Textile & Leather Review

ISSN 2623-6281 | www.tlr-journal.com | 10.31881/TLR

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How to cite: Ahmed T, Ogulata RT, Kalam MA. Investigation of the Shape Mechanism of Green Synthesized Silver Nanoparticles on Cotton Fabrics. Textile & Leather Review. 2024; 7:517-533. https://doi.org/10.31881/TLR.2024.005

How to link: https://doi.org/10.31881/TLR.2024.005

Published: 31 March 2024

Investigation of the Shape Mechanism of Green Synthesized Silver Nanoparticles on Cotton Fabrics

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Article
https://doi.org/10.31881/TLR.2024.005
Received 11 February 2024; Accepted 25 March 2024; Published 31 March 2024

ABSTRACT
Silver nanoparticles (AgNPs) can be of various shapes such as spherical, nanorod, cylindrical, cubic, irregular, etc on textile materials. However, there is a huge scarcity of literature on the mechanisms of different shapes of AgNPs. In this study, 3 sets of fabric samples were prepared by pretreating with sodium hydroxide (NaOH), citric acid, and non-ionic detergent (span-80). To investigate the diverse shape mechanism green synthesized AgNPs by Calendula arvensis leaves, Citrus reticulate peel, and Cucumis sativus peel extracts were incorporated into the fabric samples. The samples were characterized by UV-VIS Spectroscopy, X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). The UV-VIS spectra confirmed successful AgNP synthesis for Calendula arvensis and Citrus reticulata, but Cucumis sativus failed AgNP synthesis. The AgNPs were incorporated into the treated fabrics by padding and in-situ method. Then the SEM and XRD images were analyzed meticulously to delve into the nanoparticle shape-building mechanism in light of pH, incorporation methods, and crystallography. It was seen, that pH was the core factor in shape diversity. A pH lower than 7.0 produced predominately closed-pack crystals (111) and due to the low pH, the Gibbs free energy (GFE) was weaker and hence resulted in spherical nanoparticles. Again, the pH range from 7.1 to 8.0 produced cubic shapes due to a high number of open-pack crystals (110) and moderate Gibbs free energy (GFE). On the other hand, pH greater than 8.0 provided high Gibbs free energy, which expedited the reaction and led the nanoparticle shapes to anisotropy.

KEYWORDS
AgNP shapes, green synthesis, textiles, crystallography, free energy

INTRODUCTION

Silver nanoparticle possesses distinct physical, chemical, electrical, optical, and biological properties that set them apart from their counterparts. It has a broad spectrum of usage ranging from electronics to personal care including medical equipment, nanocomposite film, optical applications, and many more. The obnoxious behaviour of available chemical sterilizing agents made the silver nanoparticles (AgNPs) an excellent alternative on account of their excellent antimicrobial and antiviral ability [1].

AgNPs can be synthesized from $AgNO_3$ by multiple methods. These methods are broadly classified into two groups: top-down and bottom-up. The bottom-up process involves using chemicals for reducing

and stabilizing, which are sometimes toxic, costly, and non-eco-friendly. In this regard, organic extract may be an ideal solution. The organic extracts are abundant in nature. Moreover, it can simultaneously and efficiently reduce and stabilize the AgNPs at room temperature [2]. The shapes of AgNPs are paramount in determining thermal, optical, antibacterial, and catalytic capabilities.

The nanoparticle size is directly dependent on the concentration of OH-. The ratio of [OH-] and [M+] determines the AgNPs' size. If this ratio is more than 40 then the nanoparticles aggregate and chain-like nanoparticles are formed due to a high rate of reduction which is proportional to the OH- concentration. On the contrary, the ratio below 20 causes incomplete reduction. Similarly, Kodama et al. reported that high concentrations of OH- and metal ions produce bigger particles due to aggregation [3]. Sun and Xia determined that the nanoparticle size depends on the growth time and concentration of $AgNO_3$ [4].

AgNPs can be of different shapes such as nanorod, spherical, Quasi-spherical, triangular, hexagonal, cubic, irregular, etc. [5]. The shape of nanoparticles depends on stabilizers, inductors, and preparation methods [6]. It is also influenced by the volume ratio of the reducing agent and $AgNO_3$, temperature, and concentration of $AgNO_3$. Ahmed et al. claimed that plant extract can determine the silver nanoparticle's shape in green synthesis [7]. Besides, temperature also affects the nanoparticle shapes. The $AgNO_3$, ethylene glycol, and PBP (Pentabromophenol) produced cubic-shaped AgNPs at 161 ^oC. whereas, irregularly shaped nanoparticles are formed when lowering the temperature to 120 ^oC or raising it to 190 ^oC [4].

Cotton is the most important fibre for clothing and is unparalleled regarding comfort. But it is very congenial for microbial and fungal growth, which causes staining, bad odour, strength loss, etc. To get rid of these problems AgNPs are widely used to make the cotton fabrics antimicrobial. To the best of our knowledge, very few studies on the shaping mechanism of AgNPs on cotton fibre were reported. Du et al. showed time is a factor of spherical to square shape transformation in the case of di-aldehyde cellulose (DAC) [8]. Pillai et al. investigated citrate ions' influence on particle growth and showed that the Ag^{2+}-citrate complex undergoes a slower transformation leading to a larger silver cluster compared to uncomplexed Ag^{2+} [9].

The silver nanoparticles (AgNPs) can be incorporated into fabrics by both in-situ and ex-situ methods. Different types of ex-situ and in-situ methods are employed to embed AgNPs into the fabric. The *in-situ* method depends on various external stimuli such as low-pressure cold plasma for water vapor synthesis as reported by Khatabi et al. [10]. On the other hand, ex-situ methods include coating, padding, spray, etc. Ainur et al. synthesized AgNPs by Na-carboxymethyl starch (NaCMS) by the combined action of ultraviolet radiation and ultrasonication and incorporated AgNPs by spray coating method [11]. Maghimaa et al. synthesized AgNPs from the aqueous extract of Curcuma longa and

applied them to the fabric by dip coating method [12]. This study aims to investigate the shape mechanism of AgNPs, produced from green synthesis on cotton fabrics and the shape diversity as a function of pH, reducing agents, and padding pressure.

EXPERIMENTAL

Materials

For this study analytical grade $AgNO_3$, NaOH pellets, citric acid, and non-ionic detergent (span-80) were purchased from Merck, Germany. Two types of cotton fabrics were used: plain, and twill (3/1) having 123 and 254 GSM, respectively. The fabrics were collected from Bossa Textiles, Turkiye.

Methods

The green synthesis method was used to synthesize silver nanoparticles (AgNPs) on different cotton fabrics. To determine the effect of various pH of cotton fabrics on AgNP shape- the cotton fabrics were pretreated with acid (citric acid), alkali (NaOH), and non-ionic surfactant (span-80). Again, to incorporate the AgNPs into cotton fabrics in-situ and padding methods were used. AgNPs were synthesized using *Calendula arvensis* (field marigold), *Citrus raticulata* (mandarin orange) peel, and *Cucumis sativus* (cucumber) extract.

Plant extract preparation

Calendula arvensis (field marigold leaves) was collected from the Cukurova University garden in February, and *Cucumis sativus* (cucumber) and *Citrus reticulate* (Mandarin orange) were collected from the university agricultural research centre. The leaves of *C.arvensis* and peels of cucumber and orange were separated and dried in the shade for several days. Then, they were cut into small pieces.

5 g of *C.arvensis* leaves were immersed in 200 ml distilled water in a glass beaker and heated at 90 ^oC until the volume got reduced to 100 ml. After cooling, this solution was filtered with Whatman No 1 filter paper and preserved in a bottle labelled with *C.arvensis*. The bottle was stored at 3 ^oC for future use. In the same way, *C.reticulata* and *C.sativus* peel extract were prepared and filtered in a bottle labeled with appropriate names and stored at 3 ^oC.

Silver nanoparticle (AgNP) synthesis

Before synthesizing AgNPs, all the reagents and ingredients were heated separately at above 60 ^oC. Then, four drops of *C.arvensis* leaves extract solution was added to 100 ml $AgNO_3$ (0.002 M). After a few minutes, the colour of $AgNO_3$ started to change from colourless to yellowish which indicated the

production of AgNPs. In the same way, Orange extract and cucumber extract were used to synthesize AgNPs. All the synthesized AgNPs were analyzed using UV-VIS spectroscopy for further confirmation.

Fabric pretreatment

To evaluate the effect of different pretreatments of cotton fabrics on AgNPs, 3 sets of samples were prepared with NaOH (4 g/L), Citric acid (2 g/L), and Span-80 (0.5ml/L). The designations of the samples are as follows:

F1- Treated with NaOH

F2- Treated with Citric acid

F3- Treated with Span-80

For preparing F1 samples 2 g NaOH pellets were dissolved in 500 ml double distilled water and boiled with a magnetic stirrer (20 rpm) and then the samples were added in the solution. The fabric samples were washed with distilled water and again boiled for 20 minutes to reduce alkalinity. Finally, they were washed again and dried in an air dryer cabinet (10 minutes at 70 ^{o}C). The same procedure was followed for F2 and F3 samples using 1 g citric acid and 0.25 ml Sapn-80 in 500 ml distilled water, respectively.

Incorporation of AgNPs into cotton fabric

AgNPs were incorporated into cotton fabrics employing in-situ and padding methods:

In-situ

In this method, the silver nanoparticle (AgNPs) synthesis and incorporation are done simultaneously. For this process, two vessels were used containing $AgNO_3$ and plant extract. At first, the fabric samples were immersed in the $AgNO_3$ solution for 5 minutes, then the $AgNO_3$-soaked samples were immersed in the plant extract solution for 5 minutes. Finally, the samples were washed with distilled water and dried in an air-drying cabinet at 70 ^{o}C for 10 minutes.

Padding

For the padding method, AgNPs were synthesized first in a vessel. Then the fabric samples were dipped in the vessel and padded with a padding mangle (Labrotex, Rapid, Turkiye). The pressure of the padding mangle was set to ensure 80% wet pick-up. Finally, the padded samples were dried at 60 ^{o}C for 20 minutes and cured at 90 °C for 10 minutes.

Characterizations

pH test

The pH of the fabrics was measured according to the ISO 3071 method. In this method, at first 2 g of fabric sample was cut into small pieces. Then, 100 ml distilled water was taken in a glass beaker and the small pieces of fabric were put in it followed by stirring for 2 hours at 30 rpm. Finally, the pH of this solution was measured using a pH meter (PHS-3C, China).

UV-VIS spectroscopy

To confirm the AgNP production, samples were analyzed by using a UV-VIS spectrometer (Shimdazo UV-1800, Japan). The absorption spectra were collected in the wavelength range of 300 - 650 nm.

Scanning Electron Microscope (SEM)

The AgNP shapes were observed by using a scanning electron microscope (FEI, Quanta 650) with a 5 kV accelerating voltage. The samples were coated with a gold (Au) plate.

X-ray diffraction (XRD)

To observe the structure of AgNPs, X-ray diffraction (XRD) analysis was done. XRD pattern of the AgNPs was obtained using a PANalytical diffractometer (EMPYREAN XRD, UK) operating under Cu Kα radiation at 40 kV and 40 mA in reflection mode with a wavelength of 1.541 A^o. The sample was scanned from 20^o to 80^o with a scattering angle of 2θ.

RESULTS AND DISCUSSIONS

The *C.arvensis* plant extract contains various phytochemicals such as flavonoids, phenolic acid, and different natural components (z-jasmone, ß-sitosterol, l-threonic acid, etc.) [13]. *C. reticulata* peels are enriched with flavonoids, vitamin C, dietary fibres, essential oils, carotenoids, etc. [14].
The NADPH-contained phytochemicals reduce the Ag+ to Ag atom and polar phytochemicals cap the growth of Ag atoms as shown in Figure 1.

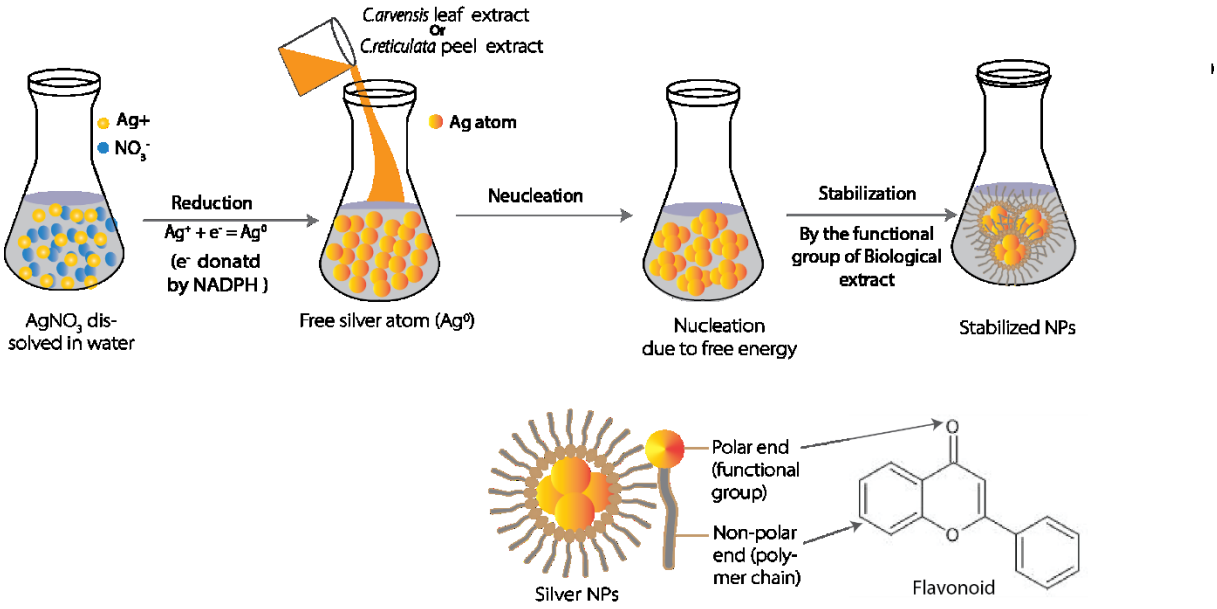


Figure 1 Green synthesis mechanism [15]

UV-VIS spectroscopic analysis of the as-prepared AgNPs was carried out to determine the surface Plasmon Resonance (SPR) band. A qualitative idea regarding AgNPs' shapes can be achieved from the position, width, and shape of the SPR band. Single narrow SPR refers to uniform spherical sizes whereas broadband refers to a wide distribution of particle sizes [16]. From Figure 2, it is seen that in the absorbance spectra of the $AgNO_3$ solution, no absorption has occurred, thus no AgNPs are formed. However, the cucumber plant extract synthesized solution shows some absorption but not in the range (350-500 nm) of the AgNPs absorbance band, the produced silver particles are not nanoparticles [17]. It is also observed that orange extract synthesized AgNPs have sharp peaks at 417 nm indicating the formation of smaller-size spherical AgNPs. On the other hand, in the case of *C. arvensis* extract the synthesized AgNPs comparatively broad peak at 422 nm is seen, indicating a slightly bigger sized AgNPs formation has taken place, which is also reported by Mulvaney [18]. In this case, no shoulder appeared along with the broad peak unlike Riaz et al. [16], which confirmed that the AgNPs contained in the solution were spherical. All absorbance spectra showed a single bell-shaped peak demonstrating the formation of spherical AgNPs [19].

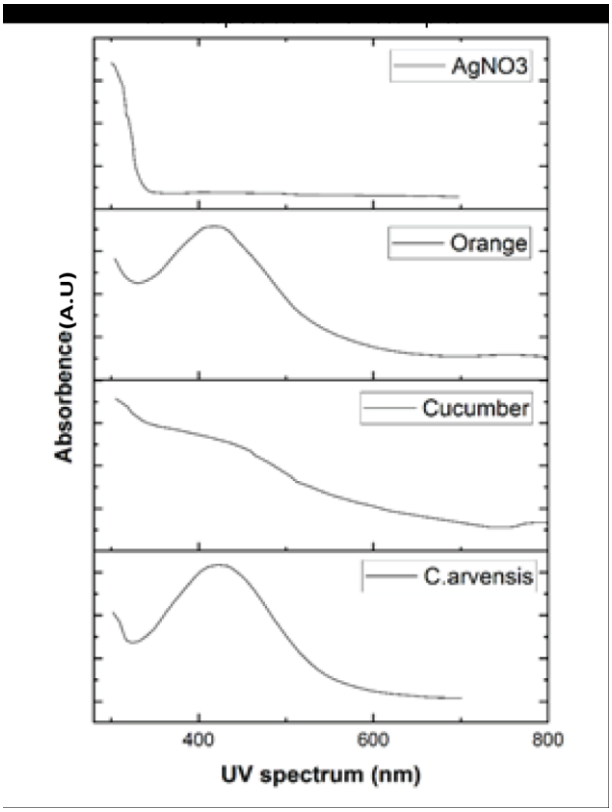
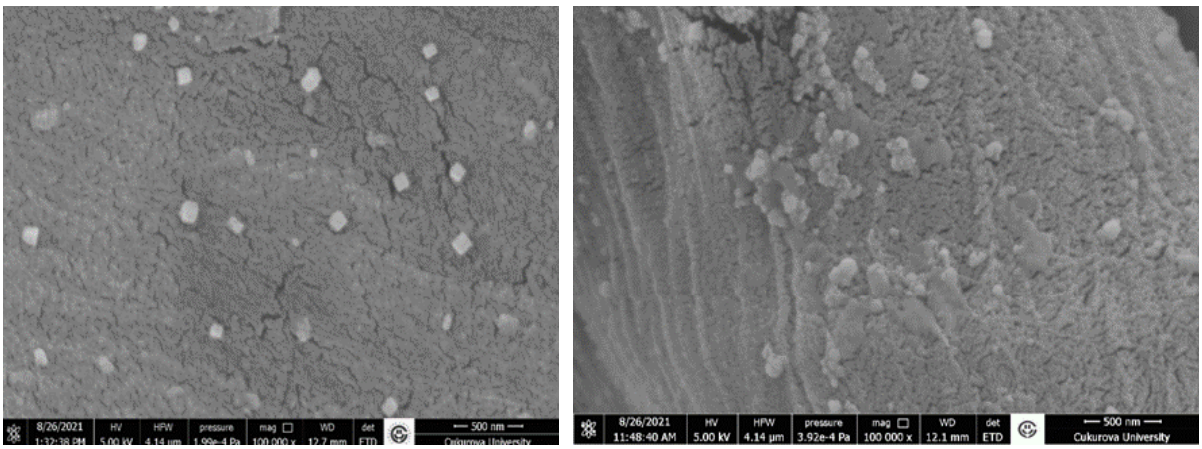
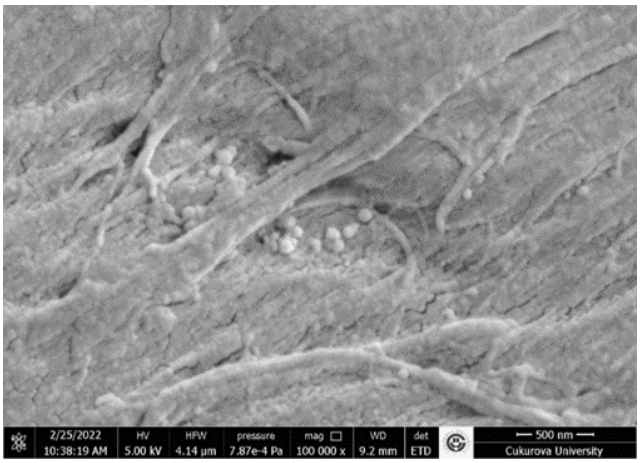


Figure 2. UV –VIS spectra of different plant extract synthesized AgNPs

Figure 3 shows the SEM images of AgNPs synthesized using *C.arvensis* and Orange peel extract on fabrics with different pH (due to the pretreatments). It is shown that cubic-shaped nanoparticles were obtained when the cotton fabrics were pretreated with NaOH and subsequently washed with water to ensure a pH range between 7 to 8 using *C.arvensis* plant extract (Figure 3-a). On the other hand, irregularly shaped nanoparticles were produced when pH was maintained more than 8 (Figure 3-b). Spherical nanoparticles were produced when orange peel extract was used and the samples' pH was less than 8 (Figure 3-c).



a) b)



c)

Figure 3. SEM images of different shapes of AgNPs produced by using different plant extracts and pH; (a) *C.arvensis* synthesized AgNPs on fabric having 7.1<pH < 8 by in-situ method; (b) *C.arvensis* synthesized AgNPs on fabric having pH > 8 by in-situ method; (c) Orange peel synthesized AgNPs on fabric having pH < 8 by in-situ method

Factors on AgNPs shape:

The shapes of silver nitrate ($AgNO_3$) on fabrics depend on multiple factors such as the pH of the fabrics, gram per square meter (GSM) of the fabrics, incorporation methods, etc. On a textile sample, there would be different shapes of AgNPs such as some are cubic, some are spherical and some are irregular as shown in Figure 7. The pivotal role is played by the pH of the fabric. The pH depends predominately on fabric pretreatment and fabric GSM.

Pretreatment effect on AgNPs shape

The pretreatment process showed a tremendous effect on the silver nanoparticle shape when *C.arvensis* extract was used. When fabrics (both low and high GSM) were pretreated with NaOH (F1), cubic and irregular-shaped nanoparticles were produced as shown in Figure 3 and Table 1 (sample 1 and sample 2). For low GSM fabrics, the pH range was 7.1 to 8.0 and in this case, cubic-shaped AgNPs were produced. Here the specified pH range (7.1 to 8.0) deviated the fabric samples from the thermodynamic equilibrium condition (as shown in Figure 4). Additionally, the entropy of the fabric samples increased following equation 1. According to equation 1, the Gibbs Free Energy (GFE) decreased with the increase in entropy. This weaker GFE led to a weak driving force, which ultimately formed loose-packed (110) orthorhombic crystal systems as shown in Figure 6-a. Again, The loosely packed crystals possessed high surface free energy [20]. For the large surface free energy the crystals were oriented in a cubic shape since the cubic shape owns maximum free surfaces. In the same way, the lowest surface free energy forms the spherical shape.

The Gibbs Free Energy (GFE) can be calculated from the following equation where the pressure is zero, and the temperature of the system is T [20].

$$g(T) = u(T) - Ts(T) \quad (1)$$

Where $u(T)$ is the internal energy/ atom and $s(T)$ is the specific entropy.

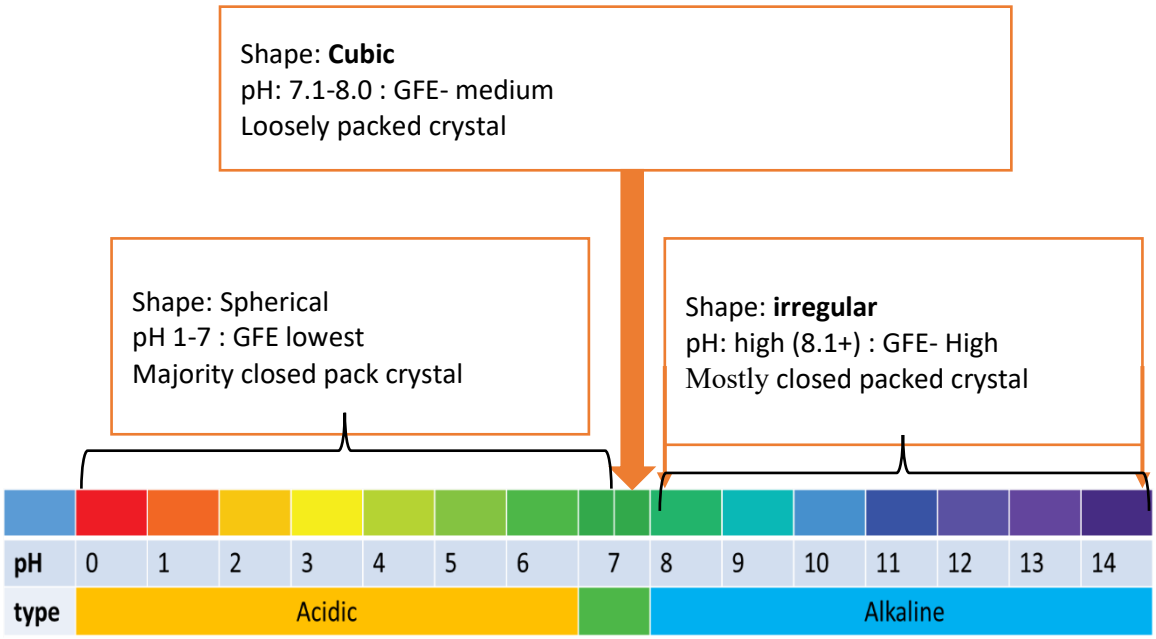


Figure 4. AgNPs shape mechanism in textile materials

On the other hand, spherical AgNPs were obtained in the case of *C.reticulata* (orange peel extract). Here, the pH of the extract was less than 7.0, so it had the lowest Gibbs Free Energy (GFE) and hence had no significant influence on shape, which ultimately led to retaining the original shape (spherical). The pivotal role in determining the AgNPs' shapes was played by the reducing agent. Primarily, the plant extract (reducing agent) synthesized spherical nanoparticles, as the low pH of plant extract provided a weaker driving force which formed the majority closed packed lattice (Figure 6-b). In this case, no additional small crystals formed since there were no extra reducing agents (-OH). This hypothesis is supported by the nanoparticle's size according to their shapes, where spherical shapes were the smallest followed by square and followed by irregular shapes (Figure- 5).

On the other hand, in alkaline conditions (pH > 8.1), the driving force was so strong that irregularly shaped AgNPs were produced, a similar result was reported by Meng, Tang, and Vongehr [21]. Additionally, the driving force dictated the growth rate, which was impacted by the surface energy differences in different crystallographic axes resulting in anisotropy [21]. High GFE caused irregular AgNPs which were closed-packed crystals (111) as evident in Figure 6-c, unlike spherical shapes, there

were some residual reducing ions (such as –OH), which caused some additional small crystals formation.

Among all the shapes the spherical shapes are the smallest in size (average size 50 nm), whereas the irregular shapes are the biggest (average size 72 nm) having a range of 10 to 250 nm. On the other hand, the cubic-shaped nanoparticles have an average size of 55 nm (Figure 5).

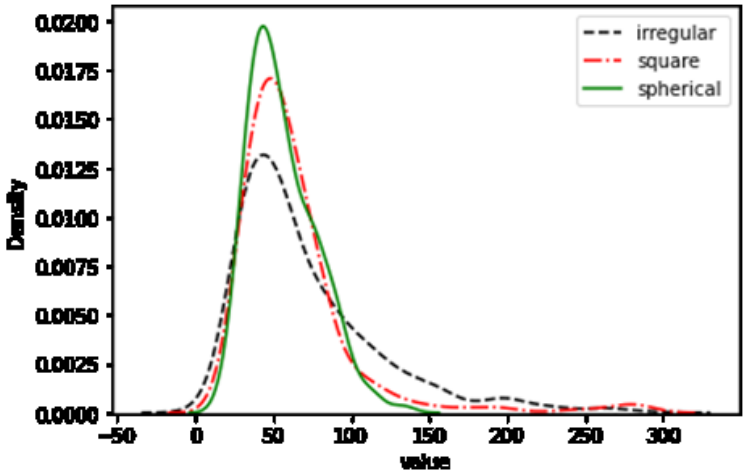


Figure 5. Nanoparticle size distribution of various-shaped nanoparticles

From Figure 6-d, it is seen that a spherical shape has many close-packed crystals, whereas a cubic shape has a large number of loosely packed crystals. The loosely packed crystals have more free energy, and hence they orient more robustly. Additionally, the little bit of added alkaline condition (pH 7.1-pH 8.00) produces some additional free atoms, which are attached to the mainstream nanoparticles. In this way, they form a cubic shape. Hence, the cubic shapes are a little bit bigger than the spherical ones.

For high GSM fabrics, the fiber density is higher which absorbs more pretreatment agents, hence for NaOH-treated samples, the pH was higher (pH > 8.2). The high pH produced irregular-shaped nanoparticles in both in-situ and padding methods (sample 3-4 in Table 1). This hypothesis is supported by Dong et al. because of the fast reaction [14,15].

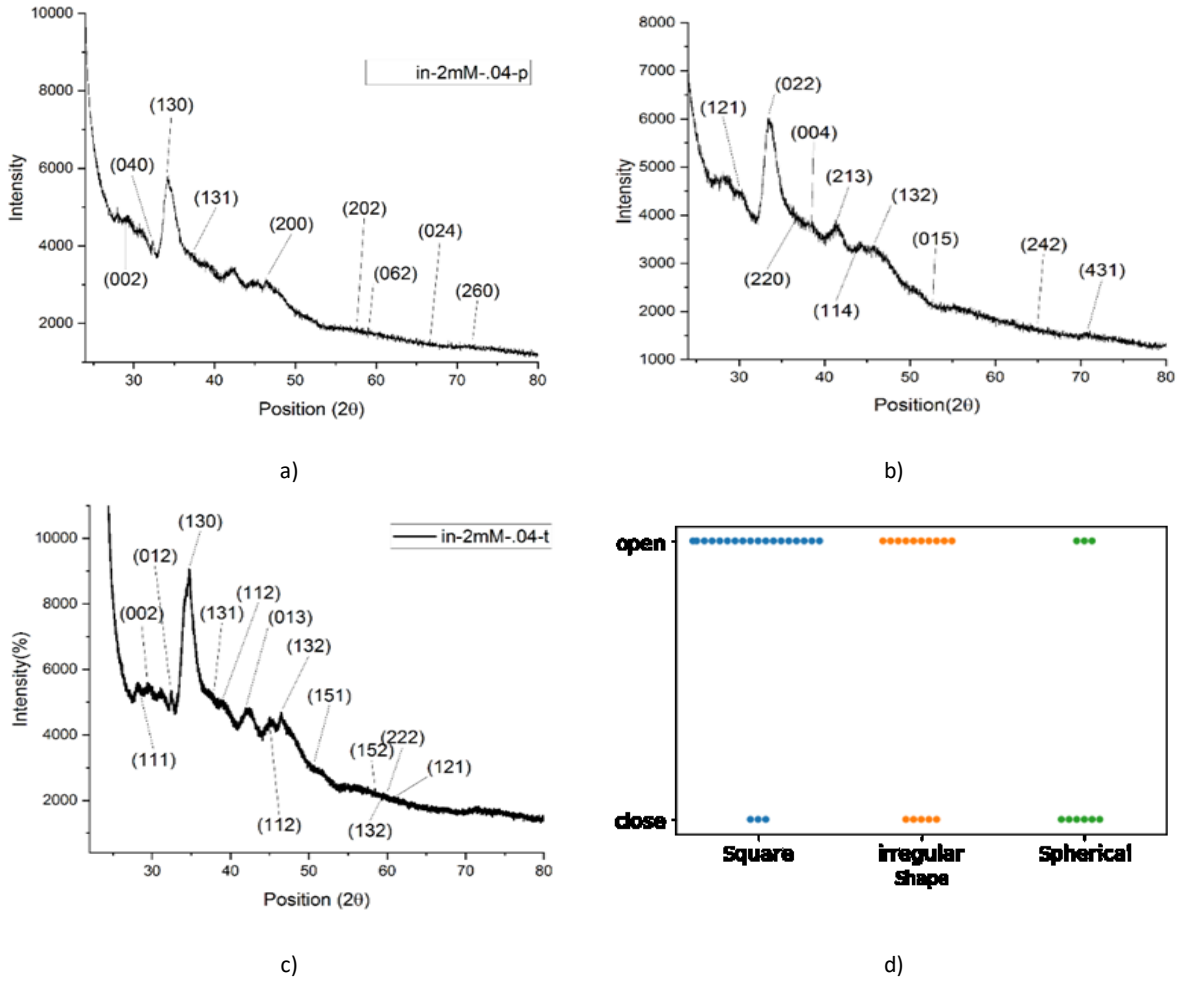


Figure 6. XRD spectra of different shaped AgNPs; (a) XRD spectrum of cubic-shaped AgNPs; (b) XRD spectrum of Spherical AgNPs; (c) XRD spectrum of irregularly shaped AgNPs; (d) XRD spectrum of close and open pack distribution for different shapes

Plant extracts on AgNPs shape

It is conjectured that the *C.arvensis* synthesized spherical AgNPs in solution. However, the shape changes when the residual Ag^{+} is reduced by residual NaOH (from the *pretreatment* of fabric) to produce smaller AgNPs. Later the newly created small nanoparticles attached to the typical AgNPs in an anisotropic manner which ultimately produced irregular shapes. This hypothesis is a close match to the work of Dong et al. [15,16].

On the other hand, orange peel extracts consistently produced spherical nanoparticles irrespective of pretreatments and methods. Besides, in the case of citric acid and span-80 *pretreated* (F2 and F3) fabrics (both low and high GSM) spherical and irregular-shaped nanoparticles of various sizes were produced, respectively in both in-situ and padding methods (table 1: sample 5-12). The pH of the samples was less than 2 for citric acid *pretreated* samples. At this low pH, the weak driving force produced spherical nanoparticles complying with the Lamer model [23]. The pH range for the Span-80

pretreatment was 6.2–7.0. However, being a surfactant Span-80 increased the surface energy of the fabrics, reinforced the driving force, and produced irregularly shaped nanoparticles. In addition, surfactants reduced the liquid's surface tension, facilitated the easier dispersion of $AgNO_3$ suspension, and also decreased the interfacial tension between $AgNO_3$ solution and fabrics, which resulted in the creation of AgNPs with irregular shapes [24].

Table 1. Shapes and sizes of different AgNPs

Sample name	No. of AgNPs	Size (nm)	Shape	Pre-treatment	Molarity of $AgNO_3$ (M)	pH	GSM	Method
1	193	49	cubic	NaoH	0.002 M	7.2	Low	In-situ
2	93	45	irregular	NaoH	0.002 M	7.2	Low	padding
3	214	54	irregular	NaoH	0.002 M	8.3	High	In-situ
4	142	45	irregular	NaoH	0.002 M	8.3	High	Padding
5	40	41	spherical	Citric Acid		1.7	Citric	In-situ
6	40	40	spherical	Citric Acid	0.002 M	1.7	Low	Padding
7	42	43	spherical	Citric Acid		1.4	High	In-situ
8	40	45	spherical	Citric Acid	0.002 M	1.4	High	Padding
9	800	129	irregular	Span -80	0.002 M	6	Low	In-situ
10	68	57	irregular	Span- 80	0.002 M	7.2	Low	padding
11	913	140	irregular	Span -80	0.002 M	6.5	High	In-situ
12	68	57	irregular	Span-80	0.002 M	7.4	High	padding

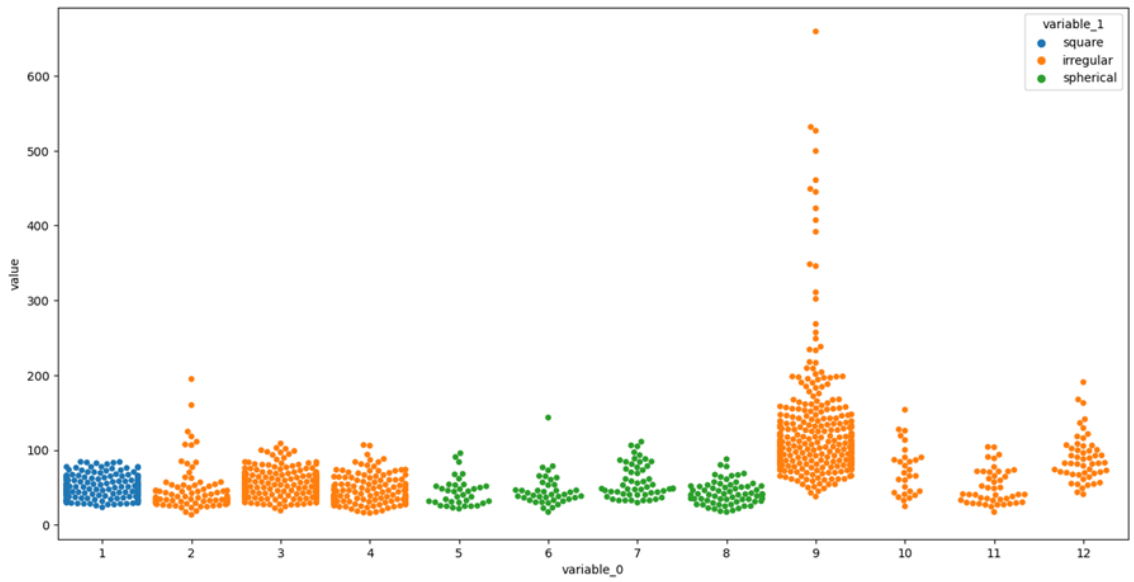


Figure 7. Distribution of AgNPs spherical and cubic shapes

Incorporation methods on AgNPs shape

The pH influenced the low GSM fabrics for the *in-situ* method but not the padding method (pressure 2 kg/cm2). Because, in the padding method, the padding pressure of the padding method, changed the created required thermodynamic non-equilibrium condition of NaOH-treated samples and formed the majority of irregular-shaped nanoparticles (Table 1).

Here, the spherical AgNPs were synthesized in the AgNPs suspension which were incorporated into the fabric samples, then the pressure was applied on the fabric during padding, and the entropy of the system increased because of non-equilibrium conditions which resulted in weak Gibbs free energy according to equation (1). Hence, the padding method produced irregular and spherical shapes (Table 1). However, this non-equilibrium condition created by padding pressure did not overpower the effect of pH, for which low pH agents (citric acid or orange peel extract) resulted in spherical nanoparticles even in the padding method.

To evaluate the influence of padding pressure the *in-situ* and padding method were combined. Here the scoured fabrics (pH 8.1) were first dipped into plant extract and then padded with a padding mangle, then again dipped in the $AgNO_3$ solution for in-situ AgNPs synthesis and again padded for a second time. In this way, some big cubic-shaped AgNPs were created (Figure 8).

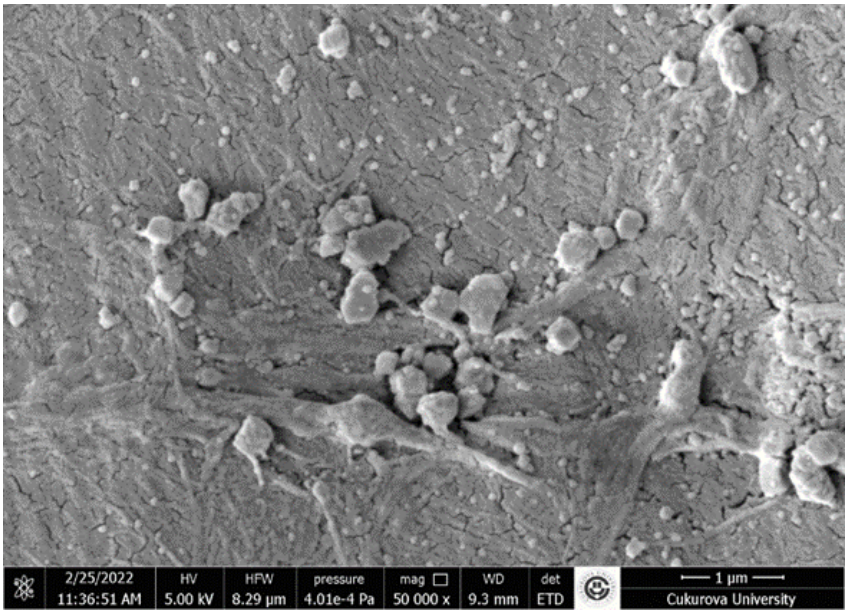


Figure 8. In-situ-pad (mixed cubic and irregular) NaOH treated + padding pressure

In this *in-situ-padding* method, at first, the fabrics were pressurized with plant extract solution first. So, thermodynamic non-equilibrium was created and within this non-equilibrium condition, the fabrics were immersed in an $AgNO_3$ solution. In wet conditions, the fabrics try to get into thermodynamic equilibrium quickly. At this point, the fabric was again padded by the padding mangles and a

thermodynamic non-equilibrium condition was created again. As the AgNPs synthesized in a stage of transformation from thermodynamic non-equilibrium to thermodynamic equilibrium; hence, cubic shapes were created here. However, when fabric was treated with NaOH the first squeezing or padding squeezed out a substantial amount of NaOH and located –OH groups unevenly on the fabric surface, which synthesized the AgNPs very quickly at the non-thermodynamic condition, which caused cubic shapes. However, due to the quick relaxation of the fabric, only a few cubic shapes were produced.

CONCLUSION

Silver nanoparticles (AgNPs) showed multiple shapes in textile materials. It was found that the *C.reticulata* synthesized AgNPs were consistently spherical whereas the *C.arvensis* synthesized AgNPs are of different shapes. This study investigated the reason behind the diversity of AgNPs' shapes. The pH was found as the most crucial factor in determining AgNPs' shape. It influences the Gibbs Free Energy (GFE) and crystal packing systems. At pH ≤7 the GFE is very weak and the crystals are closed-packed which leads a weak surface free energy and subsequently produces spherical nanoparticles. Again, the pH ranged from 7.1-8.0 produces a medium level of GFE and creates an environment for open pack crystal, the weak GFE and large surface free energy (due to open pack crystal) lead the nanoparticles to cubic shape, as cubic shape is more stable regarding the total energy. On the contrary, the pH > 8.1 provides a high GFE and high reaction rate which leads the nanoparticle to anisotropy. The average sizes of nanoparticles were found 50 nm, 58 nm, and 72 nm for pH ≤ 7, 7.1 < pH < 8.0, and pH > 8.0, respectively.

Author Contributions

Conceptualization – Ahmed T; methodology – Ahmed T; formal analysis – Ahmed T and Kalam M.A.; investigation – Ahmed T; resources – Ogulata R.T; writing-original draft preparation – Ahmed T; writing-review and editing – Ahmed T and Kalam M.A.; visualization – Ahmed T; supervision – Ogulata R.T. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

Funding

The research work was funded by Cukurova University Scientific Research Fund, Project number: FDK-2021-13527.

Acknowledgements

We are grateful to Prof. Dr. Osman Gülnaz for this support for UV-VIS Spectroscopy and the Cukurova University Central Laboratory for characterization tests.

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