

Preparation of amine coated silver nanoparticles using triethylenetetramine

L RAMAJO*, R PARRA, M REBOREDO and M CASTRO

Institute of Research in Materials Science and Technology (INTEMA),
(CONICET – University of Mar del Plata), Juan B Justo 4302 (B7608FDQ), Mar del Plata, Argentina
e-mail: lramajo@fi.mdp.edu.ar

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Abstract. This article presents a simple method towards the preparation of functionalized silver nanoparticles in a continuous medium. Silver nanoparticles were obtained through AgNO_3 chemical reduction in ethanol and triethylenetetramine was used to stabilize and functionalize the metal. The product was characterized with X-ray diffraction (XRD), Fourier-transformed infrared spectroscopy (FTIR), UV-visible spectroscopy, thermal gravimetric analysis (TGA) and transmission electron microscopy (TEM). Monocrystalline silver particles with cubic structure and an average size of 20 nm were obtained. The results reveal that it is possible to synthesize Ag nanoparticles functionalized with amine groups and that particle size is influenced by the processing route.

Keywords. Chemical reduction; electron microscopy (STEM, TEM and SEM); optical properties.

1. Introduction

Metal nanoparticles are being intensively investigated because of their unique optical, electric, and catalytic properties which make them a potential material for utilization in the field of medicine, optoelectronics, composites and in many other frontier areas of science and technology.^{1–3}

Much work has been done to improve the electrical and mechanical properties of epoxy-based electrically conductive adhesives in the past decade.⁴ Some results also showed that a good interface between silver particles and the epoxy resin can promote the conductivity, which play an important role for the performance of dielectric composites. In this way, amine coated Ag nanocomposite can be used by increasing the Ag/epoxy composite conductivity employing a low Ag amount.

In general, silver and gold nanoparticles can be synthesized by several methods, for example: chemical reduction in aqueous solutions,^{5–7} chemical and photo reduction^{8,9} and ultrasonic irradiation.^{10,11} However, most of these procedures only render stable silver dispersions at a relatively low concentration of the metal; hence, they are not suitable for

large-scale manufacturing.¹² To prepare a stable colloidal solution of metal nanoparticles it is necessary to cap the metal with an appropriate chemical agent like a polymer or a surfactant with specific functional groups that can interact with the metal surface.¹³

In the surfactant-assisted synthesis, various physicochemical properties, including the relative concentration of the surfactant, its molecular weight and the pH of the solution, among others, have a great influence on the morphology of the particles as well as on the final optical, electrical, catalytic and/or magnetic properties.^{14,15}

The objective of this work is to study the synthesis of Ag nanoparticles with amine functional groups for applications in electronics. The nanoparticles were obtained by chemical reduction of AgNO_3 in ethanol, using triethylenetetramine as surfactant, according to a simple method developed by Frattini and co-workers.¹⁶ They prepared a diluted Ag nanoparticle solution by chemical reduction in alcoholic medium using aminosilanes as surfactants in different concentrations without the precipitation of particles. In this work, an analysis of the temperature influence on the precipitation of silver nanoparticles was carried out. Also, the nanoparticles were functionalized using triethylenetetramine in order to improve the adhesion between the epoxy resin and the filler.

*For correspondence

2. Experimental

The chemicals used during this research were of high purity. The triethylenetetramine (DEH 24) was supplied by Dow Chemical, whereas the ethanol (99.5%) and silver nitrate (AgNO_3 ; 99.5%) were obtained from Cicarelli and Fluka, respectively.

300 mg of AgNO_3 were added to 200 ml of ethanol in a glass container at two different temperatures, 50 and 70°C, under constant stirring. The triethylenetetramine, previously dissolved in ethanol, was dispersed into the AgNO_3 alcoholic solution in order to obtain a 1 : 10 AgNO_3 : Amine ratio. The UV-Vis absorption spectra of these samples were afterwards acquired with a Shimadzu PC160A Plus UV-vis spectrophotometer using ethanol as reference.

The systems were precipitated by alcohol evaporation at 90°C for 2 h. The solution prepared at 50°C and treated at 90°C was labelled M1 whereas the system prepared at 70°C and treated at 90°C was labelled M2. The latter showed the precipitation of particles before the evaporation of the alcohol. As a result, a solution of amine with precipitated silver nanoparticles was achieved.

These samples were characterized by X-ray diffraction with a Philips PW1030 equipment running with $\text{CoK}\alpha$ radiation and an Fe filter at 40 kV and 30 mA. The crystallite size, L , was estimated with the Scherrer's equation ($L = K\gamma/(\beta\cos\theta)$);¹⁷ where γ is the wavelength of the source (0.179 nm), β is the full width at half-maximum intensity (fwhm) of the diffraction line, θ is the Bragg angle for the corresponding peak and K is a constant equal to 0.9.¹⁰

Transmission electron microscopy (TEM) was performed with a Philips CM200 with an acceleration voltage of 200 kV. The detection of amine groups in the product after the synthesis was achieved by FTIR using a Mattson Genesis II spectrometer.

Finally, amine-coated particles were analysed by thermogravimetric analysis (TGA, Shimadzu TGA-50) under a flow of synthetic air at a heating rate of 10°C/min from room temperature to 700°C.

3. Results and discussion

Figure 1 shows the UV-Vis absorption spectra of M1 and M2 obtained before the alcohol evaporation. The samples exhibited the usual yellow colour and the characteristic absorption band between 350–450 nm. It can be assumed that the small intensity of the band in M1 is attenuated in M2 because of pre-

cipitation. This plasmon band is produced by the conduction electrons of silver which move collectively around the particle, perturbing the electron density, and generating the oscillation of the charges. It usually appears at 415 nm; however, in our samples, the band shift could be attributed to the agglomeration of particles and to their non-spherical shape.¹⁸

The XRD patterns registered for M1 and M2 are shown in figure 2. Both samples showed similar patterns with the characteristic peaks of the cubic structure of Ag [JCPDS 04-0783]. Due to the small particle size, the diffracted planes were translated into quite

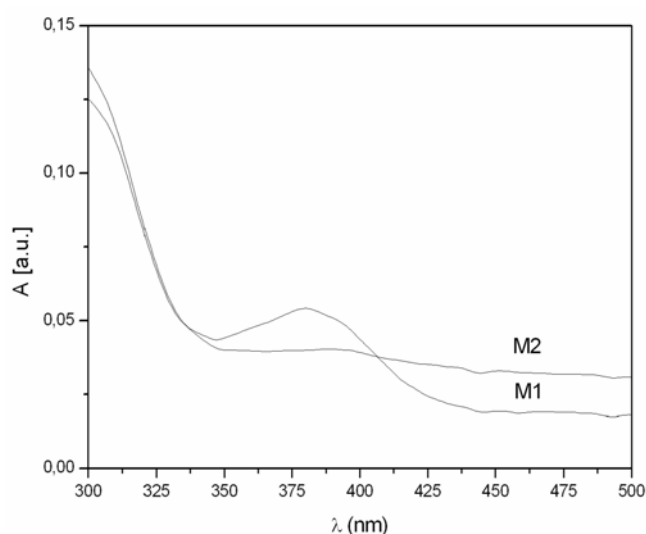


Figure 1. UV-Vis absorption spectra of dissolution M1 and M2 obtained before alcohol evaporation.

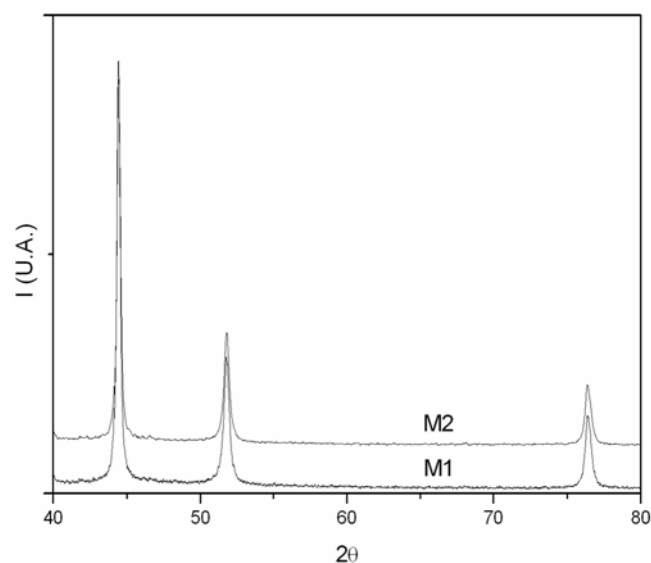


Figure 2. XRD patterns of samples M1 and M2.

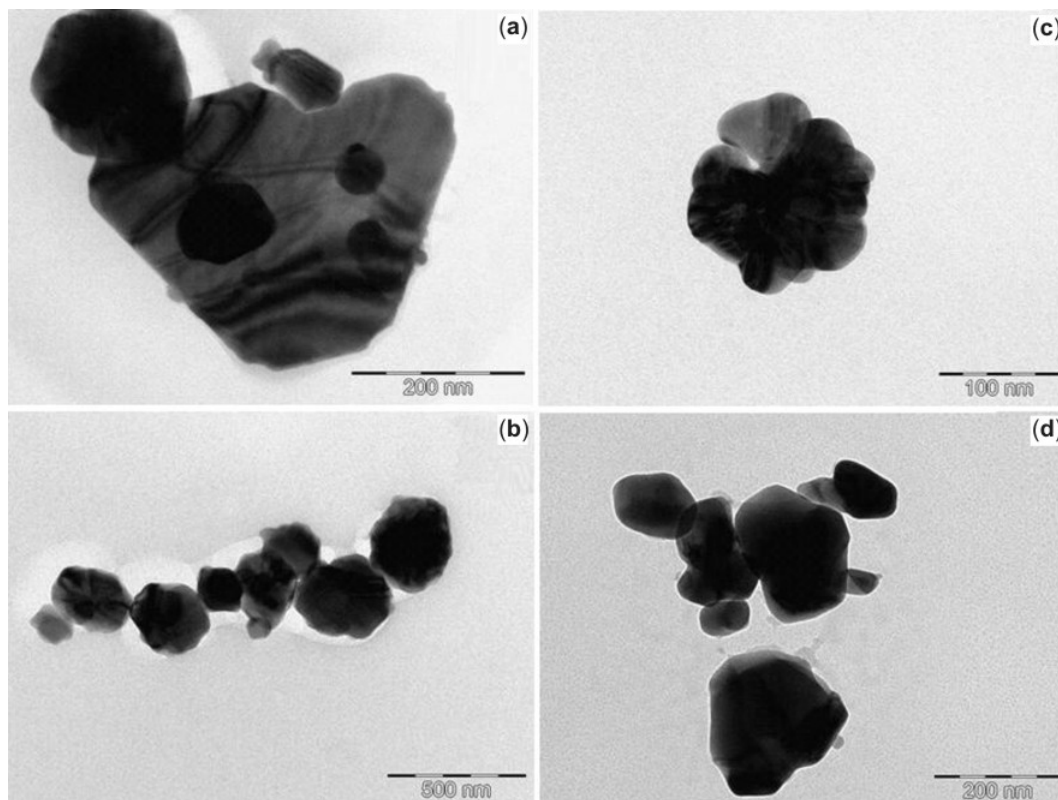


Figure 3. TEM pattern of the silver nanoparticles obtained through different processing routes. (A, B: M1; C, D: M2).

broad signals. For this reason, the equation of Scherrer was used in order to gain more information of the particle size. The silver average particle size calculated was approximately 20 nm.

The TEM images of samples M1 and M2 are shown in figures 3(a, b) and (c, d), respectively. Aggregates of particles with irregular size can be differentiated. Furthermore, the particles are not spherical and the average particle size calculated with the Scherrer's equation does not match with the TEM results because of the agglomeration. M1 displayed a higher average particle size and a higher degree of agglomeration than M2. Sizes range from 50 to 400 nm for M1 sample, and from 25 to 200 nm for M2 are observed.

The agglomeration effect can be ascribed to the adsorption of a molecule of triethylenetetramine at different Ag nanoparticles simultaneously. In general, it is believed that samples prepared at higher temperatures (M2) have a better morphology. At low temperature, the silver reduction is slower and the amine nuclei may form and grow in solution. On the other hand, at higher temperature, silver reduction proceeds faster and the formation of the complex Ag-amine is possible.¹⁹

TEM analyses were complemented with EDS and with the acquisition of SAED patterns (figure 4) for phase identification and chemical characterization of the sample M2. The SAED pattern (figure 4a) was indexed as cubic phase monocrystalline silver (JCPDS 04-0783), with a unit cell of 4.086 Å. The EDS spectrum showed the presence of Ag and Cu from the copper grid.

The FTIR spectra (3750–750 cm^{-1}) of triethylenetetramine and samples M1 and M2 are shown in figure 5. The bands at 2850 and 2950 cm^{-1} observed in every sample are characteristic of the vibration modes ν_a and ν_b of the methylene groups ($-\text{CH}_2-$). Also, the bands at 1120 and 1480 cm^{-1} are typical of the ν -C-OC, δ_s - CH_2 and δ_a - CH_3 vibrations, respectively.²⁰ These vibration modes are invariant with respect to the formation of the complex and to the adsorption at the nanoparticles surface. Then, it is suggested that the alkyl chains adopt the stretched conformation irrespectively of the complex formation.

The spectra also show peaks at 1321, 1580 and 3400 cm^{-1} attributed to ν -C-N, δ - NH_2 and ν_a -NH, respectively.²¹ The position and relative intensity of these bands change with respect to the pure amine. The variation of the $-\text{NH}_2$ and $-\text{NH}$ infrared bands

suggests the formation of links between the nanoparticles.²¹

In figure 6, a scheme with a single molecule linking two Ag nanoparticles is presented.²² In this model, the amine is linked to the Ag particles through the amine groups and no direct contact is established between the silver nanoparticles. Some researchers have attributed a key role to the amine in the Ag^+ reduction due to its decrease in the potential of Ag^+/Ag ($E_{\text{Ag}^+/\text{Ag}}$) promoting the reaction.¹⁶ However, there is still no substantial evidence that confirms this assumption.

The variation of the sample weight, and of its derivative ($\Delta W/\Delta T$), with temperature for M1 and M2 can be observed in figures 7a and b, respectively. According to both TGA curves, the thermal decomposition process is represented by multiple falls in

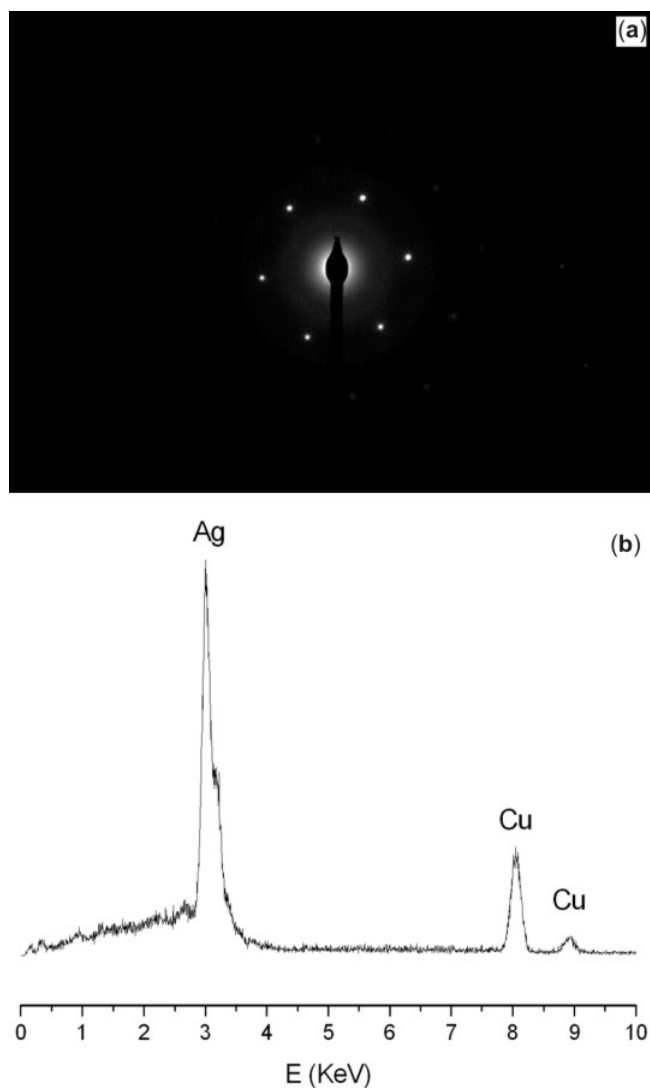


Figure 4. (a) SAD pattern and (b) EDS of the silver nanoparticles presented in the figure 3b.

weight over the temperature ranges from 50 to 125, 125 to 230, 230 to 310 and 400 to 550°C. Each of these changes was seen as a peak in the derivative curves. The weight loss between 50 and 125°C was attributed to residual alcohol evaporation, whereas the rest are due to the decomposition of triethylenetetramine. The residual mass (at 700°C), in both samples was similar, 37 and 38%, indicating the

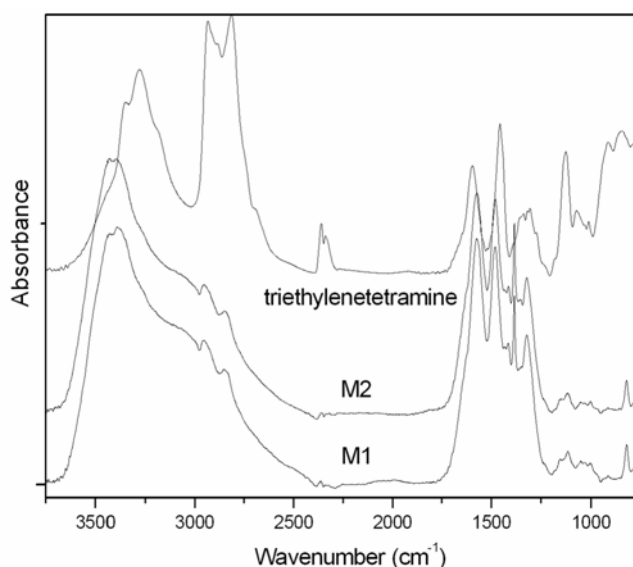


Figure 5. FTIR spectra of triethylenetetramine and Ag nanoparticles in M1 and M2.

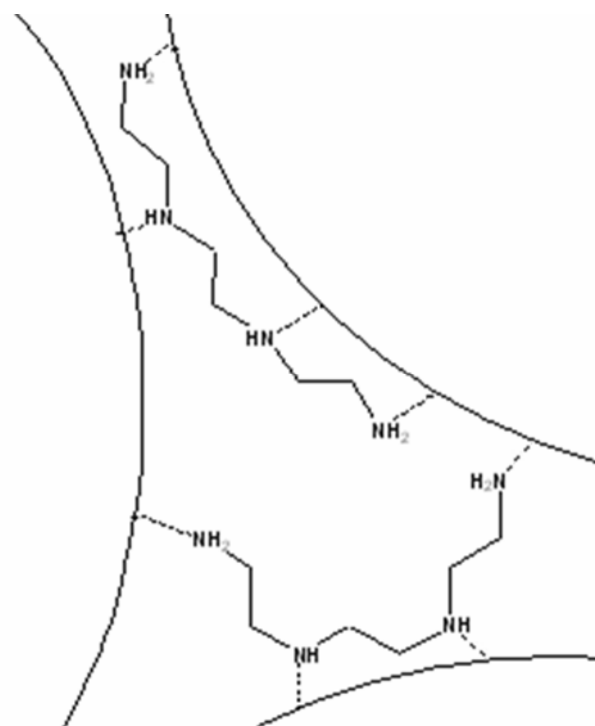


Figure 6. Schematic diagram of the mechanism of amine-induced nucleation of silver nanoparticles.

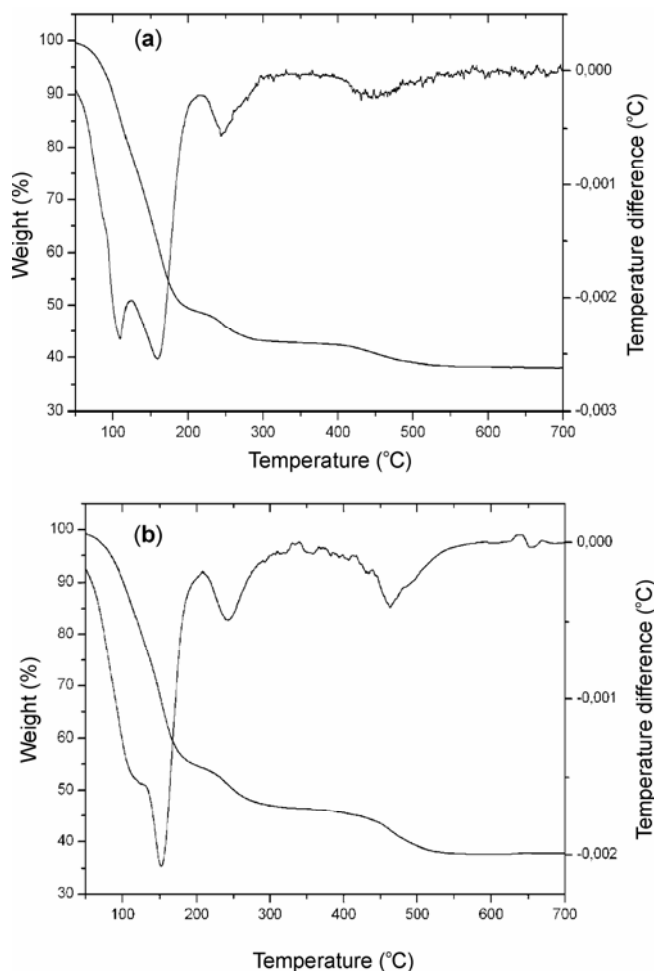


Figure 7. TG curves of Ag nanoparticles synthesized by (a) M1 and (b) M2 routes.

high amount of organics in M1 and M2. On the other hand, it can be recognized that M2 did not show a well-defined peak at 100°C, as M1 did. It can be due to a higher amount of alcohol in M1. In this way, the residual mass at 100°C in M1 was 90.5%, while M2 presented 90.25%.

4. Conclusions

Silver nanoparticles functionalized with an amine group were obtained via chemical reduction of AgNO_3 in an alcoholic solution at two different temperatures, 50 and 70°C.

Before alcohol evaporation, the systems prepared at the highest temperature presented a poor precipitation and did not show a plasmon band. After the alcohol was evaporated, both systems showed similar XRD patterns, FTIR spectra and TGA curves. Different morphologies were observed with TEM as samples prepared at 70°C showed a smaller average particle size.

Non-spherical nanoparticles were obtained and the presence of agglomerates was detected in both systems, although M2 sample presented less agglomeration. Triethylenetetramine was confirmed to act as a surface modifier and linking agent.

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