

Biocompatible silver nanoparticles prepared with amino acids and a green method

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Abstract The synthesis of nanoparticles is usually carried out by chemical reduction, which is effective but uses many toxic substances, making the process potentially harmful to the environment. Hence, as part of the search for environmentally friendly or green synthetic methods, this study aimed to produce silver nanoparticles (AgNPs) using only AgNO₃, Milli-Q water, white light from a xenon lamp (Xe) and amino acids. Nanoparticles were synthesized using 21 amino acids, and the shapes and sizes of the resultant nanoparticles were evaluated. The products were characterized by UV–Vis, zeta potential measurements and transmission electron microscopy. The synthesis of silver nanoparticles with tryptophan and tyrosine, methionine, cystine and histidine was possible through photoreduction method. Spherical nanoparticles were produced, with sizes ranging from 15 to 30 nm. Tryptophan does not require illumination nor heating, and the solution color changes immediately after the mixing of reagents if sodium hydroxide is added to the solution (pH = 10). The Xe illumination acts as sodium hydroxide in the nanoparticles synthesis, releases H⁺ and allows the reduction of silver ions (Ag⁺) in metallic silver (Ag⁰).

Keywords Amino acid · Light · Nanoparticle · Photoreduction · Silver · Cystine · Histidine · Methionine · Tyrosine · Tryptophan

Introduction

Recently, silver nanoparticles (AgNPs) have emerged as promising candidates as new antibacterial agents (Makarov et al. 2014). Their powerful antibacterial and broad-spectrum activity against morphologically and metabolically different microorganisms seems to be correlated with a multifaceted mechanism by which nanoparticles interact with the microbes (Kim et al. 2007; Roni et al. 2015; Franci et al. 2015). For this reason, AgNPs applications cover biomedical and food packaging, clothing to water filters, cosmetics, children toys, orthopedics, pharmaceuticals and medical devices, among others (Shustak and Jerusalem 2011). Materials for nanoparticles surface modification may have biological origin, such as enzymes (Durán et al. 2015), plant extracts (Contino et al. 2016), biodegradable polymers (Shustak and Jerusalem 2011), and microorganisms (Sweet et al. 2012). Amino acids have been shown to be useful in the synthesis of metal nanoparticles, as first reported in the early 2000s. Mandal et al. (2002) described the synthesis of gold nanoparticles by the reduction of chloroaurate ions using aspartic acid.

The amino acids are required for the production of various biomolecules and vitamins which are needed for proper body growth. All amino acids possess the functional amino (–NH₂) and carboxyl (–COOH) groups, as well as a side chain (–R group). The amino acids can act as reducing as well as capping agents in the preparation of AgNPs with different shapes and sizes (Shankar and Rhim 2015; Selvakannan et al. 2004).

AgNPs have been produced by chemical reduction methods, physical methods (photoreduction (Callegari et al. 2003), microwave dielectric heating (Horikoshi et al. 2010), ultrasonic irradiation (Gottesman et al. 2011), radiolysis (Tung et al. 2012)), and biological routes (Roni

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Table 1 Utilized reagents

Amino acid	From	CAS	Molecular formula	Molecular weight (g/mol)	Polarizability (cm ⁻³)
L-Aspartic acid (Asp. D)	Vetec	617-45-8	C ₄ H ₇ NO ₄	133.10	24.9
L-Glutamic acid (Glu. E)	Vetec	56-86-0	C ₅ H ₉ NO ₄	147.13	29.5
L-Alanine (Ala. A)	Synth	56-41-7	C ₃ H ₇ NO ₂	89.09	18.6
L-Arginine base (Arg. R)	Synth	74-79-3	C ₆ H ₁₄ N ₄ O ₂	174.20	42.2
L-Asparagine monohydrate (Asn. N)	Vetec	5794-24-1	C ₄ H ₈ N ₂ O ₃ ·H ₂ O	150.13	28.4
L-Cysteine hydrochloride (Cys. C)	Sigma-Aldrich	52-89-1	C ₃ H ₇ NO ₂ ·S·HCl	157.62	26.4
L-Cystine (Cys2)	Sigma-Aldrich	56-89-3	C ₆ H ₁₂ N ₂ O ₄ S ₂	240.30	
L-Phenylalanine (Phe. F)	Vetec	63-91-2	C ₉ H ₁₁ NO ₂	165.19	37.8
Glycine (Gly. G)	Sigma-Aldrich	56-40-6	C ₂ H ₅ NO ₂	75.07	14.0
L-Glutamine (Gln. Q)	Synth	56-85-9	C ₅ H ₁₀ N ₂ O ₃	146.15	36.1
L-Histidine (His. H)	Vetec	71-00-1	C ₆ H ₉ N ₃ O ₂	155.16	39.5
L-Isoleucine hydrochloride (Ile. I)	Sigma-Aldrich	17694-98-3	C ₆ H ₁₃ NO ₂ ·HCl	167.63	32.6
L-Leucine (Leu. L)	Vetec	61-90-5	C ₆ H ₁₃ NO ₂	131.18	32.6
L-Lysine hydrochloride (Lys. K)	Vetec	657-27-2	C ₆ H ₁₄ N ₂ O ₂ ·HCl	182.65	36.0
L-Methionine (Met. M)	Vetec	63-68-3	C ₅ H ₁₁ NO ₂ S	149.20	35.9
L-Proline (Pro. P)	Vetec	147-85-3	C ₅ H ₉ NO ₂	115.13	26.9
L-Serine (Ser. S)	Synth	56-45-1	C ₃ H ₇ NO ₃	105.09	20.2
L-Tyrosine (Tyr. Y)	Vetec	60-18-4	C ₉ H ₁₁ NO ₃	181.19	40.3
L-Threonine (Thr. T)	Vetec	72-19-5	C ₄ H ₉ NO ₃	119.12	24.8
L-Tryptophan (Trp. W)	Vetec	73-22-3	C ₁₁ H ₁₂ N ₂ O ₂	204.22	54.1
L-Valine (Val. V)	Vetec	72-18-4	C ₅ H ₁₁ NO ₂	117.15	27.9

et al. 2015; de Matos and Courrol 2014). With the growing emphasis on the green environmental aspect of chemical processes, the green synthesis of AgNPs has attracted great attention to the development of environmental friendly technologies.

Photochemical reduction, or photoreduction, in which Ag⁺ is reduced to Ag⁰ by hydrated electrons or free organic radicals, is one of the mildest and simplest processes to synthesize silver nanoparticles. The free electrons or radicals are produced under visible and UV light irradiation, which is both temporally and spatially controllable. When the photochemical method is used to reduce Ag ions, silver nanoparticles can be prepared by controlling the reaction conditions. AgNPs was reported using tyrosine and tryptophan previously by Shankar et al. (2015) and Selvakannan et al. (2004). Selvakannan et al. (Shankar and Rhim 2015; Selvakannan et al. 2004) demonstrate that the amino acid tyrosine is an excellent reducing agent under alkaline conditions and may be used to reduce Ag⁺ ions to synthesize stable silver nanoparticles in water. Kshirsagar et al. (2014) demonstrated an efficient synthesis of AgNPs by a simple photoreduction method using tyrosine as the photoreducing and stabilizing agent. Tomita et al. (2014) obtained AgNPs using tryptophan and light, and observed their lethal effects against bacteria.

This study was aimed at developing a simple, fast, cheap, and environmentally benign method for the synthesis of

spherical AgNPs using aqueous solutions of amino acids, AgNO₃ and incoherent white light. No additives, such as organic solvents, surfactants, or specific reducing agents were used.

Materials and methods

A preliminary study was carried out to select the most appropriate amino acids for the silver nanoparticles synthesis. The amino acids selection was based on their stability after synthesis (as evaluated by zeta potential measurement), and on the intensity of their UV–Vis absorption spectra.

The reagents used in this work are shown in Table 1. For the synthesis of the nanoparticles, each amino acid was mixed with AgNO₃, followed by the addition of Milli-Q water. The solutions were then stirred in a vortex mixer (Fisatom Equipamentos Científicos) for 5 min and exposed to a 150-W Xenon (Xe) lamp (Cermex, Excelitas Technology). The Xe lamp was positioned at 10 cm of the recipient containing the solution. The illuminated region covered exactly the recipient diameter and the intensity at the solution was estimated to be 3.6 W/cm².

The effects of the amino acid/metal concentration ratio, irradiation time, temperature, and pH on the nanoparticles formation were evaluated by ultraviolet–visible (UV–Vis)

absorption and fluorescence spectroscopy, and transmission electron microscopy (TEM) for each of the 21 amino acids. The AgNPs synthesis parameters are presented in Table 2.

The absorption measurements were carried out on an UV–Vis spectrophotometer (Shimadzu Multispec-1501), and the samples were analyzed using quartz cuvettes with 10 mm optical paths, immediately after stirring at room temperature.

Microscopic analyses were performed on a LEO 906E transmission electron microscope (Zeiss, Germany), with images captured using a Megaview III camera (Zeiss) and processed using the iTEM—Universal software HAS Imaging Platform (Olympus Soft Imaging Solutions GmbH, Germany). For analysis, 5 μl of each sample were deposited on a square copper mesh (37 $\mu\text{m}/\text{side}$), previously coated with parlodium and an amorphous carbon film. After allowing the sample to soak into the mesh (3 min), the excess sample was removed using absorbent paper and subjected to analysis. The ImageJ 1.46 software program was used to determine the average size of the nanoparticles by applying the Gaussian fitting in Origin 8.

Zeta potential measurements were performed by focusing a 633 nm laser on the colloidal suspension (Malvern Zetasizer NanoZS). During analysis, the changes in the pH and zeta potential (mV) of the nanoparticles were monitored.

Results and discussion

The AgNO_3 and AgNO_3 in the presence of amino acids water solutions are colorless. After light irradiation, the water and amino acids solutions changed to brownish/yellow hues for five amino acids: Cystine (Cys2), Histidine (His), Methionine (Met), Tyrosine (Tyr) and Tryptophan (Trp), indicating the presence of silver nanoparticles in the suspensions, as can be seen in the Fig. 1.

The absorption spectra for all amino acids solutions are shown in Fig. 2, where a–e present the spectra for the five amino acids (Cys2, His, Met, Tyr and Trp) in which nanoparticles were formed, before and after irradiation; (f) presents the spectra after irradiation for the other 16 amino acids, evidencing that nanoparticles were not formed. In the absorption spectra, the presence of a band at ~ 420 nm (Surface Plasmon Resonance—SPR band) indicates the formation of spherical AgNPs. The position of the SPR band peaks was 402 nm for Tyr (a), 410 nm for Met (b), 416 nm for Trp (c), 427 nm for Cys2 (d) and 475 nm for His (e). For all the other amino acids, the SPR band was not observed (f). The full-width at half maximum (FWHM) of the UV–Vis spectral bands indicates the size distribution of the colloidal dispersion (Kelly et al. 2003). The smaller

the FWHM, lower the polydispersity and more homogeneous the nanoparticle size. The amino acids Tyr and Trp show lower FWHM indicating solutions that have more homogeneous nanoparticles.

To better understand the synthesis process, the concentration dependence and irradiation times were studied for the amino acid Tryptophan (TrpAgNPs) and the results are discussed in the next sections.

Variations of the silver nitrate concentration

The absorbance of the silver colloidal tryptophan solutions (~ 12 mM) with varying AgNO_3 concentration and irradiated by 1 min, were measured. The area under SPR band between 340 and 800 nm was calculated and is plotted in Fig. 3 as a function of the AgNO_3 concentration, showing that the SPR band increases with the silver concentration, indicating that more particles are formed. Data were fitted by a logistic equation (Eq. 1) (Barlow and Blake 1989), and the fit parameters are shown in the inset in Fig. 3. In our case, describe the fraction of AgNPs produced as a function of the AgNO_3 concentration.

$$y = V_{\max} \frac{x^n}{k^n + x^n} \quad (1)$$

In this equation, X represents the AgNO_3 concentration, V_{\max} is the maximal AgNPs production, K is the concentration producing half this effect, and the power, n determines the slope of the curve.

Xenon light irradiation time

Tryptophan (12 mM) and silver nitrate (5 mM) water solution does not show SPR absorption bands characteristic of silver nanoparticles since amino acids by itself are not an adequate reducing agent for the reduction of silver. Therefore, for nanoparticles production starting from AgNO_3 , the reduction $\text{Ag}^+ + 1\text{e}^- \rightarrow \text{Ag}^0$ must occur, leading to the formation of silver clusters, subsequent nucleation and growth of the nanoparticles. Illumination with white light is essential for the formation of nanoparticles since it promotes, through light absorption, the reduction of silver ions (Ag^+) to metallic silver (Ag^0), starting the process outlined, being a catalyst for the formation of AgNPs. Xenon lamps are used due to their blue shifted spectra, which contain more energetic photons that are more efficient at reducing the silver ions. Simultaneously, amino acids control the agglomeration of silver particles, thereby stabilizing the colloidal suspension (McGilvray et al. 2011). Each amino acid has a different oxidation potential, which depends on its size and the spatial arrangement of its atoms.

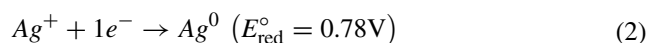
Table 2 AgNPs synthesis parameters

AgNPs		Histidine		Methionine		Tyrosine		Tryptophan	
Cystine									
$T_{amb} = 25\text{ }^{\circ}\text{C}/2'\text{ Xe}$		$T_{amb} = 25\text{ }^{\circ}\text{C}/2'\text{ Xe}$	$T_{amb} = 25\text{ }^{\circ}\text{C}/22.55'\text{ Xe}$	$T_{amb} = 25\text{ }^{\circ}\text{C}/2'\text{ Xe}$	$T_{amb} = 25\text{ }^{\circ}\text{C}/2'\text{ Xe}$	$T_{amb} = 25\text{ }^{\circ}\text{C}/2'\text{ Xe}$	$T_{amb} = 25\text{ }^{\circ}\text{C}/2'\text{ Xe}$	$T_{amb} = 25\text{ }^{\circ}\text{C}/2'\text{ Xe}$	$T_{amb} = 25\text{ }^{\circ}\text{C}/2'\text{ Xe}$
pH final = 9.1		pH final = 7.8	pH final = 4.0	pH final = 10.6	pH final = 9.3				
[Ag] mmol/L	[Cyst] mmol/L	[Ag] mmol/L	[His] mmol/L	[Ag] mmol/L	[Met] mmol/L	[Ag] mmol/L	[Tyr] mmol/L	[Ag] mmol/L	[Tri] mmol/L
2.01	0.23	2.01	4.03	2.01	9.82	2.01	1.00	2.01	2.01
Ratio: 0.1		Ratio: 2.0		Ratio: 4.9		Ratio: 0.5		Ratio: 1.0	

The SPR band area, between 340 and 800 nm was calculated and plotted as a function of the Xe irradiation time. The effect of the irradiation time is shown in Fig. 4. The experimental points were fitted by Hill equation, and the fit parameters are shown in the inset in Fig. 4. By this figure, it is observed that the increase in the nanoparticles concentration is light irradiation dependent. The k (half-saturation dose) was $\sim 6177\text{ s} \times \text{intensity (max)}$ with a Hill coefficient of 0.9. The dependence of the potentiation of the nanoparticle-induced formation on the light exposure time further confirms that light irradiation can potentiate nanoparticles production.

The tryptophan, tyrosine, Histidine, methionine and cystine can promote silver nanoparticles formation under xenon lamp illumination conditions. The role of this amino acids/mechanism is described below:

The illumination promotes both oxidation of amino acids and silver reduction:



Each amino acid has a different reduction potential, which depends on its size and the spatial arrangement of its atoms. The higher the reduction potential, greater is the tendency of the species in gaining electrons (reducing), as well as smaller the reduction potential, greater is the tendency of species to donate electrons (oxidizing). To facilitate and/or accelerate the oxidation process, the use of electromagnetic radiation (xenon lamp) is necessary. The combination of the photons and temperature supplied by the xenon lamp can facilitate the loss of electrons (oxidation), enabling the reduction of the metal species and nanoparticle formation. After the reduction, silver clusters are formed with the subsequent nucleation and growth of the nanoparticles. Thus, light is a catalyst for the formation of the AgNPs.

We also observe a correlation between tendency of an amino acid oxidation and the formation of dipole moment in this amino acid, a property known as polarizability, which is closely linked to the size of the electronic cloud. According to the literature, the polarizability of amino acid residues in neutral medium is proportional to the molar mass (Pethig 1979).

Of the five amino acids selected to silver nanoparticles synthesis (tryptophan, tyrosine, Histidine, methionine and cystine), three correspond to four amino acids that have higher polarizability (tryptophan, tyrosine and Histidine), the other two (methionine and cystine), although intermediate polarizability feature, present sulfur in its structure, which has high affinity for silver, enabling the AgNPs synthesis (Choi et al. 2003). As polarizability increases, the dispersion forces also become stronger. Thus, silver atoms attract oneanother more vigorously and nanoparticles are formed. It was observed that even showing a high

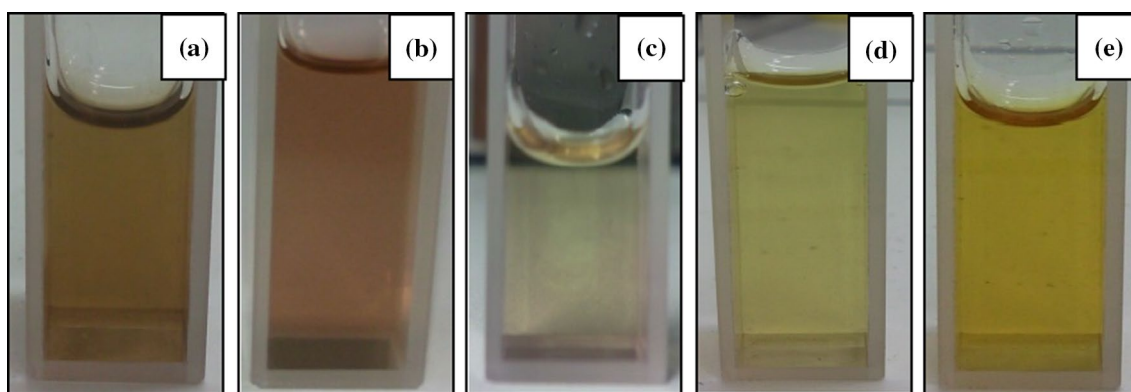


Fig. 1 Colored solutions prepared with **a** Cys2, **b** His, **c** Met, **d** Tyr, and **e** Trp, indicating the formation of silver nanoparticles

polarizability, the synthesis of silver nanoparticles with the amino acids arginine and as the phenylalanine was not efficient. A color modification was observed during illumination but the solutions were not stable after the irradiation with light Xe.

Temperature variation with Xe irradiation time

A Xe lamp radiates over a wide spectral range, from the ultraviolet to the infrared (185 nm to 2000 nm). Figure 5 shows that with longer irradiation times the temperature of the silver particles solutions increases. The biggest temperature variation ($\Delta T = T_{\text{final}} - T_{\text{initial}}$, where T_{initial} is before irradiation and T_{final} is after irradiation), 45 °C, was observed in tryptophan AgNPs irradiated for 5 min, while the smallest variation, 30 °C, was observed for Cys2 and Met.

Experimentally, it was observed that the heat accelerated the formation of silver nanoparticles, leaving them even more homogeneous.

Importance of pH in nanoparticles stability

Tryptophan does not require illumination or heating for producing silver nanoparticles, and the solution color changes immediately after the mixing of reagents if sodium hydroxide is added to the solution (pH = 10), showing the importance of pH adjustment for nanoparticles production. In this case, sodium hydroxide raises the pH, releases H^+ and allows the reduction of silver ions (Ag^+) to metallic silver (Ag^0).

The Xe illumination has a similar role as sodium hydroxide in the nanoparticles synthesis. The evolution of pH before and after Xe irradiation to light for Trp, Tyr, Cys2, Met and His is shown the Fig. 6. The following pH

changes ($\Delta\text{pH} = \text{pH}_{\text{afterXe}} - \text{pH}_{\text{beforeXe}}$) were observed after irradiation for 2 min: Trp = -0.8 , Tyr = -2.0 , His = $+1.0$, Cys = -2.0 and Met = -2.0 . After Xe light irradiation, the Trp, Tyr, Met, and Cys solutions become more acidic, probably due to the release of H^+ by the oxidation of amino acids. An opposite effect was observed for His, probably due to its basic side chains at neutral pH. Histidine is a unique amino acid, as it can exist in neutral or positively charged forms within the physiological pH range of 5.0–7.0, and have both hydrogen donor and acceptor atoms in its side chains (Patronov et al. 2014).

The zeta potential for silver nanoparticles synthesized with the parameters described in the Table 2 are shown in Fig. 7. For His, Cys2, Trp and Tyr, the zeta potential measurements indicates that higher stability ($> |20 \text{ mV}|$) may be achieved while maintaining the basic pH. The zeta potential of TrpAgNPs irradiated with Xe light, changes exponentially with the solution pH (Tomita et al. 2014). The pH increase modifies the amino acids structure, enabling nanoparticle stabilization against agglomeration and precipitation. Nevertheless, it was observed that Met presents a positive potential, differently from the other amino acids.

Amino acids and AgNPs interact by the pairs Ag–O, Ag–N, Ag–S and Ag–ring, i.e., regions with electrons with the metallic surface (Ramezani et al. 2015). These interactions are a mixture of covalent character (sharing of electrons) and electrostatic, and Lewis acid–base pair. It has been found by zeta potential measurements that in basic media the nanoparticles surface charge is negative, resulting in the formation of negatively charged species (anions); these species confer charge to the nanoparticles, which repel each other because they have equal

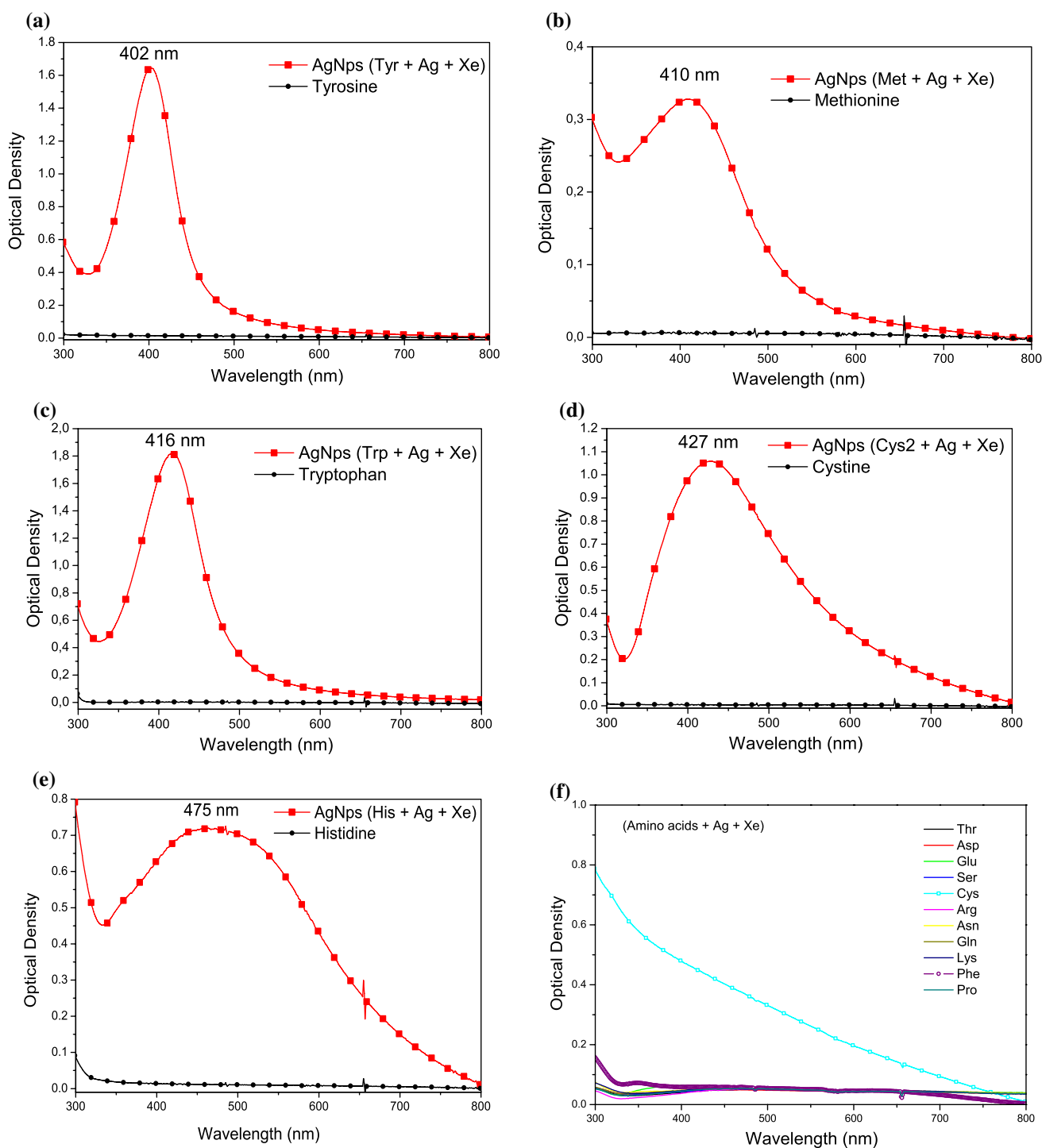


Fig. 2 UV-Vis spectra (amino acids + AgNO₃ + Xe light) of the reaction mixtures for Tyr (a), Met (b), Trp (c), Cys2 (d), and His (e). All the others amino acids (f). The synthesis parameter for each amino acids + AgNO₃ + Xe light can be obtained in the Table 2

sign charges, avoiding clutter. In an acid medium, the surface charge is predominantly positive (protonated species).

It was observed that the increase of pH value for methionine significantly harms the stability of the suspension, justifying the maintenance of an acidic medium (~4/5). A

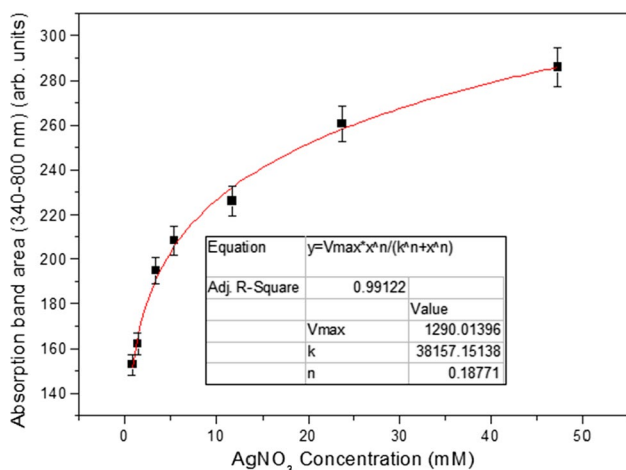


Fig. 3 Area of the SPR absorption bands of silver nanoparticles formed with illumination for 1 min by a Xe lamp as a function of the silver concentration

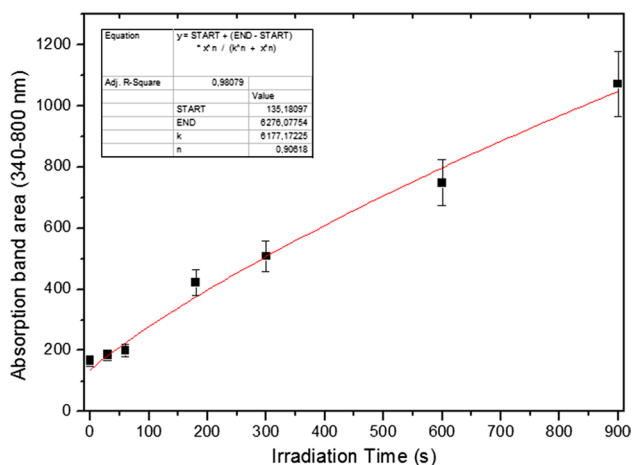


Fig. 4 Area of the SPR absorption bands of silver nanoparticles produced using different Xe lamp light illumination times

similar effect was observed in the literature for cysteine that has a covalent bond with the $-SH$ group and the electrostatic binding with the $-NH_3^+$ group (Li et al. 2006). With the basification of the medium, there is progressive carboxylic group ionization. So, in basic media, with the carboxyl radical deprotonated, there will be two regions of strong interaction with the nanoparticle, shortening the distance d between two nanoparticles, which leads to increased agglomeration and precipitation, as schematized in Fig. 8.

TEM images

TEM was used to characterize the size, shape and morphology of the synthesized AgNPs prepared with Tyr, Met, Trp,

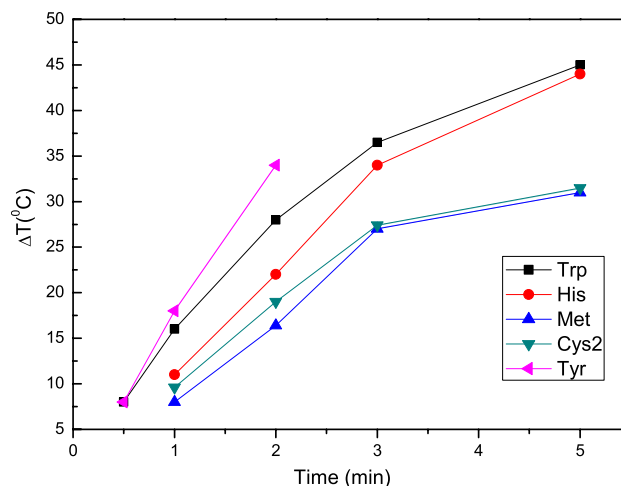


Fig. 5 Temperature variation as a function of Xe irradiation time for AgNPs/Tryptophan. T_{initial} = before light e T_{final} = after light

Cys2 and His. For all these amino acids the AgNPs morphology is nearly spherical. The AgNPs sizes ranged from 16 to 30 nm, as shown in Fig. 9.

Conclusions

AgNPs were obtained with five of the 21 studied amino acids under Xe light irradiation: tyrosine, methionine, tryptophan, cystine and histidine. The light reduces silver ions (Ag^+) into metallic silver (Ag^0), and amino acids prevent the agglomeration of nanoparticles adhering to the surface (steric effects and load).

Tryptophan does not require illumination or heating to form nanoparticles and the solution color changes immediately after the mixing of reagents if sodium hydroxide is added to the solution. This occurs because sodium hydroxide releases H^+ and allows the reduction of silver ions (Ag^+) to metallic silver (Ag^0). For the other amino acids, the Xe illumination plays a similar role as the sodium hydroxide in the nanoparticles synthesis. With illumination, the SPR band area increase following a Hill growth curve with $AgNO_3$ concentration and irradiation time for TrpAgNPs solutions.

Zeta potential measurements indicated that the stability of the colloidal suspensions was higher in basic media, in which there is greater surface charge formation, particularly negative charge, except for methionine.

The light is a catalyst for the formation of the AgNPs, changing solutions pH and temperature. Simultaneously, amino acids control the agglomeration of silver particles, thereby stabilizing the colloidal suspension. This method is simple, cheap and fast. This study opens the possibility of applying such nanoparticles in biological systems

Fig. 6 pH values of AgNO_3 and amino acids solutions before and after Xe irradiation for **a** Trp (16.1 mM), **b** Tyr (15.1 mM), **c** His (1.8 mM), **d** Met (15.1 mM), **e** Cys2 (0.3 mM), AgNO_3 (10.5 mM), milli-Q water (pH = 5.4) and pH adjustment with NaOH

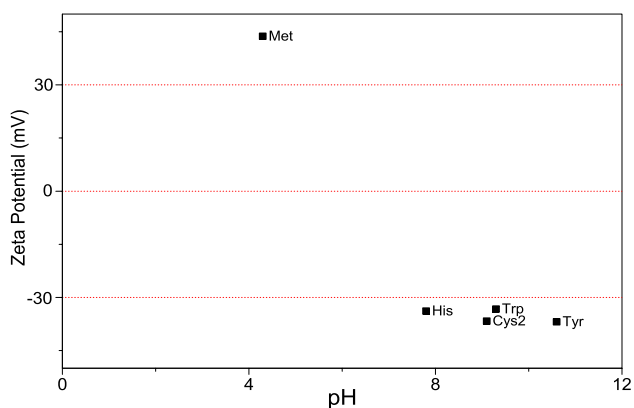
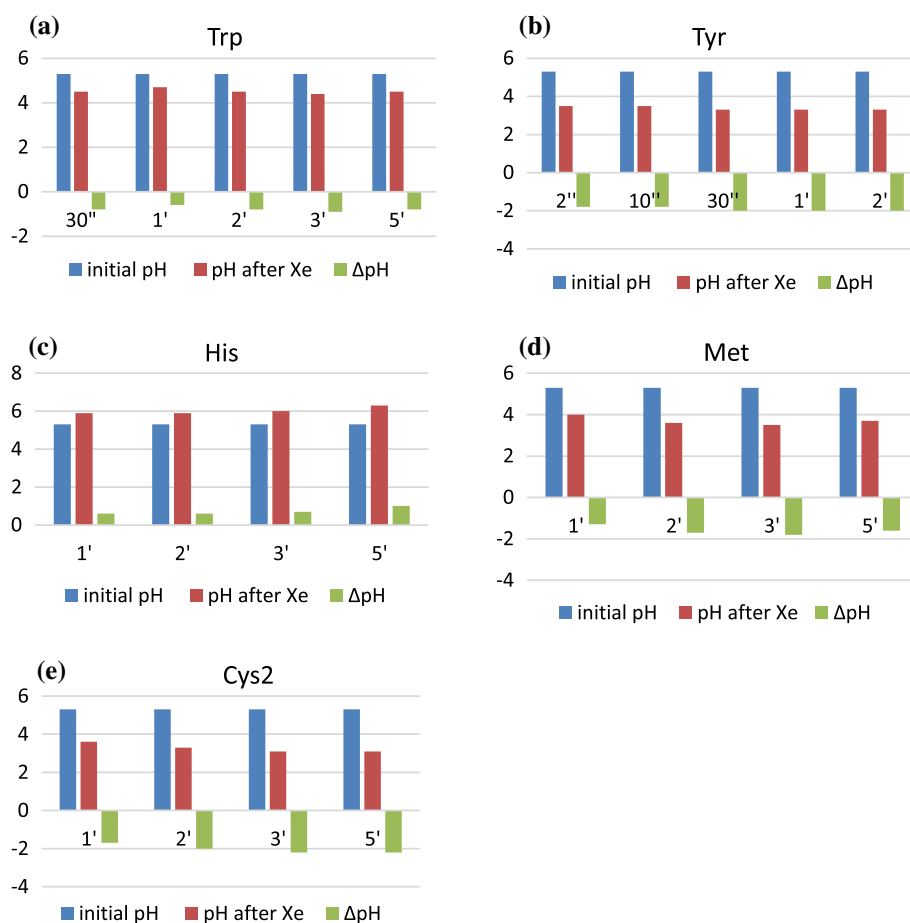


Fig. 7 Zeta potential of Met, His, Cys2, Trp and Tyr as a function of pH

due to the biocompatibility of the amino acids and pH control, e.g., the in situ synthesis of nanoparticles or the functionalization of metal nanoparticles with amino acids/proteins. This could portend advances in areas, such as microbiology.

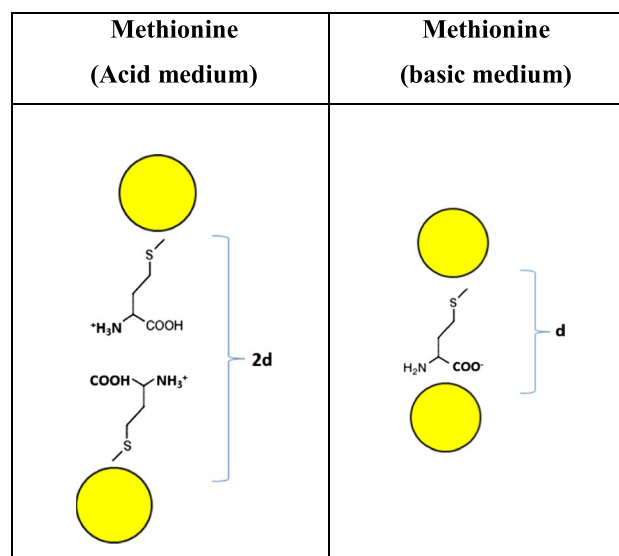
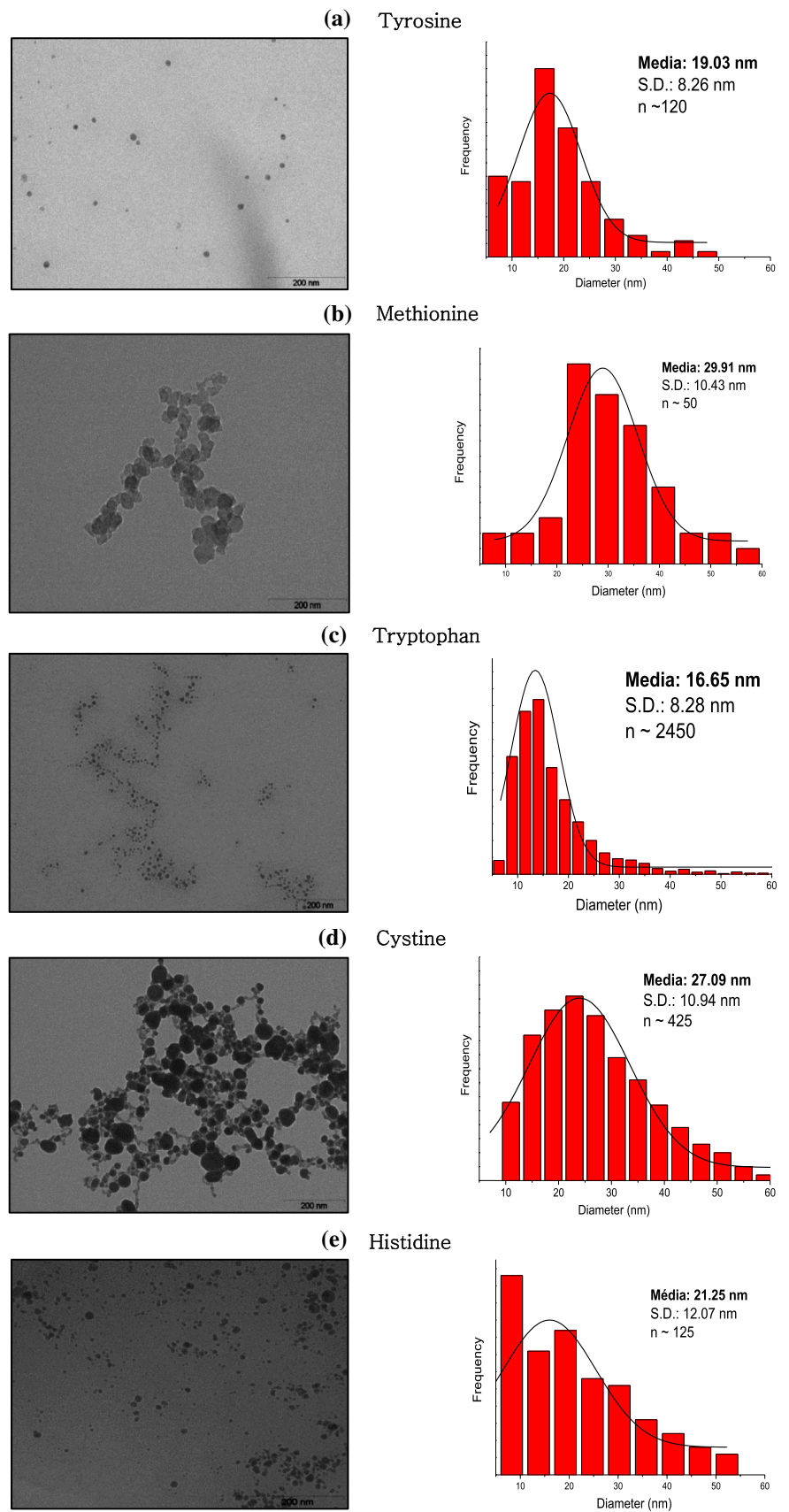


Fig. 8 Interaction of methionine with silver nanoparticles in acid and basic media. In a basic medium, with the carboxylic group deprotonation, two regions of strong interaction with nanoparticles will occur, shortening the distance (d) between two nanoparticles and resulting in agglomeration and precipitation

Fig. 9 TEM images, and average sizes of the AgNPs prepared with Tyr (a), Met (b), Trp (c), Cys2 (d) and His (e)



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Compliance with ethical standards

Conflict of interest No conflict of interest to disclose.

Human and animal rights This article does not contain any studies with human participants or animals performed by any of the authors.

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