 1 – Synthesis flow chart

SAMPLE	%Au (mol/mol)	%Ag (mol/mol)	Ag/Au (mol/mol)	Metals Conc [mM]
Au	100	0	-	11
(Au)Ag01	67	33	0.5	15
(Au)Ag02	40	60	1.5	8.3
(Au)Ag03	18	82	4.5	6.1
Ag	0	100	-	50
(Ag)Au01	67	33	0.5	15
(Ag)Au02	40	60	1.5	8.3
(Ag)Au03	18	82	4.5	6.1

Table 1 – Prepared bimetallic nanoparticles

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 Catalytic reaction

The catalytic reduction of 4-nitrophenol by NaBH_4 was studied at room temperature (25°C) in a standard quartz cuvette with 1 cm path length and about 3 mL volume. Due to their lowest dimension, only the Au-Core samples were considered for the catalytic characterization. The prepared samples were properly diluted with distilled water in order to achieve a metal concentration of 1.1×10^{-2} mM. Thus 10 ml of diluted suspensions were mixed with 5 mL of a 4-nitrophenol solution (9.0×10^{-2} mM) and with 1 mL of a NaBH_4 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 through measuring the change in absorbance at 400 nm, corresponding to 4-NP, as a function of time.

2.4 Ceramic application

Prepared nanosuspensions were properly diluted and applied on porcelain stoneware throughout an aerospray gun, taking care that each tiles received the same quantities of pigment. Ceramic tiles were fired at 1150°C for 10 minutes.

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) and by the STEM mode with microanalysis EDX. The colour of ceramics was measured by diffuse reflectance spectroscopy (Miniscan MSXP4000, Hunter Lab, Reston, USA) in the 400-700 nm range (illuminant D65, observer 10°) taking a white glazed tile as reference.

3 RESULTS AND DISCUSSION

3.1 Nanoparticles synthesis

Since particles composition influences their optical properties, the UV-VIS spectra collected for bimetallic structure showed a clear shift with respect to single metal spectra. In fact, while the pure Au nanoparticles solution has a characteristic resonance peak at 520 nm, Au-Ag samples evidenced a clear blue-shifting of the plasmon resonance band increasing the silver content. Figure 1 shows the shift of UV-VIS spectra collected for the Ag-core series. The plasmon resonance shifting confirmed the formation of multi-component nanostructures, in fact for a physical mixing two distinct bands would be observed: at 400 nm for silver and at 520 nm for gold (Fig. 2). The prepared sols show excellent stability up to several months of storage, indicating that no nanoparticles aggregation occurred. Hydrodynamic diameter (HD) measured by DLS (Fig. 3) evidenced that with respect to Ag nanoparticles, Au nanoparticles have a lower HD and samples containing Ag exhibited a progressive increase in particle size. Furthermore, it was clearly observed that the diameter

of the particle used as seed influenced the final core-shell size, in fact the size of the Au-Core particles was lower than Ag-Core samples.

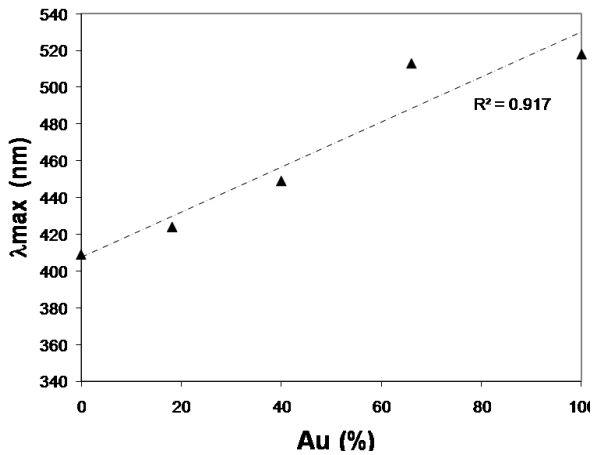


Figure 1 - Surface plasmon resonance shift in Ag-core series depending on particle composition.

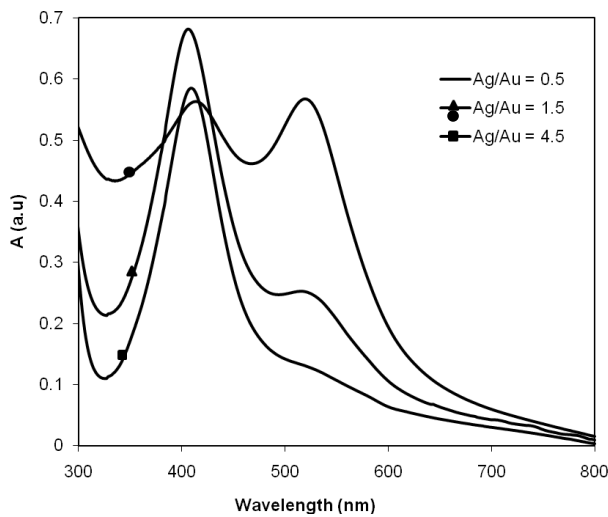


Figure 2 - Extinction spectra of Au-Ag physical mixing

Since DLS values correspond to the hydrodynamic diameter, HRTEM analysis generally indicated a lower nanoparticle diameter (Fig. 4a), highlighting the difference between hydrodynamic diameter, comprehensive of coordination sphere, and real size. However, HRTEM indicated that nanoparticles are typically spherical and polycrystalline and confirmed that samples containing higher shell element concentration exhibited a slight increase in the diameter, indicating that reduction/deposition rather than other process dominates the coating process.

EDX-STEM line scanning across the nanoparticles was carried out to analyze the distribution of the chemical composition. For example in Au core systems, in the samples with Ag/Au ratio of 1.5 or 4.5, the maximum of the Au signal in the center of the nanoparticles, supports the formation of Au-core Ag-shell nanostructures (Fig. 4b). On

the contrary, samples with low amount of Ag exhibit a typical Au-Ag alloy behaviour.

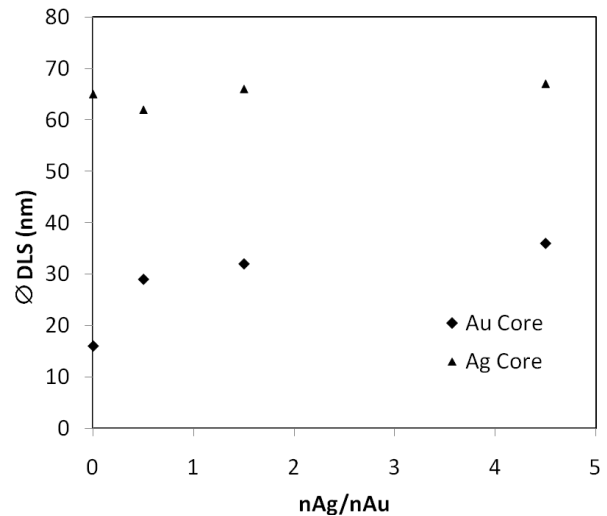


Figure 3 – Mean hydrodynamic diameter measured by DLS for Au-Core and Ag-Core series.

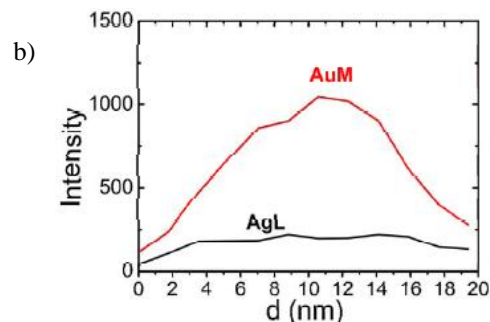
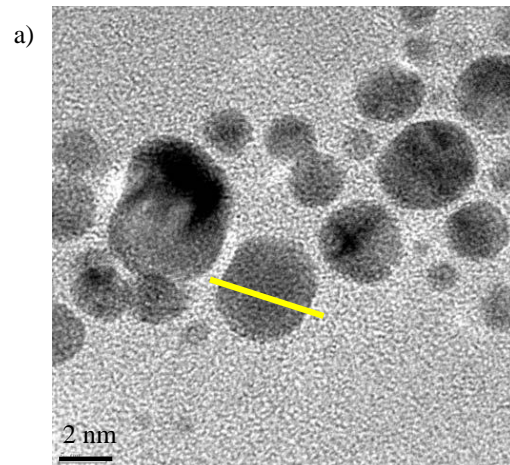


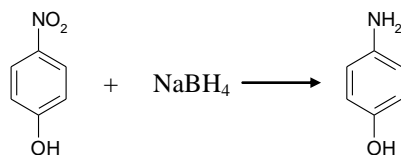
Figure 4 – a) HRTEM analysis of sample (Au)Ag02; b) EDX analysis of a particle profile

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. This synthesis method has been extended to the preparation of bimetallic nanocluster of Au-Cu, both as core-shell structure and as alloy.

3.2 Catalytic behavior

Synthesized nanocrystal of Au, Ag and AuAg act as effective catalyst for the hydrogenation of p-nitrophenol in the presence of NaBH_4 .



4- Nitrophenol (4-NP) 4- Aminophenol (4-AP)

Since NaBH_4 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 (Fig. 5). The pseudo-first-order rate constants reported in table 2, were calculated by the decreasing of the band of 4-NP, considering the slope of the $\ln(A_t/A_0)$ function of time. The final kinetic constants resulted similar to literature values. Increasing the silver amount, a lower catalytic activity was observed, confirming the lower activity of Ag in this reaction.

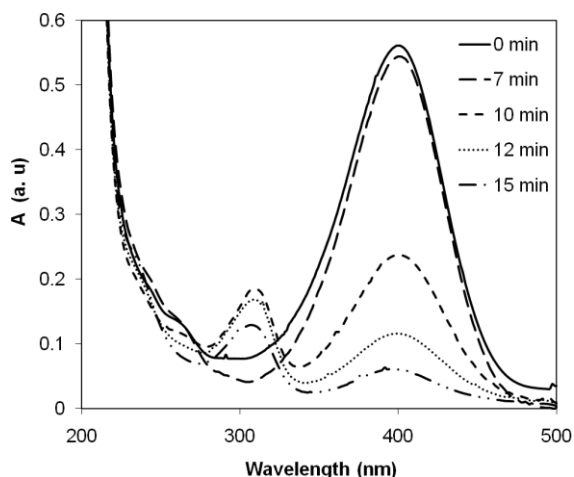


Figure 5 – UV-Vis spectra of 4-NP reduction for sample AuAg 03.

SAMPLE	Ag/Au (mol/mol)	Kinetic Constant (s^{-1})
Au	-	1.75×10^{-2}
(Au)Ag01	0.5	0.71×10^{-2}
(Au)Ag02	1.5	0.48×10^{-2}
(Au)Ag03	4.5	0.31×10^{-2}
Ag	-	0.17×10^{-2}

Table 2 – Calculated kinetic constants for Au-Core samples.

3.3 Colouring performance

Preliminary tests showed that the red component of coating colour is directly correlated with gold concentration. Bimetallic nanopigments behave similarly to Au nanoparticles. Their colouring performance, in fact, is nearly the same of gold nanoparticles given the same Au concentration. Ag-Core samples are characterized by a better colouring performance with respect to Au-Core ones. In particular, sample (Ag)Au02 exhibited the best behaviour, as its performance is practically the same of nanopigments with higher gold concentration.

However from preliminary testes it was noticed that silver seems not to affect significantly the colour quality and despite the deep yellow shade of Ag nanoparticles suspensions, little contribution is given to the pigment-bearing coatings in terms of yellow component (b^*).

3.4 Conclusions

Au-Ag stable bimetallic nanoparticles were synthesized by a microwave assisted route, by using an eco-friendly method that provided a total reaction yield. Both UV-VIS spectroscopy and microscopy data confirmed the formation of bimetallic nanostructures, in the form of core-shell or alloy. Catalytic tests showed that prepared nanostructure of Au, Ag and AuAg act as effective catalyst in the hydrogenation of p-nitrophenol, resulting in agreement with literature data, but with a decreased activity for higher silver content.

The best colouring performance was observed for Ag-Core samples, further analysis are ongoing to explain the reasons of this behavior.

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