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Effect of amine groups in the synthesis of Ag nanoparticles using aminosilanes

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Abstract

This work presents a simple method to produce silver nanoparticles through $AgNO_3$ chemical reduction in a continuous media. Aminosilanes act as catalytic reactors and superficial modifiers of Ag nanoparticles, inhibiting their growth and avoiding aggregation. Nanoparticles formation is studied by UV–vis spectroscopy, atomic force microscopy (AFM) and dynamic light scattering (DLS) techniques. The extent of the reduction reaction increases with either a higher aminosilane concentration or with aminosilanes with a higher number of amine groups. The number of amine groups in the aminosilane has also a strong effect on the size of the resulting Ag particles. The morphology of the Ag nanoparticles obtained is spherical and the mean size is of approximately 5 nm.

Keywords: Chemical reduction; Atomic force microscopy (AFM); Optical properties

1. Introduction

Noble metal nanoparticles have been intensely investigated due to their optical, catalytic and electric properties. These characteristics make them suitable for a variety of potential applications on microelectronics. Metallic silver, in particular, either in bulk or in nanoparticles, is a technologically important material. It shows unique properties normally related to noble metals (excellent conductivity, chemical stability, catalytic activity) besides other specific ones that can be controlled depending on the particles size, the size distribution and shape (antibacteriostatic effects, non-linear optical behavior, etc.) with an acceptable production cost [1]. Consequently, there is a remarkable interest in developing procedures to produce silver nanoparticles dispersions on a large scale.

Several methods have been reported for metallic nanoparticles synthesis, including Ag ions chemical reduction in aqueous solutions with or without stabilizing agents [2–5], thermal decomposition in organic solvents [6], chemical and photo reduction in reverse micelles [7,8], radiation chemical reduction [9] and microwave assisted [10], with typical advantages and disadvantages in each case.

However, most of the procedures previously described, yield stable silver dispersions only at relatively low concentrations of metal; hence, they are not suitable for large-scale manufacturing.

This work describes a simple method to produce Ag nanoparticles in a continuous media. The silver nanoparticles are obtained from $AgNO_3$ chemical reduction in ethanol, using aminosilanes as catalysts and colloidal suspension stabilizers. This reaction is attained employing aminosilanes with different amine groups in alcoholic solution in order to achieve nanoparticles isolation and stable colloidal suspension to control size. These compounds were used in different $AgNO_3$:aminosilane ratio (w/w). Besides, aminosilanes work as surface modifiers that avoid particles agglomeration, and their action allows future manipulation of nanoparticles.

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2. Experimental steps

In a dark container to prevent early photoreduction, 300 mg of $AgNO_3$ (Fluka, 99.95%) are added to 180 cm^3 of ethanol (Merck, 99.8%) at a temperature of 60 °C, stirring constantly. Different aminosilanes are dissolved in ethanol and then dispersed in a solution of alcohol–$AgNO_3$ previously prepared under stirring to finally obtain $AgNO_3$:aminosilane ratios of 1:5, 1:10 and 1:15.

The aminosilanes used were:

- 3-aminopropyltrimethoxysilane (APS) (Aldrich, 97%);
- 3-(2-aminoethylaminopropyl)trimethoxysilane (AES) (Aldrich, 97%);
- *N*-[3-(trimethoxysilyl)propyl]diethylenetriamine (ATS) (Aldrich Tech.).

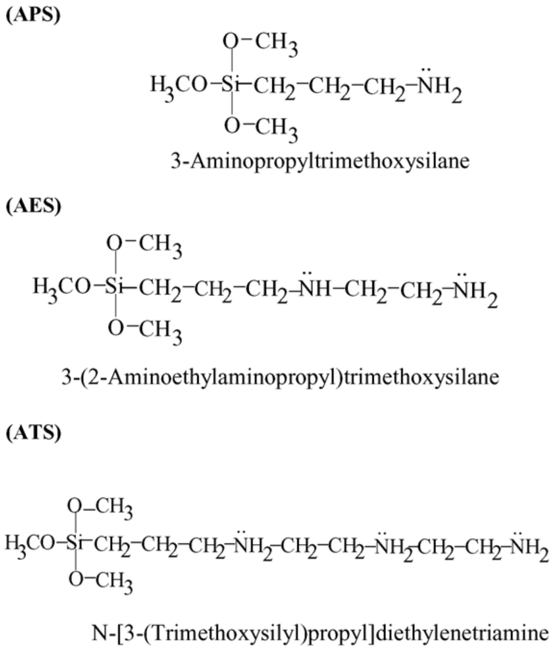
The chemical structure of the three compounds is shown in Fig. 1.

After the preparation of the solution, an air or nitrogen reflux process is carried out during 1 h. Then, the Ag nanoparticles covered with aminosilanes are stored in amber flasks.

For atomic force microscopy (AFM) images, a drop of nanoparticles alcoholic solution is placed over a pristine mica substrate on air atmosphere, the solvent evaporates naturally and then the AFM measurements are taken.

The AFM images were obtained using NanoTec ELECTRONICA equipment with tapping mode configuration at room air temperature. A SiN tip supported by a silicon cantilever (0.76 $N\,m^{-1}$ spring constant and 71 kHz resonance frequency) was used.

UV–vis spectra were performed employing a diluted Ag nanoparticles solution and ethanol as reference. The instrument used was a JASCO Model V-530 UV–vis spectrophotometer.



$H_3CO{-}Si(OCH_3)_2{-}CH_2{-}CH_2{-}CH_2{-}\ddot{N}H_2$

$H_3CO{-}Si(OCH_3)_2{-}CH_2{-}CH_2{-}CH_2{-}\ddot{N}H{-}CH_2{-}CH_2{-}\ddot{N}H_2$

$H_3CO{-}Si(OCH_3)_2{-}CH_2{-}CH_2{-}CH_2{-}\ddot{N}H_2{-}CH_2{-}CH_2{-}\ddot{N}H_2{-}CH_2{-}CH_2{-}\ddot{N}H_2$

Fig. 1. Chemical structure of aminosilanes used as superficial modifiers.

Dynamic light scattering (DLS), Nicomp particle size (Model 380 PSS, Santa Barbara, USA), was used to measure the diameter distribution function of nanoparticles at a fixed scattering angle of 90°.

3. Results and discussion

The reduction of silver ions in different solutions generally yields colloidal silver with particle diameter of several nanometers. These particles have specific optical properties indicated by the presence of intense absorption band at 400–415 nm caused by collective excitation of all the free electrons in the particles [11]. It is known that the presence of catalysts during the formation of metal nanoparticles can influence the resulting nanoparticles morphology and size [12]. Ag nanoparticles formation can be identified by a color change in the solution without precipitation and by UV–vis spectra of the prepared products.

Table 1 shows that Ag nanoparticles formation is favored when the aminosilane concentration increases as well as when the number of amine groups is greater in the aminosilane.

The progress of reduction reaction and formation of silver nanoparticles was monitored by the appearance and increase of the characteristic plasmon absorption band centered around 410 nm and the vanishing of the peaks located around 280 nm that are attributed to the absorption by complexes of Ag^+ and the $Ag_4{}^{2+}$ intermediate reduced species or by small clusters of Ag atoms.

For 1:10 $AgNO_3$:ATS ratio (Fig. 2), the reaction is almost completed after 1 h of refluxing treatment, only a very weak absorption band is observed around 280 nm. A very homogenous colloidal suspension (transparent and yellowish brown color) of nanosized particles was obtained. The following evolution of the absorption spectra shows that the completion of the process occurs between 4 and 24 h, while the plasmon absorption peak is blue-shifted [5,7].

In order to study long-term stability of the Ag nanoparticles in colloidal solutions, normalized UV–vis spectra were obtained for an ethanol solution containing ATS covered Ag nanoparticles (1:5 $AgNO_3$:ATS ratio), at different periods of storage (after refluxing process), as shown in Fig. 3. An absorption band around 400 nm is observed in all spectra due to Ag nanoparticles surface plasmon resonance. A very weak absorption at 280 nm is also observed, indicating an almost

Table 1
Ag nanoparticles formation for different $AgNO_3$:aminosilanes ratio

	1:5	1:10	1:15
APS	No	No	Yes
AES	No	Yes	Not studied
ATS	Yes	Yes	Not studied

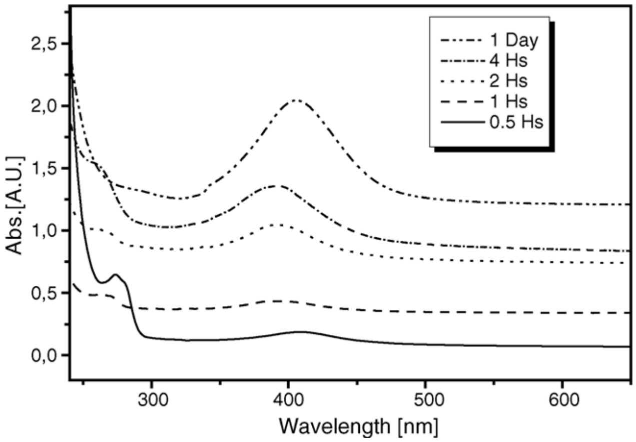


Fig. 2. UV–vis spectra of Ag nanoparticles covered with ATS and prepared under nitrogen atmosphere, 1:10 ratio.

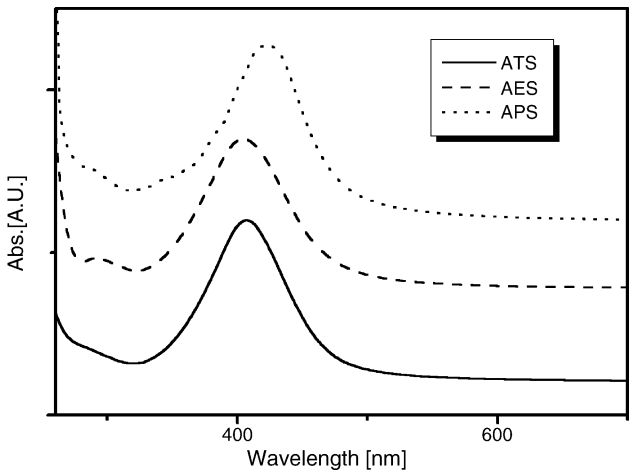


Fig. 4. UV–vis spectra of Ag nanoparticles covered with ATS (1:10), AES (1:10) and APS (1:15).

complete $AgNO_3$ reduction. Besides, no remarkable differences were observed between nanoparticles solution spectra taken at 7 days, 15 days and 3 months from preparation, suggesting system stability.

In Fig. 4, a comparison between APS (1:15 $AgNO_3$:APS ratio), AES (1:10 $AgNO_3$:AES ratio) and ATS (1:10 $AgNO_3$:ATS ratio) covered nanoparticles is shown. The UV–vis absorption spectra of the AES and ATS covered nanoparticles exhibit similar features with peaks centered at 403 and 407 nm and full wave of half maximum (FWHM) of 0.53 and 0.48 eV, respectively. Taking into consideration the fact that the average size of the ATS covered particles is around 5 nm (shown below in Fig. 6). These results would evidence that the size of particles synthesized with AES and ATS are located on the intrinsic size region, where the dipole approximation is valid and occurs in a $1/R$ dependence of the plasmon bandwidth [13].

Consequently and considering that the bandwidth is not inhomogeneously broadened due to different particle size distributions, it is possible to infer that AES covered particles are smaller than ATS covered ones. On the other hand, the APS covered particles show a plasmon absorption band centered at 422 nm and a narrower FWHM (0.42 eV). That great red-shift of the plasmon absorption as well as the narrower bandwidth, if the dipole approximation upholds valid for this size range, indicate that the APS covered particles are much bigger than the ones synthesized with AES and ATS.

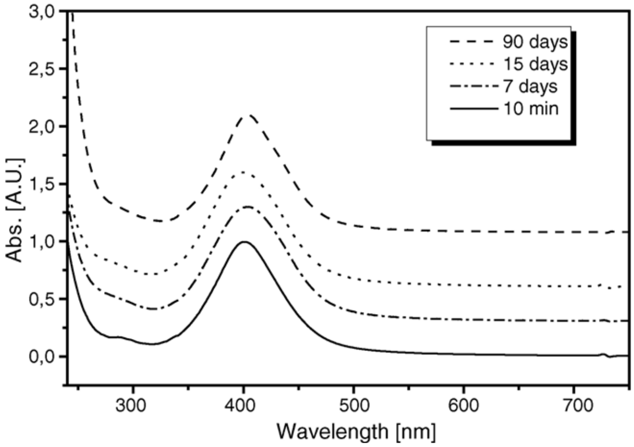


Fig. 3. UV–vis spectra of Ag nanoparticles covered with ATS and prepared under nitrogen atmosphere, 1:5 ratio.

Finally, to study Ag nanoparticles isolated from their dispersing environment, a nanoparticles powder was prepared evaporating ethanol, and then stored in a sealed flask under nitrogen atmosphere.

A portion of this powder was redispersed in ethanol producing stable colloids with extinction spectra very similar to the original ones (Fig. 5). This result is very important because it proves that there is no degradation of Ag nanoparticles when they are separated from their dispersing environment.

Typical AFM images of surface morphology (two-dimensional (2D) view in Fig. 6) do not show nanoparticles clustering due to the fact that aminosilanes act as superficial

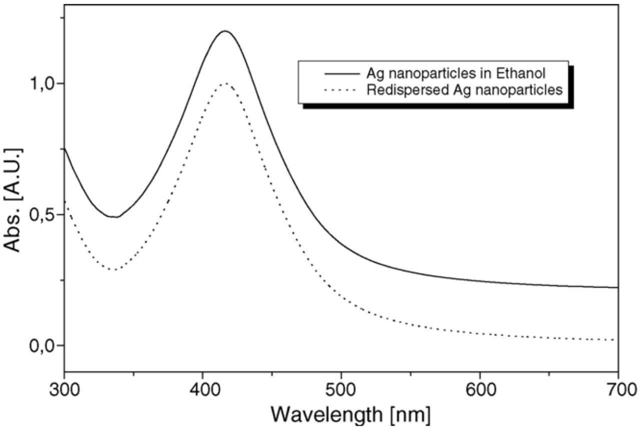


Fig. 5. UV–vis spectra of Ag nanoparticles in ethanol before and after re-dissolution.

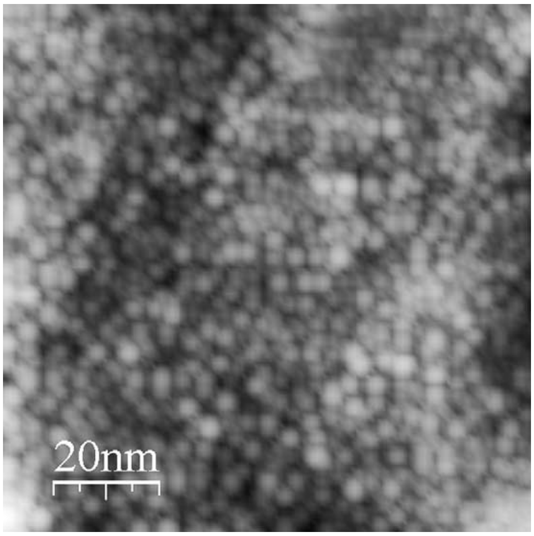


Fig. 6. Two-dimensional (2D) AFM topographic image of Ag nanoparticles covered with ATS (1:5) placed over a mica substrate.

modifiers avoiding this harmful behavior. Although in AFM images, particles seem to be very close to each other, they keep their morphology and individuality, and the geometry of the particles is spherical. This characteristic is repeated in different areas of the sample, with higher or lower population density of nanoparticles. The size of the nanoparticles can be inferred from the AFM images (Fig. 7a) and this study gives an average diameter of 5.14 nm with S.D. 1.02, showing a good particle size distribution.

Furthermore, the average hydrodynamic radius of these particles was measured by DLS showing an average size of 5.3 nm with S.D. 1.1 nm (20.2%) consistent with the results described above. The distribution is shown in Fig. 7b.

The reduction of Ag^+ to Ag requires a relatively high negative redox potential. The reduction of silver ion at 60 °C in a polar Lewis base solvent (ethanol) with aminosilanes, resulted in spontaneous reduction of the silver salt and the growth of silver nanoparticles depending on the number of amino groups in aminosilanes used and on their concentration. For ATS, although the reaction takes more than 4 h to be completed, the formation of nanosize Ag particles starts almost immediately after the catalyst agent is added to the $AgNO_3$/ethanol solution, irrespective of the $AgNO_3$:ATS ratio used. In contrast, in the case of the $AgNO_3$ solution in ethanol with APS, precipitation over flask walls occurred after longer refluxing times and no absorption band characteristic of surface plasmon resonance was observed in remnant solutions for 1:5 and 1:10 $AgNO_3$:APS ratios. A stable Ag particles colloidal solution was only obtained using a higher $AgNO_3$:APS ratio, which was equal to 1:15.

Amine groups can be attributed a key role in the reduction of Ag^+. And this may be due to the coordination between N and Ag^+, which may decrease the potential of Ag^+/Ag

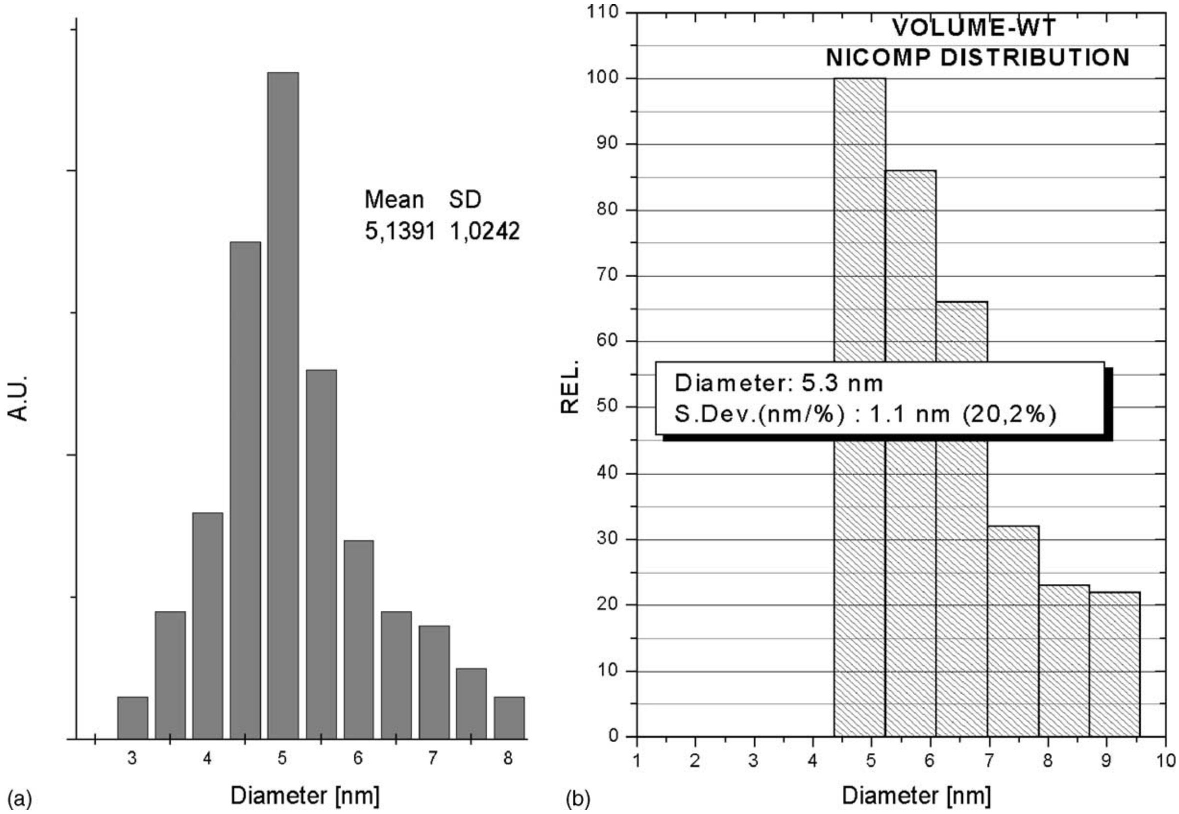


Fig. 7. (a) Ag nanoparticles size distribution from AFM images and (b) obtained by DLS.

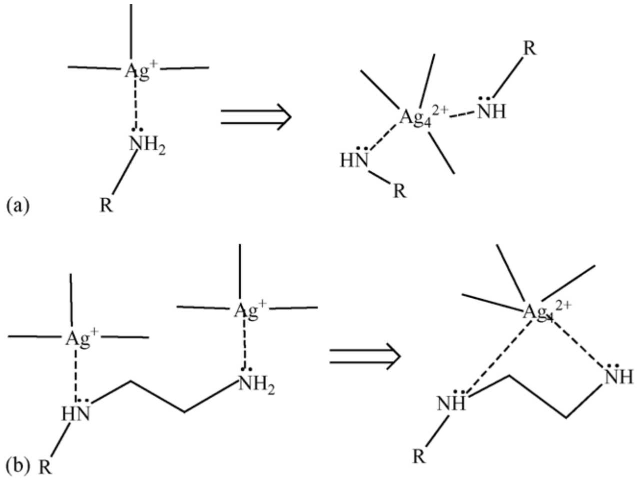


Fig. 8. Coordination of amine groups for (a) APS and (b) AES and ATS.

($E_{Ag+/Ag}$) and promote the reduction of Ag^+. The extent of the reduction reaction increases with either a higher aminosilane concentration or with aminosilanes with a higher number of amine groups. The number of amine groups in the aminosilane has also a strong effect on the size of the resulting Ag particles. However, the size differences are mainly between the Ag particles synthesized with APS (one amine group) and the ones prepared with AES (two amine groups) or ATS (three amine groups). This behavior would be attributed to the different manners of coordination of the Ag^+ ions by the APS and the AES or the ATS. The APS with one amine group behaves as a monodentate ligand (Fig. 8a). Contrarily, the AES and ATS with two and three amine groups, respectively, could behave as bidentate ligand, chelating and/or bridging. Although, the formation of chelates with a central Ag^+ ion would be restricted by steric effects, the bridging of two or three Ag^+ ions is feasible, each amine group of same molecule of AES or ATS ligands to one Ag^+ ions (Fig. 8b). The manner of coordination would be strongly affecting the formation of the intermediate reduced species, such as Ag_4^{2+}, as well as its subsequent evolution for forming particles. Consequently, the AES and ATS attached molecules to the intermediate species would restrict more the growing of the particles than the APS molecules.

4. Conclusions

Ag nanoparticles dispersions, 5 nm average size, were obtained by chemical reduction of $AgNO_3$ in aminosilanes alcoholic solution.

Formation of Ag nanoparticles is favored with aminosilanes concentration increase and with the number of amine groups in the aminosilanes. The number of amine groups in the aminosilane has also a strong effect on the size of the resulting Ag particles.

Colloidal solutions are stable for long periods and particles can be redispersed after the separation of their alcoholic environment without modification of their properties.

Aminosilanes act as superficial modifiers and catalytic reactors of Ag nanoparticles, inhibiting their growth and avoiding aggregation.

Acknowledgements

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