Production of silver nanoparticles by green synthesis using artichoke (Cynara scolymus L.) aqueous extract and measurement of their electrical conductivity

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Abstract
This work reports the production of silver nanoparticles (AgNPs) by a green method using, for the first time, an extract of artichoke (Cynara scolymus L.), and we explore their electrical properties with the aim of using, for the first time, totally green AgNPs on the preparation of highly conductive inks. The ultraviolet-visible spectroscopy (UV–Vis) studies monitored the surface plasmon resonance phenomenon of green-synthesized silver nanoparticles. Biomolecules of Cynara scolymus L. (CS) extract flower were suggested to be responsible for reducing and capping of AgNPs, by Fourier transformed infrared spectroscopy (FTIR) measurements. Elemental analysis was determined by energy dispersive spectroscopy (EDS). Transmission electron microscopy analysis showed nearly spherical silver nanoparticles surrounded and connected by CS extract material with size varying from 30–80 nm. Scanning electron microscope studies revealed films of AgNPs surrounded by CS extract with nearly spherical and uniformly dispersed silver nanoparticles. The peaks in x-ray diffraction pattern are in good match with that of face-centred-cubic form of metallic silver. The purity and thermal stability of the formed AgNP was detected by differential scanning calorimetry-thermal gravimetric analysis, the melting point at 973.22 °C through this analysis was closely related to bulk metallic silver which indicates its purity. Moreover, the electrical resistivity test, the four probe method, confirmed that the green synthesized AgNP using artichoke flower extract had highly electrical conductivity: the resistivity of AgNP films was of c.a. 5.1 × 10⁻⁸ Ω × m after sintering treatment at 100 °C for 30 min, which was about three times that of bulk silver (1.59 × 10⁻⁸ Ω × m). Hence, green synthesis can be a prospective way to develop metallic nanoparticles for the preparation of highly conductive inks with low sintering temperature.

Keywords: silver nanoparticles, conductive inks, green synthesis, printed electronics, low sintering temperature
Classification numbers: 2.04, 2.07, 4.03, 4.10
1. Introduction

The introduction of printing techniques to produce the electrical circuits in substrates with the use of metallic nanoparticles inks, has given new possibilities for the electronic market by reducing application material costs, adding new functionalities to existing products, enabling new applications and increasing production yield. Such applications comprise display devices, photovoltaic, lighting, radio-frequency identification (RFID) and other devices [1].

Metallic nanoparticles inks, among the different conductive inks, are especially promising for designing electrical circuits, mainly for inkjet printing technologies. Undeniably, due to the high bulk conductivity of silver together with its environmental resistance to oxidation, makes silver nanoparticles inks the most used these days [2]. However, the accomplishment of a high colloidal stability with such metallic particles is still complex. Generally to avoid the aggregation of silver nanoparticles, solvents, capping agents and additives are needed. In addition, after producing the electrical circuits with these metallic nanoparticles inks, a sintering or drying process is usually needed to guarantee sufficient interconnected conduction paths to exhibit high electrical conduction, unlike larger silver particles that are used in other printing processes such as flexography or screen printing [3]. The printing substrate requires then to endure high levels of temperature involved in this step without degradation or deformations, and it limits the substrate choice [4].

The printed electronic requirements also brought the promise to produce more environmental-friendly electronic products, and it can be addressed with water-based ink formulations for example. In addition, market analysts expect the printed electronics market to approximately reach $73 billion in 2025, which is an exponentially growth [5].

Nanoparticles productions through different physical and chemical routes have their own drawbacks as they are inevitably associated with the use of hazardous chemicals as per reductants, cappings and organic solvents, and the employed techniques have requirements such as high energy radiation, microwave irradiation and inert gas condensation [6]. Thus, there is a demand for ‘green chemistry’ that guarantees clean, non-toxic, and environment-friendly methods to produce nanoparticles.

In recent years, synthesis of silver nanoparticles, employing either microorganisms or plant extracts, has emerged as a green alternative in comparison with conventional physical and chemical methods [7]. The production of nanoparticles using naturally occurring biomolecules from plant extracts, and microorganisms acting both as reducing and capping agents are considered advantageous [8]. Plant extracts is the best approach for producing AgNP (simpler, quicker, efficient and economical method) and many plant extracts have reportedly been used in the preparation of silver nanoparticles, mainly for antimicrobial activity or other biomedical applications [9]. Different plants and plants portion (e.g. leaves, fruit, peel, seeds, root and stem) resulted in Ag nanoparticles of different sizes and shapes (mostly spherical) and distinct pharmaceutical and other biomedical applications [7]. Almost, no studies addressed the electrical characterization of green synthesized nanoparticles. Although a recent work reported a green method of synthesizing silver nanoparticles (AgNPs) using glucose, a natural compound acting as reducing agent, but the capping agent was a synthetic polymer, polyvinylpyrrolidone (PVP). The work showed that after UV sintering, the conductivity ($2.3 \times 10^5$ S m$^{-1}$) and mechanical properties of prepared conductive ink were good [10]. Our approach is novel due to the fact that we produced silver nanoparticles by a totally green method using, for the first time, an extract of artichoke (Cynara scolymus L.), and we explore their electrical properties with the aim of using, for the first time, totally green AgNPs on the preparation of highly conductive inks.

In this regard flower heads (globe) extract of artichoke (Cynara scolymus L.), a species from the family of Asteraceae, was used in this work for bioconversion of silver ions to nanoparticles. There are several biologically active constituents in Cynara scolymus L. (CS) flower. These include carbohydrates, proteins and phenolic compounds, which can be used in the reduction and capping of silver ions. CS is a rich source of polyphenolic compounds with the main chemical components being mono- and dicafeoylquinic acids. The cyanarin is the most well-known caffeoylquinic acid derivative. The other phenolics are the flavones apigenin and luteolin, and the anthocyanidinscyanidin, peonidin, and delphinidin have also been found [11]. In spite of its nutritional and pharmaceutical applications, the wastes originated by the industry (e.g. canning industry) are high, constituting c.a. 80%–85% of the total biomass of the plant [12]. In 2016, the global production of artichoke almost reached 1.5 Mton [13]. The potential of CS for biosynthesis of AgNPs is therefore huge.

Due to their low cost and environmental-friendly nature with their highly reducing properties, Cynara scolymus L. was selected as the reducing and capping agent to prepare silver nanoparticles. The green synthesized AgNPs by CS extract were characterized, and the produced films of AgNPs were tested for electrical resistivity by the four probe method. To our knowledge this is the first report for the green synthesis of silver nanoparticles using flower heads extract of artichoke (Cynara scolymus L.). Although there is one report of green synthesized AgNPs using the leaf extract of artichoke, the authors did not present any study on the synthesis, these particles were used only for comparative purposes [14].

The use of green synthesized silver nanoparticles offers numerous benefits for electronic applications as they do not use toxic chemicals and the natural organic capping agent can be removed at low temperature to ensure a metallic continuum for the electrical conduction.

2. Materials and methods

2.1. Chemicals

Silver nitrate (AgNO$_3$) was purchased from Sigma-Aldrich. Fresh artichoke (Cynara scolymus L.) flower heads were obtained from a local market (Braga, Portugal).
2.2. Preparation of extract

Fresh *Cynara scolymus* L. (CS) flower heads were purchased from the local market, they were washed with tap water in order to remove residues and other types of contaminants, and dried at air. To prepare the CS extract, 20 g of finely cut and well washed flower petals were put in a beaker and making the volume to 100 ml with distilled water followed by boiling for 15 min. The extract was cooled at room temperature, then filtered, and then stored at about 4 °C for further studies.

2.3. Green synthesis of silver nanoparticles using *Cynara scolymus* L. aqueous extract

Silver nanoparticles were synthesized by the reduction of AgNO\(_3\) solution by aqueous *Cynara scolymus* L. (CS) extract. Briefly, 5 ml of 20 mM of AgNO\(_3\) was slowly added to 15 ml of CS aqueous extract in a 50 ml beaker with continuous stirring at 40°C and pH 7.0. The reduction of AgNO\(_3\) to silver nanoparticles by CS extract was visualised by the colour change of the solution, it changed from light yellow to reddish brown. After synthesis, the solution with AgNPs was centrifuged at 8,000 rpm for 10 min, in an appropriate high-speed centrifuge (Universal 320—Hettich (Zentrifugen)). The final colloidal solution was stored at about 4 °C for further studies.

The concentration ratio of the CS extract and AgNO\(_3\) was optimized through two approaches: (i) with the increment on the concentrations of CS extract (12, 15, 17 ml) at constant concentration of silver nitrate (5 ml of 20 mM); and (ii) with the increment on the concentrations of silver nitrate (5, 10 and 20 mM) while keeping the volume of CS extract constant (15 ml). For both approaches, after 30 min of reaction at 40°C and pH 7.0, the absorbance of the resulting solution was measured spectrophotometrically. The pH of the reaction was also optimized by varying the pH (pH 6.0, pH 7.0 and pH 8.0), the pH was adjusted by 0.1 N NaOH solution. After 30 min of reaction at 40°C, the absorbance of the resulting solution was measured spectrophotometrically.

2.4. Characterization of green synthesized silver nanoparticles

Green synthesis of silver nanoparticles was confirmed by measuring the absorbance in UV-Vis spectra at a wavelength range of 200–800 nm, at a resolution of 1 nm (spectrophotometer UV-240 1 PC, Shimadzu). Attenuated total reflectance (ATR)-FTIR spectra were obtained using a Jasco FTIR-4100 (Jasco, Tokyo, Japan) with a deuterated cell to identify the biomolecules in *Cynara scolymus* L., which were responsible for reduction and capping of AgNPs, at a wavelength range of 4000–600 cm\(^{-1}\). The size and morphology of AgNPs were observed by TEM (JEOL 2100 Lab6 microscope) at 200 kV acceleration. The microstructure of the synthesized nanoparticles films was observed by scanning electron microscope SEM (Leica-Cambridge S360 scanning electron microscope and the NanoSEM-FEI Nova 200 (FEG/SEM)). The elemental composition was analyzed by an energy dispersive spectrometer (EDS, combined with SEM). The crystalline structure of the nanoparticles was characterized by XRD (Rigaku D/ max 2500 V) at a setting of 30 kV/40 mA, equipped with Cu-K\(_{α}\) radiation source at an angle of 2θ. Simultaneous DSC-TGA (TA Instruments, model SDT 2920) analysis were performed to measure temperature and heat flow associated with thermal transitions, as well as the weight loss in green synthesized silver nanoparticles, between 30°C and 1000°C, argon was used for the inert atmosphere. The electrical resistance measurements were performed based on the Van der Pauw technique at ambient temperature. Films were tested using a DMM 3706A System Switch/Multimeter and Plug-in Card from Keithly and in-house sample assembly jig with four flat ohmic contact probes of phosphor Bronze with 2.54 mm diameter. And also a digital multimeter (Fluke 8846A) was used to detect the resistance of AgNP films.

3. Results and discussion

3.1. Green synthesis of silver nanoparticles

The addition of aqueous solution of silver nitrate into beakers containing plant extract of artichoke (*Cynara scolymus* L.), in all experiments, resulted in colour change of the solution; it changed from yellowish to reddish brown within reaction time, owing to the surface plasmon resonance phenomenon of silver nanoparticles [15]. On addition of 5 ml of aqueous silver nitrate solution at concentration of 20 mM to different concentrations (12–17 ml) of CS extract, the reaction solution changed its colour from yellow light to reddish light and lastly to reddish brown, which indicated the formation of silver nanoparticles. Other parameters were also optimized such as silver nitrate concentration and pH, which also directly affect the formation of silver nanoparticles.

3.2. Characterization of green synthesized silver nanoparticles

3.2.1. UV-Vis spectroscopic measurements of AgNP. The formation of AgNP as a result of the reduction of AgNO\(_3\) by CS extract was observed visually by the colour change of the reaction solution; it changed from light yellow to reddish brown (figure 1). The change in the colour of the reaction was due to surface plasmon resonance (SPR) phenomenon. Metal nanoparticles exhibit characteristic SPR absorption bands, due to the free electrons present in the nanoparticles oscillating resonantly with light waves [16]. This resonance creates the SPR peak in the absorption spectra. The appearance in the absorbance spectra of a peak in the range of 350–600 nm shows the characteristics of surface plasmon resonance of silver nanoparticles [17, 18].

Figure 2 shows the recorded absorption spectra at a wavelength range of 360–800 nm of green synthesized AgNP with different concentrations of CS extract of 12, 15 and 20 ml (for 20 mM of AgNO\(_3\) and pH = 7.0). As the concentration of the extract increases from 12 to 15 ml there is a decrease in the wavelength and there is an increase in the peak absorbance. The shift towards the shorter wavelength after increasing CS extract concentration signifies a diminution in particle size.
that might be a result of an increase in nucleation owing to enhanced reduction process. The increase in the peak absorbance with increasing extract concentration indicates that nanoparticles production also increased. Distinctly, with further increase in extract concentration from 15 to 17 ml, there is an increase in the wavelength from 445 nm to 465 nm and there is a decrease in the peak absorbance. The shift towards the higher wavelength is characteristic of an increase in particle size. Further increase in the CS extract concentration (that also enhanced the reduction process) might result in further growth (Ostwald ripening) of the nanoparticles and consequently formed nanoparticles with larger diameters. The diminution of the maximum absorbance suggests aggregation and precipitation of the nanoparticles. The double peak at 17 ml CS extract evidences the formation of a bimodal particle diameter distribution. The extract concentration of 15 ml gave the maximum AgNPs formation with the absorption peak at 445 nm. Thus, this 15 ml extract concentration was considered as optimum and is used for further experiments. Similarly, other works reported AgNP exhibiting characteristic surface
Figure 3 shows the recorded absorption spectra at a wavelength range of 360–800 nm of green synthesized AgNPs with different concentrations of silver nitrate of 5 mM, 10 mM and 20 mM (for 15 ml of CS extract; pH = 7.0). It is observed that as the concentration of silver nitrate increases that the intensity of absorption peaks increases. Figure 3 also shows that 20 mM concentration of silver nitrate gave the maximum absorbance peak at 449 nm using CS extract as a reducing agent, indicating the maximum AgNPs formation. For 5 mM of AgNO₃, and for 15 ml concentrations of CS extract and pH of 7.0, there is no formation of AgNPs around 400 to 500 nm, and a very low intensity and broad peak is shown for high wavelengths 600 to 700 nm, which may indicate the formation of Ag particles of large diameter [21].

The pH value of reaction also plays an important role in the formation of AgNPs [22]. The change in pH may lead to the change of the charge of natural phytochemicals in the extract. This charge change impacts the interactions of silver ions to the biomolecules and it may affect the reduction of silver ions to AgNP. The solution was adjusted in different pH and the concentration ratio of CS extract and silver nitrate was kept at constant values, according to the previous results. The absorption spectra of AgNP synthesised at different pH are presented in figure 4. The minimum silver nanoparticles formation was at pH = 6.0 and the maximum AgNP synthesis at pH = 7.0 with maximum absorbance peak at 453 nm. Similarly, the work of Sarsar et al [23] on the synthesis of the silver nanoparticles using Psidium guajava (P. guajava) leaf extract, reported the maximum synthesis of the AgNP at pH 7.0. Interestingly, at pH of 8.0 there is a formation of an additional broad peak at 670 nm, reflecting the formation of AgNPs with larger diameter. The AgNP might undergo agglomeration into bigger particles, resulting in a bimodal distribution of AgNPs sizes [21]. Therefore, to ensure smaller nanoparticles with a narrower size distribution and maximum production of AgNPs, the synthesis conditions were set at 15 ml CS extract, 20 mM AgNO₃, and pH 7.0. These AgNPs with optimized synthesis conditions were further characterized.

3.2.2. TEM analysis of green synthesized AgNPs. Figure 5 shows the morphology and size of the optimized green synthesized silver nanoparticles assessed by TEM. TEM images of powder AgNP, directly applied to the carbon side of the sample support grid, shows that the nanoparticles are attached to each other (figure 5(a)) and that there is a less electron dense material surrounding and connecting the nanoparticles, which might be the biomolecules of the CS extract. As a test to better distribute the nanoparticles the sample was exposed to a strong electron beam of the microscope with the aim to charge the particles and separate them (figure 5(b)). Separated nanoparticles with clear less electron dense connection vary in size mainly from about 30–80 nm in diameter, atomic lattice structures are observed in nanoparticles which can lead to straight edges of nanoparticles, i.e. nanoparticles are not perfectly spherical.

3.2.3. SEM and EDS analysis of green synthesized AgNPs. Figure 6 shows typical results of the studies of silver films (produced with optimized synthesis of AgNPs) deposited on a carbon strip by means of scanning electron microscopy (SEM). SEM was used to characterize the shape, size and morphology of films from green synthesised AgNP. It reveals that films of silver nanoparticles surrounded by CS extract material have uniformed dispersed nearly spherical nanoparticles, with particle size in the range of 50 nm to 80 nm (the smaller nanoparticles were only visible by TEM). Figure 6 also shows the effect of thermal treatment (sintering process) of the AgNP films at 60°C and at 100°C for 30 min (figures 6(a) and (b), respectively).

At 60°C (figure 6(a)), the nearly spherical silver nanoparticles begin to gradually organize in clusters, but as observed, with many voids between them affecting the percolating paths. When increasing the sintering temperature to 100°C (figure 6(b)) the well dispersed nanoparticles strongly clustered, diminishing the voids between them and ensuring interconnected paths for the electrical conduction.

The sintering temperature might have induced evaporation of the aqueous extract during the samples treatment or might have induced in situ generation of new nanoparticles, some
AgNO₃ ions might have been further reduced by the biomolecules present in the CS extract, and new AgNP were formed or resulted in further growth of the nanoparticles, decreasing the inter-particle spacing (the voids).

Energy dispersive spectroscopy (EDS) analysis was used to characterize the elemental composition of the green synthesized AgNPs (figure 7). The intense peak shown at 3 keV is typical of the elemental silver nanocrystals. Other elements are shown in EDS analysis and are carbon, oxygen, chlorine, silica, calcium and magnesium. Since AgNPs were synthesized using the aqueous extract of artichoke (*Cynara scolymus* L.), these elements present in small amounts indicates the participation of plant phytochemical groups in reducing and capping of the synthesized AgNPs. The compositions obtained from EDS analysis for sample from figure 7(a) (sintering treatment at 60°C) were silver 65.01%, carbon 16.11%, oxygen 10.91%, chlorine 3.66%, silica 1.99%, calcium 1.60% and magnesium 0.72%; and for sample from figure 7(b) (sintering treatment at 100°C) were silver 75.44%, carbon 13.44%, oxygen 5.34% and chlorine 5.78%. This quantitative analysis proved high silver contents (75.44%) in the sample treated at higher temperature, but lower C and O and higher chlorine content, which might indicate a better evaporation of the aqueous extract or an on-going nanoparticles nucleation/growth during sample treatment at 100°C for 30 min.

3.2.4. XRD analysis of green synthesized AgNPs. The structural characterization of AgNP was performed by powder XRD analysis. Figure 8 shows the XRD pattern of green synthesized AgNP. The diffractogram has been matched with JCPDS card No. 04-0783. The peaks at 2θ values of 38.24°, 44.32°, 64.56°, and 77.52° corresponding to (hkl) planes of (111), (200), (220) and (311) can be attributed to face-centred-cubic structure of silver nanocrystals. The other two peaks in the diffractogram of 32.28 and 44.36° might be due to AgNO₃ involved in the synthesis that remained in the sample.
3.2.5. DSC-TGA analysis of green synthesized AgNPs. The purity and thermal stability of AgNPs were assessed by simultaneous DSC-TGA analysis. Figure 9 shows the DSC-TGA curves of silver nanoparticles synthesized by CS extract. The obtained melting point at 973.22 °C was closely related to the reported metallic silver of 960.54 °C [24], which indicates the purity of the synthesized AgNPs. The total loss of weight of about 26.71% showed that the metallic core is surrounded by biomolecules. TGA plot suggested that the weight loss in the temperature of 30 °C to 100 °C is mainly due to moisture. Degradation pattern of organic compounds was mainly between 80 °C–500 °C. There was nearly no degradation above 500 °C that accounts for the weight of silver.

3.2.6. (ATR)-FTIR analysis of green synthesized AgNPs. Attenuated total reflectance (ATR)-FTIR measurements were taken to understand the possible phytomolecules responsible for reducing and capping of AgNPs synthesized by artichoke (Cynara scolymus L.) extract. Figure 10 shows the (ATR)-FTIR spectra of dried aqueous CS extract and synthesised AgNPs. In the CS extract, the peak IR bands observed at 3245 cm⁻¹ correspond to OH stretching vibrations (of water, alcohols, phenols, carbohydrates, peroxides), while the band at 2927 cm⁻¹ is assigned to C–H stretching vibrations of CH₂ and CH₃ from lipids, methoxy derivatives, C–H (aldehydes) [25]. The peak at 1604 cm⁻¹ corresponds to aromatic domain and N–H (amino acids) bending vibrations. The band observed at 1400 cm⁻¹ corresponds to stretching vibrations C–O (amide) and C–H bending vibrations. The strong intense peak at 1024 cm⁻¹ is related to C–O–C linkages or C–O stretching from phenolic compounds, mainly attributed to flavonoids and cynarin excessively present in Cynara scolymus L. extract [11]. And the peak located at 669 cm⁻¹ could be assigned to C–alkyl chloride as well as the vibrations of the methil, –CH₃ group.

In the case of silver nanoparticles, a broad peak at 3218 cm⁻¹ is characteristic of OH stretch, the peak at 1608 cm⁻¹ shows the presence of aromatic ring (C=C) and the stretching vibrations of amides, the 1317 cm⁻¹ band corresponds to the NO₃ stretching which is due to the residue of silver nitrate, and the peak at 1027 cm⁻¹ with decreased band intensity (compared to the extract) is related to the C–O–C linkages or C–O stretching from phenolic compounds. The bands at 1400 cm⁻¹ and at 1261 cm⁻¹ existing in the spectrum of CS extract, are missing in the FTIR spectra of the AgNPs, inferring that the O–H group of the phenolic compounds and carboxylate groups of the extract might have bond to silver ions. The spectrum also validates the interaction of amino (–NH₂) or carboxylate (–COO⁻) groups in compounds of the Cynara scolymus L. extract with AgNPs surface. The reduction and capping of synthesized AgNPs might be due to cynarin, flavonoids and proteins present in CS extract. A recent study also evidenced the involvement of water-soluble flavonoid in the reduction of AgNP using plant extracts [26]. These results obtain good agreement with the literatures [10, 25]. From FTIR analysis, it can be inferred that these phytomolecules from CS extract formed a strong coating/capping on the AgNP.
which indicates its purity. The four probe method measured the electrical resistivity of AgNP films and it had a low resistivity in the range of $5.1 \times 10^{-8} \Omega \times \text{m}$ after thermal treatment at 100 °C for 30 min (about three times that of bulk silver of $1.59 \times 10^{-8} \Omega \times \text{m}$).

The benefits of using plant extract (green synthesis) for synthesis of Ag nanoparticles with high electrical conductivity are enormous. It is an environmental-friendly process that promotes energy efficiency, cost effectiveness, and protects human health while leads to inherently safer products and lesser waste. The *Cynara scolymus* L. extract proved to be effective to produce AgNPs with high electrical conductivity. The use of *Cynara scolymus* L. extract from industrial wastes, which are not suitable for human consumption, could be used as raw material to produce Ag nanoparticles. As a competitive alternative to conventional physical and chemical methods, this environmental-friendly method of synthesizing silver nanoparticles has an enormous potential to be used in low cost electronic applications.

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