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Use of H_2O_2 for the Morphology Control of Silver Nanostructures †

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Abstract: Nanotechnology is a field that has advanced significantly in the last decades. Nanomaterials, as a result of their nanometric dimensions, exhibit unique properties that enhance their technological and biomedical applications. Metallic nanoparticles, like silver nanoparticles (AgNPs), have stood out due to their intrinsic properties, such as the localized surface plasmon resonance, which can be controlled by their size and shape. Thus, in this work, we developed a practical synthetic procedure to obtain AgNPs with controlled morphology. AgNPs were prepared in water by the chemical reduction methodology, using different stabilizers under room temperature or with heating, and sodium borohydride as the reducing agent. The results obtained showed that the AgNPs were successfully prepared, using polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) as the stabilizing agents. The AgNPs' shape could be controlled by the absence or presence of H_2O_2, forming nanospheres or nanoprisms, respectively. The nanomaterials prepared exhibited colloidal stability with a negative surface charge, and TEM images confirmed their spherical and prismatic morphology. Furthermore, the results showed that the two synthesis conditions, room temperature and heating, afforded AgNPs in spherical and prismatic shapes, however, with temperature the size distribution was lower. Thus, this methodology has the potential to be expanded to other stabilizing agents as a simple and practical method to prepare silver nanostructures with controlled morphology.

Keywords: nanotechnology; synthesis; silver nanostructures; spherical shape; prismatic shape

1. Introduction

Nanotechnology is a field of science that has developed notably in recent times, attracting more and more, the interest of researchers. This science involves the development and application of nanomaterials with specific properties related to their dimension [1]. These properties allow the improvement and/or the appearance of physico-chemical properties, potentiating the technological and scientific development of this field.

One of the main factors that contribute to the properties of nanoparticles (NPs), is the increase of the surface to volume ratio of these structures, thus, the atoms of the surface have a smaller number of neighbors, presenting unsatisfied chemical bonds, which makes them more reactive, with greater mobility and higher free energy [2].

Metallic NPs are among the most used nanomaterials, since they present interesting optical properties, which depend on the shape and size of the particles [3]. The behavior of these properties, as well as their applications, is associated with plasmonic effects. Metallic NPs act as antennas to convert light into localized electric fields or as guides to direct light to specific locations, making it possible to actively manipulate light at the nanoscale by controlling the shape and size of the particles [4]. Among these types of nanomaterials, silver nanoparticles (AgNPs) stand out, in addition to the optical properties already mentioned, the ease of obtaining as well as the relatively low cost make colloidal Ag NPs quite attractive. [5–9].

The synthetic route selected to obtain the NPs can be crucial to effectively achieve nanomaterials with controlled shape, size, narrow size distribution, low agglomeration, and its respective optical properties. Moreover, the choice of synthetic method and the manipulation of parameters such as temperature, reagents, order of addition of reagents, pH, concentration, stabilizer, and solvent, can produce NPs with different shapes (spheres, prisms, rods, cubes, and so on) and different sizes [10,11].

One of the methods used to control the morphology of AgNPs is the use of H_2O_2 and sodium citrate, as was confirmed by the reports performed by Zhang et al. (2011). In this study, the authors observed that a small amount of both H_2O_2 and sodium citrate, led to the formation of nanoprisms in good yield and uniformity. The nanoprisms formation was monitored using absorption spectra, observing a decrease in the intensity of the characteristic band of the nanospheres (at 400 nm) and the appearance of a new band at approximately 500 nm. Therefore, these authors concluded that the morphology can be controlled using H_2O_2 associated with a ligand, which can be sodium citrate or other di- or tricarboxylate compounds, being the shape-directing effect intrinsically related to the presence of H_2O_2. However, these authors only used polyvinylpyrrolidone (PVP) as the additional stabilizing agent [12].

Thus, in this work, we optimize and expand this methodology to other stabilizing agents. It was developed a methodology to synthesize AgNPs in spherical and prismatic shapes, in an aqueous medium, with different stabilizers: PVP, polyvinyl alcohol (PVA), and ascorbic acid (AA).

2. Materials and Methods

Silver nitrate ($AgNO_3$, 99%), sodium borohydride ($NaBH_4$, 99.99%), and polyvinyl alcohol (PVA, 99%) were purchased from Sigma-Aldrich. Trisodium citrate (TSC, 99%) and polyvinylpyrrolidone (PVP, 95%, Mw ≈ 29 K) were obtained from Dinamica (Brazil). Hydrogen peroxide (H_2O_2, 30%) was obtained from Moderna, and L-(+)-Ascorbic acid (AA, 99%) supplied by Vetec. The water used was ultrapure and all reagents were used without further purification.

As detailed in Table 1, AgNPs were synthesized with the following stabilizers: ascorbic acid (AA), polyvinyl alcohol (PVA), and polyvinylpyrrolidone (PVP). The amount of hydrogen peroxide used varied, from 0 μL to form spherical NPs to 60 μL to form prismatic ones. There were also variations in temperature conditions, with the reaction occurring at room temperature or at 70 °C, directly affecting the duration of the reaction.

Initially, a 24.75 mL aqueous solution was prepared combining silver nitrate (50 mM, 50 μL) and trisodium citrate (75 mM, 0.5 mL). Then the stabilizer, PVP (17.5 mM, 0.1 mL), PVA (17.5 mM, 0.1 mL) or AA (27.7 mM, 0.1 mL) was added. Then H_2O_2 was added to the solution (0 μL to form spheres and 60 μL to form prisms). And finally, sodium borohydride (100 mM, 250 μL) was added to start the reduction. This entire process occurred under stirring at 500 rpm and at room temperature or 70 °C. The reaction was concluded when the color of the system stabilized, and the dispersion was stored at room temperature.

Table 1. Summary of methodology parameters.

Temperature	**Duration (min)**	**Shape**	**Amount of H_2O_2 (µL)**	**Color**	**Stabilizer**	**Code**
Room Temperature (RT)	30	Sphere	0	Yellow	PVP	AgNP-RT-PVP-E
					PVA	AgNP-RT-PVA-E
					AA	AgNP-RT-AA-E
		Prism	60	Blue	PVP	AgNP-RT-PVP-P
					PVA	AgNP-RT-PVA-P
					AA	AgNP-RT-AA-P
Heating 70 °C (H)	3	Sphere	0	Yellow	PVP	AgNP-H-PVP-E
					PVA	AgNP-H-PVA-E
					AA	AgNP-H-AA-E
		Prism	60	Blue	PVP	AgNP-H-PVP-P
					PVA	AgNP-H-PVA-P
					AA	AgNP-H-AA-P

The AgNPs were characterized by UV-Vis spectroscopy (Evolution 600 s model (Thermo Scientific®), transmission electron microscopy (FEI Tecnai G2 Spirit Biotwin transmission electron microscope with a resolution of 0.34 nm and under voltage from 20 to 120 kV) and potential Zeta (Zetasizer Nano ZS90 equipment, Malvern Analytic).

3. Results

The methodology used was based on the publication by Zhang et al. (2011), in which AgNPs stabilized with PVP at room temperature were prepared in spherical and prismatic shapes. In this work, we changed some parameters in the procedure to achieve the best synthetic performance to obtain AgNPs with different stabilizers and shapes. Initially, two synthesis conditions were defined, room temperature (~25 °C) and heating (70 °C), then three different stabilizers were used, PVP, PVA, and AA. Finally, spherical and prismatic AgNPs were formed as yellow and blue colloidal dispersions, respectively

3.1. UV-Vis Spectroscopy

The syntheses were performed, in both mentioned conditions, by reducing an aqueous solution of $AgNO_3$ with the reducing agent, $NaBH_4$, in the presence of sodium citrate and the stabilizers (PVP, PVA, and AA). In this step, the reactions resulted in yellow colloidal dispersions with a plasmon band around 400 nm (Figure 1a,b), suggesting the formation of spherical NPs. For the synthesis of the nanospheres, there were no significant differences in the UV-Vis absorption spectra with changing temperatures.

For the formation of the nanoprisms, H_2O_2 (60 µL) was added to the solution, confirming the action of H_2O_2 as a shape-director agent. For these systems, it was observed a difference in the bandwidth and in the absorption band position of the NPs prepared at room temperature and under heating (Figure 1c,d). The AgNPs with PVP showed a redshift when prepared with heating, which may be related to their size increase. The inverse happened for the AgNPs with PVA, in which, there was a decrease in the size of these nanomaterials and a blueshift of the absorption band. No significative changes were observed in the absorption band for AgNPs with AA. However, it is possible to note a slight narrowing of the band near 600 nm, which may be related to the formation of a more homogeneous dispersion in size.

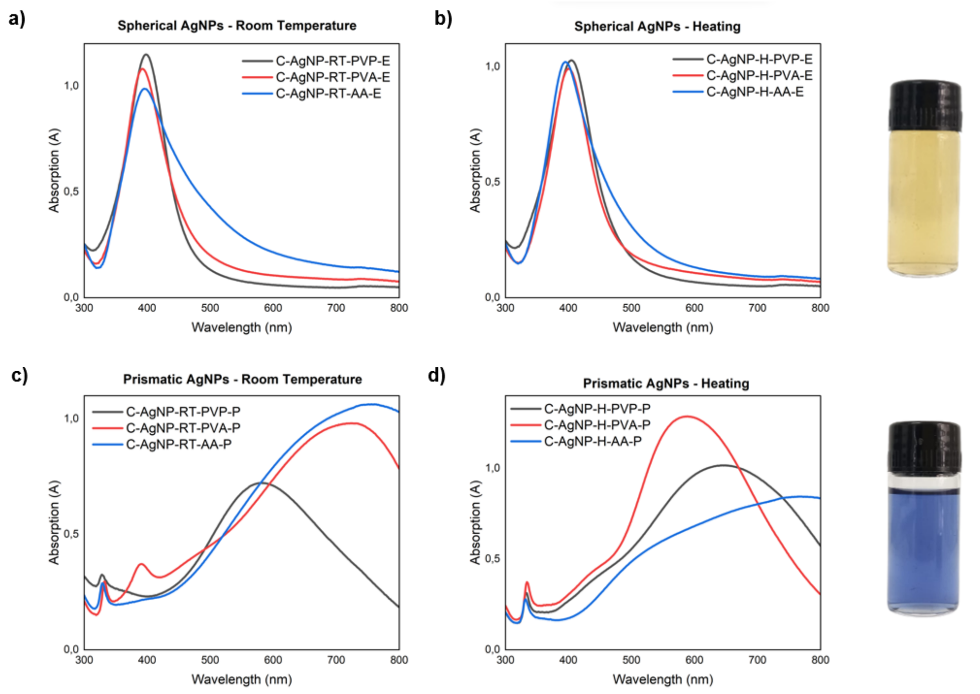

Figure 1. UV-Vis absorption spectra of samples synthesized at room temperature and with heating in (**a**,**b**) spherical and (**c**,**d**) prismatic shapes.

3.2. Transmission Electron Microscopy

The transmission electron microscopy images of the AgNPs provided, besides evidence of the NP's shape, relevant information about the size distribution (Figure 2). The spherical NPs showed a narrow size distribution, especially those synthetized under heating. The nanoprisms, on the other hand, exhibited a wider size distribution curve, both for the syntheses at room temperature and under heating.

The spherical AgNPs showed a smaller average diameter (between 7.1 and 13.5 nm), when compared to the prismatic AgNPs, especially those prepared with heating. The prismatic NPs exhibit a larger size than the spherical ones, however, the largest mean value observed for the size of the nanoprisms, is 36.7 nm, which is considered relatively low, when compared with the values found in the literature, which are usually above 50 nm [13,14]. The thickness of the prismatic AgNPs was also measured, and all showed values less than 10 nm.

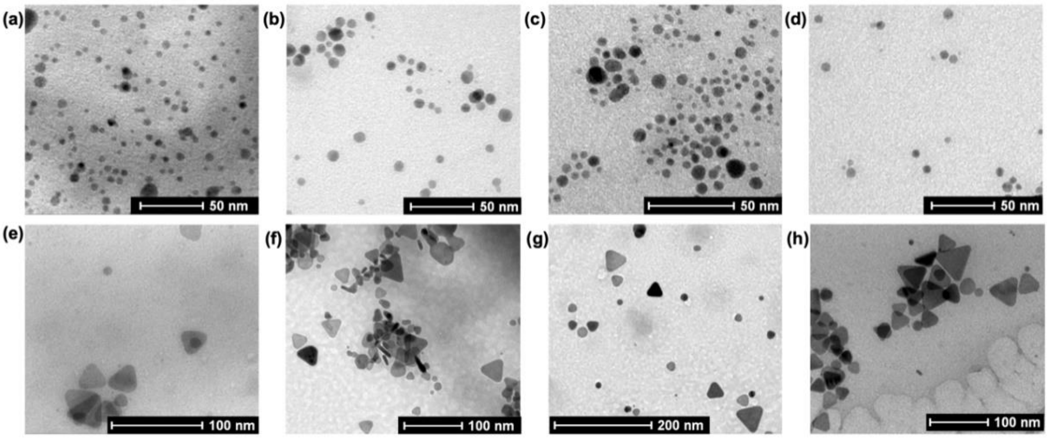

Figure 2. TEM images of the samples (**a**) AgNP-RT-PVP-E, (**b**) AgNP-RT-PVA-E, (**c**) AgNP-H-PVP-E, (**d**) AgNP-H-PVA-E, (**e**) AgNP-RT-PVP-T, (**f**) AgNP-RT-PVA-T, (**g**) AgNP-H-PVP-T e (**h**) AgNP-H-PVA-T.

3.3. Zeta Potential

All nanoparticles showed good colloidal stability, which can be evidenced by the zeta potential values, in which all nanoparticles had average values smaller than −30 mV.

4. Discussion

In this study, the prismatic shape control was achieved using H_2O_2, which was needed to prepare the nanoprisms, confirmed by UV-Vis spectroscopy and TEM. Thus, it is possible to infer that H_2O_2 can promote the formation of anisotropic structures. However, this behavior does not depend solely on peroxide since it is necessary to have a synergistic action with sodium citrate. It is known that H_2O_2 is a strong oxidizing agent, and that citrate is a stabilizing agent that can contribute to the shape direction growth of AgNPs. Citrate acts as a co-coating agent and selectively attaches itself to the {111} facets, blocking the growth along that direction and allowing ample growth in the lateral direction [15]. The results obtained here are in agreement with that reported in the literature and reinforce the mechanism proposed by Zhang et al. (2011). According to which, the addition of $NaBH_4$ partially reduces silver ions, which are stabilized by citrate and borohydride ions, temporarily. At the same time, the extensive growth of the NPs is inhibited by the oxidative attack of H_2O_2. There is a dynamic equilibrium between reduction by $NaBH_4$ and oxidation by H_2O_2, resulting in the small nanoparticle maintenance. As the $NaBH_4$ is consumed over time, the protection of the borohydride ions weakens, allowing the production of silver cores with different structures, including those with defects that favor the growth of planar nanoparticles.

5. Conclusions

In this work, silver nanoparticles with spherical and prismatic shapes, stabilized with PVP, PVA, and AA, were successfully prepared. The characterizations of AgNPs indicate the formation of stable and negatively surface-charged nanomaterials. The transmission electron microscopy images confirm the spherical and prismatic morphology of the nanostructures, with size ranging between 7.1 and 8.4 nm for spherical AgNPs and between 28.6 and 33.7 nm for prismatic AgNPs. Furthermore, we were able to expand the use of this methodology to other stabilizing agents, to yield AgNPs with controlled shapes.

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